Large area low temperature growth of optical and dielectrical materials using excimer lamps

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Abstract

This research aims to achieve large-area, low-temperature deposition of thin films with high refractive indices, low leakage currents and high dielectric constant for optical and microelectronics applications, using excimer lamps.

An efficient system consisting of four excimer lamps filled with xenon producing intense narrowband ultraviolet (UV) radiation at $\lambda=172$ nm was constructed and applied to materials’ processing. Also, deposition by a new UV assisted Injection Liquid Source™ (UVILS) developed by JIPELEC and incorporating a krypton chloride ($\lambda=222$ nm) lamp is presented. The UVILS technique combines the intense radiation from an excimer lamp with a novel injection liquid source capable of delivering precisely controllable quantities of a liquid precursor into the chemical vapour deposition (CVD) chamber. Silicon dioxide ($\text{SiO}_2$), titanium dioxide ($\text{TiO}_2$) and composite films of tantalum pentoxide ($\text{Ta}_2\text{O}_5$) doped with $\text{TiO}_2$ i.e. ($\text{Ta}_2\text{O}_5)_{1-x}\text{(TiO}_2)_x$ were grown and deposited at 400°C and below. A wide range of techniques was employed to characterise these films.

Good $\text{TiO}_2$ films with refractive indices from 2.20 - 2.54 were grown on crystalline Si and quartz by photo-CVD, with deposition rates around 50 nm/min achieved. The optical band gap of the films, $E_g$, found to be 3.35eV, is close to the accepted value of 3.5eV for $\text{TiO}_2$. ($\text{Ta}_2\text{O}_5)_{1-x}\text{(TiO}_2)_x$ films of various compositions were subsequently grown under the same conditions, with a highest dielectric constant value of 51 and band gap energies ranging between 3.2eV and 4.2eV obtained. Films of thickness and refractive indices up to 140 nm and 2.4 respectively were grown by the novel technique of photo-induced sol-gel deposition of $\text{TiO}_2$ applied to ($\text{Ta}_2\text{O}_5)_{1-x}\text{(TiO}_2)_x$ films. $\text{SiO}_2$ films of 1-3 nm thickness were grown on Si by photo-oxidation.

The excimer lamp technique requires a low thermal budget, is inexpensive in capital outlay, adaptable due to its simple application and can be easily upscaled to large-areas.
Preface

This research aims to achieve large-area, low-temperature deposition of thin films with high refractive indices, low leakage currents and high dielectric constant for optical and microelectronics applications. The main objective is to design, build then employ a novel and efficient ultraviolet (UV) lamp system for the low-temperature large area processing of optical and dielectric thin films. The films of interest in this work are silicon dioxide ($\text{SiO}_2$), titanium dioxide ($\text{TiO}_2$) and composite films of tantalum pentoxide ($\text{Ta}_2\text{O}_5$) doped with $\text{TiO}_2$ i.e. $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$ and these are processed at from room temperature to $400^\circ\text{C}$. The main techniques proposed for this research are the photo-induced sol-gel process, photo-assisted surface oxidation and photochemical vapour deposition (photo-CVD). Photo-induced sol-gel processing involves the absorption of photon energy from a UV source by the precursors dispensed on a substrate resulting in their selective breaking of bonds to produce required ceramic materials. This process is used in conjunction with a new UV assisted Injection Liquid Source™ (UV-ILS) chemical vapour deposition (CVD) developed by JIPELEC. This new technique combines the intense radiation from an excimer lamp ($\lambda=222$ nm) with a novel injection liquid source capable of delivering precisely controllable quantities of a liquid metalorganic precursor into the CVD chamber. Photo-oxidation mainly involves the irradiation of oxidising agents resulting in their breakdown or reaction producing active components that react with substrate material surfaces, resulting in oxide growth at the surface. Photo-CVD involves enhanced reactions in the vapour phase at the substrate surface. These techniques have been chosen over other conventional techniques because of advantages that include the low thermal budget, the ability to deposit films at low temperatures over wide areas, and the ability to precisely control the thickness of deposited materials. In this research, processing of all materials is carried out.
using an excimer lamp sources filled with xenon (Xe*) and an inert gas and krypton chloride (KrCl*) an inert gas - halide combination to produce intense narrowband radiation. These lamps operate \( \lambda=172 \) nm and \( \lambda=222 \) nm respectively. Characteristics of emission spectra of excimer sources, from 108 nm to 354 nm have been proven useful for thin film and surface processing. A wide range of techniques is employed to characterise the electrical and optical properties of these thin-film materials. These include Fourier transform infrared spectroscopy for the analysis of chemical bonding of the films, UV-visible infrared spectroscopy analysing optical properties at wavelengths of between 195 - 1100 nm, capacitance-voltage and current-voltage measurements for analysing electrical properties and X-ray diffraction for analysing the crystallinity of films.

The first chapter reviews the vast range of UV sources and their general applications. A brief discussion of excimer lamps is given. The second chapter describes the underlying principles of excimer lamps and their applications. The characteristic properties of vacuum ultraviolet (VUV) and UV light generated from an excimer lamp are described. The excimer lamp technique, which is relatively inexpensive in capital outlay, is adaptable because of its simplicity to apply, can be easily upscaled to large-areas and has being proven to be interesting for optical and electronic applications.

Chapter 3 provides details of the apparatus used for the deposition of thin film materials and the measurement methods employed. The design and construction of a new large area four-lamp excimer lamp system is discussed. Apparatus designed for photo-CVD including the UV-ILS system is also described.
Chapter 4 discusses the photo-CVD processing of TiO$_2$ and (Ta$_2$O$_5$)$_{1-x}$(TiO$_2$)$_x$ films using the UV-ILS source and 222 nm excimer lamps. TiO$_2$ films from around 20 - 510 nm in thickness with refractive indices from 2.20 - 2.54 were grown on crystalline Si and quartz by photo-CVD at temperatures between 50 - 350°C using KrCl* lamps. Film deposition rates around 50 nm/min were achieved at 350°C. The optical band gap of the as-grown films, $E_g$, was found to be 3.35 eV which is close to the accepted value of 3.5 eV for TiO$_2$. Composite (Ta$_2$O$_5$)$_{1-x}$(TiO$_2$)$_x$ films were also grown on quartz and crystalline p-type Si (100) by photo-CVD using 222 nm excimer lamps at temperatures from 50 - 350°C. Band gap energies ranging between 3.2 eV and 4.2 eV were obtained for films of various compositions.

The fifth chapter describes the novel technique of photo-induced sol-gel deposition of TiO$_2$ applied to (Ta$_2$O$_5$)$_{1-x}$(TiO$_2$)$_x$ films using 172 nm lamps. Films of thickness and refractive indices up to 140 nm and 2.4 respectively were grown.

Chapter 6 investigates the low-temperature deposition of ultra-thin SiO$_2$ films by photo-oxidation using 172 nm lamps in an O$_2$ atmosphere. Generally, films with good optical and dielectrical properties have been deposited. These exhibited low leakage currents.

Chapter 7 reviews the results of this research and provides recommendations for further research work. A critical view of the work done and shortcomings is presented.
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Acknowledgements

I would like to dedicate this research to my father, whose passing away happened when I was about to complete this thesis, and to my dear mother.

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Chapter 1

UV sources and general applications

1. Introduction

Thin films are materials bridging the gap between monolayer and bulk structures and they span the thickness range from ~1 nm to ~ several μm [1]. Thin films have been deposited by a myriad of techniques including pyrolysis [2], electron beam evaporation [3], metal - organic chemical vapour deposition (MOCVD) [4], molecular beam epitaxy [5], atomic layer deposition (ALD) [6], hydrolysis of organic and inorganic precursors [7], plasma enhanced chemical vapour deposition (PECVD) [8], reactive r.f sputtering [9], the liquid - phase chemical techniques [10] which include the sol - gel process [11,12], laser deposition [13] and many other methods. Some materials have also been deposited by photo processing using excimer lamp radiation [14-16].

This work explores the ultraviolet (UV) -assisted deposition of materials for optical and dielectric applications. The techniques employed include photo-oxidation, photo-induced sol-gel process and photo-assisted CVD. All these are low-temperature processes occurring over large surfaces.
Photo-oxidation involves oxygen reactions enhanced by UV radiation. Photo-CVD involves the selective decomposition of precursors in the vapour phase by irradiation, and the reaction of components at the substrate surface, resulting in the deposition and growth of required materials. During photo-induced sol-gel processing, organometallic precursors are dispensed onto substrates by the spin-on or dipping process, then irradiated to induce selective bond breaking and grow the required films. The earliest work on sol-gel processing was reported by Blodgett [17]. The sol-gel process requires a drying step that has conventionally been achieved thermally at high temperatures.

When exposed to wavelengths below 250 nm, most materials absorb radiation [18]. This initiates the low temperature photo-induced breaking of bonds in the case of sol-gel polymers during metal–organic decomposition and the formation of reactive free radical oxygen species at atomic and molecular level in the oxidation case. The desired thin oxide film product is thus formed. A full description of the sol-gel process is covered in Chapter 5.

Photo-induced processing includes photo-assisted oxidation, photo-induced sol-gel and photo-CVD and requires reliable and efficient UV radiation sources. Before these techniques are fully discussed, a review is made below of UV sources and their various applications.

1.1 UV Sources

The electromagnetic spectrum is a continuum of all sinusoidal electromagnetic waves arranged according to frequency and wavelength, and travelling at the speed of light. Table 1.1 shows some wavelength regions of the Electromagnetic Spectrum [19]
Table 1.1 Wavelength regions of the Electromagnetic Spectrum [19]

<table>
<thead>
<tr>
<th>Name</th>
<th>Lower Limit (nm)</th>
<th>Upper Limit (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard x-ray</td>
<td>0.01</td>
<td>1</td>
</tr>
<tr>
<td>Soft x-ray</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>Extreme ultraviolet (XUV)</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Vacuum ultraviolet (VUV)</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Ultraviolet (UV)</td>
<td>200</td>
<td>400</td>
</tr>
<tr>
<td>Visible</td>
<td>400</td>
<td>780</td>
</tr>
<tr>
<td>Near Infrared</td>
<td>780</td>
<td>3000</td>
</tr>
<tr>
<td>Intermediate Infrared</td>
<td>3000</td>
<td>6000</td>
</tr>
<tr>
<td>Far Infrared</td>
<td>6000</td>
<td>15000</td>
</tr>
<tr>
<td>Extreme Infrared</td>
<td>15000</td>
<td>10000000</td>
</tr>
</tbody>
</table>

A diagram of the electromagnetic spectrum is shown in figure 1.1 [20].

Figure 1.1 The electromagnetic spectrum
UV radiation refers to that part of the electromagnetic spectrum with wavelengths in the range of about 30 to 400 nm. Table 1.1 shows the extreme, vacuum ultraviolet (VUV) and UV regions, spanning the wavelength ranges 30-100, 100-200 and 200-400 nm respectively. The VUV region, corresponding to the energy range 6.2 – 12.4eV is the most interesting region for UV processing of materials. UV radiation has other sub-divisions, which are UV-A, UV-B and UV-C ranges as shown in figure 1.1 [20]. UV-A or near UV range is wavelengths from 400 nm to 315 nm. UV-B or mid UV range refers to wavelengths from 315 nm to 280 nm and UV-C or far UV refers to shorter UV wavelengths, usually 200 to 280 nm.

Generally, the conventional sources of UV are lamps and lasers. Sources of UV and VUV that have been identified include incandescent, black body radiators, mercury lamps, metal - halide lamps, electrodeless lamps, deuterium lamps, lasers, synchrotron radiation and excimers. Photons in the UV and visible are produced by spontaneous or stimulated radiative transitions between electronic energy levels in atoms and molecules, or two body radiative recombination and electron retardation. Retarding electrons travelling at high speed in circular paths are the source of synchrotron radiation. UV sources emit narrow - band UV or VUV radiation at different photon energies which are useful for photochemical processes.

1.1.1 Incandescent Sources

Incandescent sources include black body radiators, tungsten filament and tungsten halogen lamps. A black body selectively emits at 0.2% efficiency at around 3000K. The power emitted by a black body is given by the Stefan - Boltzmann law:

\[ M(T) = \sigma T^4 \]  

(1.1)

where \( M(T) \) is the total power radiated onto one hemisphere by 1cm\(^2\) of surface at T Kelvin, and the Stefan - Boltzmann constant \( \sigma = 5.6703 \times 10^{-12} \text{Wcm}^{-2}\text{K}^{-4} \) [21].
Filament lamps employ tungsten because its melting point of 3655 K is higher than any metallic element. The lamp operates in the 3000K region. The spectral emissivity of tungsten reaches maximum in the UV and visible and decreases markedly towards the infra-red. Compared to a black body, tungsten is a more efficient source of visible light because its ratio of visible light to infra-red is greater.

A tungsten halogen lamp is filled with gas to which a small amount of a halogen, iodine or bromine is added in order to prevent the tungsten from forming an opaque deposit on the inside wall of the envelope by forming a halide.

1.1.2 Mercury (Hg) lamps

These are available as the low, medium and high-pressure lamps. Hg is ideal as a filling gas for a low pressure lamp for efficient UV production because of its fairly low ionisation energy of 10.43 eV that allows the avalanche effect to take place readily. It has a vapour pressure at 40°C of 7x10^3 torr, which provides the optimum pressure for production of resonance radiation [20]. Although its ionisation energy is reasonably low, the lowest excited state which is not metastable is at such a level above the ground state that the resonance radiation appears at a useful radiation and the element is so chemically inert it can envelope the electrode materials.

Hg is more volatile than any other metal. It is introduced as a single drop and almost all the Hg remains in the liquid form during lamp operation. An inert, non-radiative Ar gas aids starting through the reduction of the starting voltage by allowing an increase in the number of collisions with electrons. Most of the radiation emitted by a low pressure Hg lamp peaks at 253.7 nm and 185.0 nm produced by the transitions 6^3P_1 \rightarrow 6^1S_0 and 6^1P_1 \rightarrow 6^1S_0 [22]. The 253.7 nm output is more pronounced than that at 185.0 nm. Self absorption is, however prevalent at these wavelengths. The low pressure Hg fluorescent lighting tube comprises a glass envelope coated on the inside with a fluorescent powder which converts the resonance Hg radiation at 253.7 nm into
white visible light. The low pressure Hg lamp however, requires a ballast in series with it for stable operation since it has a negative characteristic.

The medium pressure Hg lamp is an arc discharge operating at pressures in the range 100 - 10000 torr. The temperatures of the electrons, atoms and ions become almost identical. The plasma temperature is in the region of 5000 - 7000K. Most medium pressure Hg lamps operate from an a.c. supply with electrodes frequently interchanging the role of anode and cathode. During normal operation, electron current to the lamp is supplied by thermionic emission from the hot electrodes. Thermionic emission from an electrode is given by the Richardson - Dushman equation:

\[
J = AT^2 \exp \left( -\frac{e\phi}{kT} \right)
\]

where \( J \) is the current density (A/cm\(^2\)), \( T \) is the absolute temperature, \( e \) is the electronic charge, \( \phi \) is the work function (eV), \( k \) is the Boltzmann constant and \( A \) is the emission coefficient for a particular surface = 120Acm\(^{-2}\)K\(^{-2}\) for pure metals. Emissive materials are used to reduce the electrode temperature required for adequate thermionic emission since tungsten has a high work function. In this lamp, all the Hg evaporates with the coolest part of the tube maintained at a temperature in excess of 400°C and the main body at 600-800°C during stable operation to maintain the pressure required. The medium pressure Hg lamp circuitry must enable an arc to be established and control the current passing through the lamp and in the case of ac lamps allow the arc to be re-established every half cycle. The output of Hg lamps in the visible consists only of a few strong lines. Radiation at 436 nm contributes little to the total lumen output, and the lack of radiation in the red part of the spectrum above 600 nm gives the Hg light a characteristic blue-green colour. The lamp requires the use of a suitable ballast. Due to lamps operating at high Hg pressure they have a higher impedance per unit length of arc and consequently, long lamps require a step-up transformer.
The high pressure Hg lamps are useful where very high intensity compact sources of spectrally continuous radiation are required. These are the electrode-confined compact arc and the wall-stabilised capillary arc. The high pressure Hg arc has a spectral output, which shows strong line broadening, a strong continuum and pronounced self-absorption, particularly of 254 nm radiation.

1.1.3 Metal-halide lamps

Metal-halide lamps are constructed in the same way as medium pressure Hg lamps. The addition of metallic elements in the form of volatile halides to the discharge gives some enhancement at certain wavelengths. Chlorides, bromides and iodides which are the most volatile, are usually employed. Fluorides are too reactive. The metal halide is required to have a strong output in the spectral region needing enhancement, and have a low vapour pressure at ambient temperature. It must be stable at normal wall temperatures, have a fairly high vapour pressure at normal wall temperatures and must be unstable at the temperature of the discharge. Metal halide lamps that have been used include thallium halide (535.0 nm), gallium iodide (intense at 403.3 and 417.2 nm), lead iodide (364.0, 368.3 and 405.8 nm), iron iodide (between 350 and 450 nm), antimony iodide (between 200 and 320 nm) and magnesium iodide (many peaks between 240 and 580 nm) [20].

1.1.4 Electrodeless lamps

The electrodeless lamp uses a chamber normally filled with Hg and an inert gas. The discharge tube absorbs microwave energy fed via waveguides into a microwave chamber in which a tube is housed. The modular lamp system consists of an irradiator and a power supply. Microwave energy at 2450MHz is generated by two 1500W magnetrons and is fed through waveguides into the chamber via rectangular slots cut in the back of the reflector [20]. The magnetrons and waveguides as well as the lamp are air-cooled. The lamp with no electrodes and having a much narrower and lighter tube than a conventional electrode lamp warms up within seconds. A wide
choice of metal halide additives can be used to enhance parts of the spectrum for particular applications since the problems associated with electrodes are eliminated. Electrode losses are non-existent and the discharge fills virtually the entire length of the tube.

1.1.5 The deuterium lamp

The hydrogen or deuterium (D or $^2$H) lamp is a low pressure (5-10torr), low power (20-200W), compact source of quite high intensity. It operates between 60-120V, at a discharge current of 0.2 - 2.0A. The dc arc discharge lamp gives a line-free continuum between 170 and 350 nm, with peak output at about 200 nm. An aperture placed between the cathode and anode constricts and stabilises the arc. The lamp produces a point source with a low overall efficiency.

Figure 1.2 below [23] shows a range of laser wavelengths commonly used for materials processing as well as typical spectra of hot tungsten filament and Xe arc lamps and the strongest lines available using an Hg discharge.

1.2 Lasers

The laser comprises an active medium which may be a solid, liquid or gas containing a pair of energy levels radiatively connected by a photon energy of the required wavelength and is located in the resonant cavity, a highly reflective mirror and a partially transmissive mirror. Its principle lies in population inversion, which is the non-equilibrium situation in which the population density of the excited state is higher than the population density of the ground state. This inversion is achieved by pumping. An intense source of energetic incoherent or coherent photons is employed during pumping. The pumping processes include optical by the c.w. or pulsed laser
light emitted by a powerful lamp or a laser beam or electrical by a c w, radio-frequency or pulsed
current flowing in a conductive medium such as an ionised gas or a semiconductor. Pumping is
carried out in a three level system in which the lower laser level is also the ground state or four
level system in which the lower laser level is above ground state. A population inversion is
produced more easily in the four level system. In quasi - three level lasers, the ground level
consists of many sublevels, the lower laser level being one of these sublevels. Optical pumping by
an incoherent source involves the absorption of light from a powerful lamp by the active medium,
so that atoms are pumped into the upper laser level. X-ray pumping involves a medium excited by
a beam from an x-ray source and is similar to optical pumping. Optical pumping efficiencies range
from 3-8% [24]. Electrical pumping is accomplished by means of a sufficiently intense electrical

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*Figure 1.2* Output power and spectra from commercial UV lasers and lamps [23] with p, q, and
r representing lamps on the right hand scale; (a)-F2, (b)-ArF, (c)-KrF (d)-XeCl, (e)-N2, (f)-XeF,
(g) and (h) Ar ion laser, (i) Kr ion laser, (j) ruby laser, (k) Nd:YAG or Nd:glass laser, (l)-CO2
laser, (m)-a series of tuning curves available from various dye laser systems above and/or flash
lamps, (r)-tungsten lamp, (q)-Xenon arc lamp and (p)- Hg lamp
discharge and is particularly suited to gas and semiconductor lasers. E-beam pumping involves a medium excited by a beam of electrons from an electron beam machine.

### 1.2.1 Properties of Laser Radiation

These include:

- a) high beam power,
- b) directionality,
- c) high peak beam power density,
- d) spatial coherence,
- e) monochromaticity
- f) and pulses of very short duration (less than 1μs for inducing multiple photon dissociation, and for obtaining rapid local heating of substrates).

Whereas the radiating surface of an incoherent source emits in all directions into a hemisphere, the radiation from a laser is highly directional. As the beam is generally small in diameter, the beam power density can be very high. Laser pulses of very short duration can be obtained and Q switching produces pulses lasting a few nanoseconds.

### 1.2.2 Laser Types

Laser types discussed here are the optically pumped solid, semiconductor diode, dye, gas and excimer lasers. A discussion is further made on their advantages and disadvantages.

#### 1.2.2.1 Optically pumped solid state lasers

Optically pumped solid lasers employ ions of transition or rare earth elements as impurity dopants in crystalline or glass matrices. These include ruby lasers emitting at 694.3 nm and used in the pulsed mode and neodymium (Nd) lasers emitting at 1.06 μm and operated in c.w. mode.
Nd:YAG lasers can either operate in c.w. or pulsed mode, and can be pumped by a lamp or AlGaAs semiconductor laser. Q-switched lasers have second harmonic ($\lambda=532$nm), third harmonic ($\lambda=355$nm) fourth harmonic beams ($\lambda=266$nm) as well as mode locked lasers, with Nd:YAG lasers with intracavity second harmonic generation giving a green ($\lambda=532$nm), c.w. output power up to ~10W also available [24].

1.2.2.2 Semiconductor diode injection lasers

When a flat p-n junction is formed between p- and n- doped semiconductor crystal a forward voltage brings electrons and holes into the same region and their recombination is accompanied by emission of photons. If current density is high enough, stimulated emission occurs. Electrical energy is directly converted into coherent radiation. The laser, which has very small dimensions, is normally operated in the pulsed mode.

1.2.2.3 Dye Lasers

The organic dye laser uses an organic fluorescent material dissolved in a common solvent. The solution may be used in a cell for pulsed operation or in the form of a jet flowing from a nozzle for c.w. The laser is pumped by another laser or a flashlamp. The laser is tuneable with any wavelength required being selected by the use of a prism, grating or filter within the resonant cavity.

1.2.2.4 Gas lasers

Gases are optically homogeneous and can be circulated for cooling. Chemical lasers can be employed. Elementary chemical reactions lead to an inverted population by selectively partitioning exothermic reaction energy among non-equilibrium vibrationally excited products. Reactions take the form:
Photodissociation lasers use intense UV light to split a molecule so that one of the products is an excited state. The majority of gas lasers use electrical discharge through the gas to create the population inversion. As in the discharge lamp, energy is absorbed from the electric field by the acceleration of electrons and ions and these transfer energy to the components of the gas mix by collisions. These include the He - Ne laser operating a c.w. at low power usually only a few milliwatts at 632.8 nm, Ar ion and Kr ion lasers operating at various wavelengths in the UV and visible regions, and CO₂ lasers containing a mixture of CO₂, N₂ and He. In the CO₂ laser, energy transfer occurs from N₂ molecules in their first vibrationally excited state to CO₂ molecules. The laser is tuneable between 9.3 and 11.0μm. He enhances the excitation of N₂ by collisional energy transfer and by increasing the rate of depopulation. The CO₂ laser is capable of producing more c.w. power than any other laser. The He-Cd laser uses Cd ions to emit at 325 and 442 nm. The Cu vapour laser emits at 510 and 578 nm. The N₂ laser emitting at 337 nm uses transitions between electronic energy levels [20].

1.2.2.5 Excimer lasers

These are halogen dimer lasers F₂ (157 nm), Br₂ (292 nm), I₂ (342 nm) and rare gas halide excimer lasers that include ArF (193 nm), KrF (248 nm), XeF (352 nm), ArCl (175 nm), KrCl (222 nm), XeCl (308 nm) and XeBr (283 nm) [21,24].

Table 1.2 [25] shows a summary of characteristics of the most commonly used laser systems in materials processing.
Table 1.2. Properties of some of the commercially available high-power/energy lasers [25]

<table>
<thead>
<tr>
<th>Laser type</th>
<th>Wavelength (µm)</th>
<th>Power (W)</th>
<th>Energy (mJ)</th>
<th>Pulsewidth (ns)</th>
<th>Beam size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>9-11</td>
<td>500</td>
<td>5000</td>
<td>200</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>CO</td>
<td>5-7</td>
<td>100</td>
<td>1000</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Nd : YAG</td>
<td>1.064</td>
<td>500</td>
<td>1200</td>
<td>4-20</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Nd : glass</td>
<td>1.054</td>
<td>500</td>
<td>5000</td>
<td>4-50</td>
<td>10</td>
</tr>
<tr>
<td>He : Ne</td>
<td>0.63</td>
<td>0.01</td>
<td>5</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Nd : YAG</td>
<td>0.532</td>
<td>600</td>
<td>4-20</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Cu vapour</td>
<td>0.51-0.58</td>
<td>10</td>
<td>20</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Ar ion</td>
<td>0.48-0.51</td>
<td>20</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ar ion</td>
<td>0.35</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Nd : YAG</td>
<td>0.355</td>
<td>300</td>
<td>4-20</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Kr ion</td>
<td>0.33-0.35</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>XeF</td>
<td>0.351</td>
<td>5</td>
<td>20</td>
<td>20x10</td>
<td></td>
</tr>
<tr>
<td>XeCl</td>
<td>0.308</td>
<td>10</td>
<td>20</td>
<td>20x10</td>
<td></td>
</tr>
<tr>
<td>Nd : YAG</td>
<td>0.266</td>
<td>200</td>
<td>4-20</td>
<td></td>
<td>20x10</td>
</tr>
<tr>
<td>KrF</td>
<td>0.248</td>
<td>100</td>
<td>20</td>
<td>20x10</td>
<td></td>
</tr>
<tr>
<td>ArF</td>
<td>0.193</td>
<td>400</td>
<td>20</td>
<td>20x10</td>
<td></td>
</tr>
</tbody>
</table>

1.2.2.6 Advantages and disadvantages of conventional lamps and lasers

Laser-induced processes can occur at ambient temperature and pressure without the need for complicated vacuum equipment. Some lasers produce high power beams which lead to high photo induced rates. Lamps provide large area beams and are useful for a variety of large - area processes and are inexpensive. Most lamps have a simple construction and some, such as the electrodeless lamp have long lifetimes.

Low pressure Hg lamps contain a few millitorr of metal vapours, have relatively low VUV and UV intensities (e.g. \( \lambda = 185 \) nm, 3mW/cm²; \( \lambda = 254 \) nm, 10mW/cm²) [22], and consequently very
slow photoinduced reaction rates. Electrodeless lamps are available in one size only, with the irradiator module containing the lamp, reflector, magnetrons, waveguides and other equipment having a large size. Radiation emitted by the electrodeless lamp is attenuated in the wire mesh screen and magnetrons generate microwave energy with rather low efficiency and need replacement about every 5000 hours, thus increasing lamp running costs [20]. Conventional lamps generally produce low power low intensity radiation especially towards the DUV. Lasers are non-uniform sources, which produce monochromatic, coherent irradiation. High fluence lasers, which provide only small area beams, generally have low overall efficiencies and mean power outputs. Lasers require a huge capital outlay cost much higher than conventional incoherent sources. Their operational and maintenance costs are very high. Only a limited number of excimer laser wavelengths are available at high power levels such as $\lambda = 193$ nm (ArF*), $\lambda = 248$ nm (KrF*), $\lambda = 308$ nm (XeCl*), $\lambda = 351$ nm (XeF*) [21, 22].

1.3 Excimer lamps

Since traditional UV and VUV lamps have limitations in intensity and efficiency and slow processing rates as seen above, a demand has grown for new high-power, low cost and large-area UV and VUV sources. On the other hand, lasers have prohibitive costs and cannot pattern large areas. UV sources of wavelengths shorter than 200 nm are needed to radiate the precursor molecules and higher photon fluxes are required to achieve higher deposition rates. Excimer UV sources with high intensity are an attractive alternative to conventional UV lamps and lasers for large – area industrial applications. Excimer lamps have a long lifetime because the electrodes are not in direct contact with the discharge gases thus avoiding any corrosion during the discharge process and no contamination of the excimer gas, which occurs in conventional lamps, leading to the contamination of the discharge gas and the short lifetime of lamps. They have a simple construction and are not expensive. Sealed lamps of different planar and cylindrical geometries can be designed. Moreover, available excimer lamps have the capability of producing high power radiation from the near UV ($\lambda = 354$ nm) to the VUV ($\lambda = 108$ nm) over large areas [26 - 29]. The structure of excimer lamps is discussed in Chapter 3.
1.4 Applications of UV sources

UV and VUV have applications in microelectronics, optoelectronics, protective and decorative coatings and optical coatings [30], photo-assisted oxidation, curing of photoresins, production of ozone, water treatment and cracking of gaseous waste products, UV curing, surface modification, etching and photo-induced processing of materials. VUV photons in the order of 10eV can break chemical bonds of many compounds. Many materials absorb radiation wavelengths shorter than 250 nm, very efficiently [18]. Moreover, low temperature processing is gaining pre-eminence as a means of reducing the thermal budget in device fabrication. Photo-induced deposition of insulating or protective layers has received considerable attention as a low temperature processing method [31, 32]. Much photo-assisted processing work has been carried out by laser chemical deposition [33] and low pressure mercury lamps [30, 34] as well as deuterium lamps [22]. Excimer lamps have been successfully applied for large-area processing optical and dielectric materials [18, 35].

1.4.1 Photo-induced materials deposition

The first application of excimer lamps for the deposition of silicon dioxide (SiO₂), silicon nitride (Si₃N₄) and silicon oxynitride (SiOₓNₙ) films used mixtures of silane, nitrous oxide and ammonia [14, 35-36]. UV sources have been widely applied to deposit various dielectric and amorphous semiconductor materials including Si₃N₄ [14], a-Si:H [15], a-SiC:H [16], Ta₂O₅, [37-39], PZT [40] and many others.

1.4.2 UV-induced metal deposition

Metal deposition has been carried out by photo-decomposition of metallo-organic precursors, by laser-induced metallo-organic decomposition (L-MOD) techniques and by UV lamps. As already discussed, the latter have the advantage in the ability of processing over large surface
areas. Excimer UV lamp induced decomposition of palladium acetate films to deposit Pd of up to 80 nm thick was demonstrated at wavelengths of 308, 222 and 172 nm [18]. As expected, metal deposited at low wavelengths was found to be the thickest. Au was deposited on Al₂O₃ using a deep UV Hg/Xe lamp [41] and platinum by an argon ion laser at 515 nm [42], with Cu layers up to 50 nm grown [43]. Area-selective definition of complex circuits and interconnections by imaging technology or contact masks can be obtained without the need of photolithography. Other radiation sources that have been used for L-MOD process include argon ion lasers, excimer lasers, Nd:YAG lasers, synchrotron emission and UV lamps [44]. Considerable interest has been focused on metal deposition by laser induced decomposition of precursors [45 - 46].

1.4.3 Surface Coatings

Surface coating involves the application of a thin film of one material to another for purposes including protection against chemical attack, decoration, modification of optical properties, improvement of surface mechanical properties, modification of surface electrical properties and others. Many conventional coating materials contain environmentally unfriendly non-reactive solvents, which are also fire hazards. Photopolymerisation provides many potential advantages for UV curing of surfaces.

1.4.4 UV Curing

UV curing is a photochemical process that involves the polymerisation of special paints, inks, varnishes, coatings, adhesives and sealing compounds as a result of their irradiation with UV light instead of heat in a wide range of industrial applications. Excimer UV and VUV sources have been successfully applied for photo-polymerisation processes at ambient temperatures [47 - 48]. UV curing meets the demands for increased productivity, lower cost and greatly reduced emissions. UV light induced photo-chemical polymerisation processes are used for curing
structural adhesives for bonding glass, ceramics, ferrites, plastics and metals, potting compounds and encapsulants in the electrical, electronic and optoelectronic industries. Advantages of UV light curing processes over conventional curing processes include:

a) rapid curing times in some cases almost instantaneous, allowing immediate further processing,

b) on demand cure during which cure occurs only on exposure to UV light,

c) no solvents (100% solids) with no environmental pollution due to solvent evaporation,

d) single-component ready to use systems with no mixing, no waste, no waste disposal, no cleaning of mixing containers,

e) no problems with pot life of mixed materials,

f) no heat required thus low thermal stressing of substrate materials,

g) minimal space requirements and capital expenditure,

h) ready adaptation into existing production facilities

i) and the possibility of automatic dispensing and curing, leading to improved production efficiency.

The UV curing of polyimide for interlayer dielectrics is covered in the next chapter.

1.4.5 Photo-etching

Photo-etching involves the complete or partial removal of unwanted material from a surface through its exposure to UV irradiation. UV is suitable for native or chemical oxide etching including pre-metal oxide etch of silicon oxides. An example is the oxide etching by UV irradiation in conjunction with HF / CH3OH on the surface of silicon to control moisture level [49].
1.4.6 Water purification

There is an increasing need for ultrapure water in industry, for many processes that include the fabrication of microcircuits, production of pharmaceuticals and for use in boilers. As already discussed, UV can easily dissociate O₂ to ground state radical O atoms with the subsequent formation of ozone (O₃). This results in the UV / O₃ and UV / H₂O₂ combinations. The UV / O₃ combination is capable of reducing the organic content of water to extremely low levels, resulting in the production of water of a low total organic content [20]. This is because UV and O₃ have a very powerful oxidising action particularly in the presence of water and its vapour, with the formation OH radicals. Under the right conditions it is possible to convert all organic carbon to CO₂. The UV / O₃ combination is suitable not only for treating water, but also for deodorising air streams. Examples of contaminants, which may be removed from water, include dyes, pesticides and polynuclear aromatic hydrocarbons [20]. The UV / H₂O₂ combination also yields OH radicals and is capable of removing organics from water.

1.4.7 Surface cleaning

UV radiation is effective in removing traces of contaminants left behind after conventional solvent cleaning processes on solid surfaces such as metal and quartz. Such surface cleaning is employed in silicon IC processing for applications including pre-oxidation surface treatments, organic removal prior to metallisation and epitaxial deposition. The output of the UV source is matched to the energies required for efficient photolysis, with the best established photochemically enhanced cleaning process being the UV / O₃ removal of organic contaminants. The basic requirement is for a continuous generation of the oxidising agents, atomic oxygen and O₃.
1.4.8 Photo-chemical reactions

Some organic compounds can only be synthesised by photochemical means. One of the most important applications of industrial photochemical synthesis is the chlorination of hydrocarbons by long wavelength UV in the reaction:

\[
\text{hv} \quad \text{Cl}_2 \rightarrow 2\text{Cl}^* \quad (1.4)
\]

\[
\text{Cl}^* + \text{RH} \rightarrow \text{R}^* + \text{HCl} \quad (1.5)
\]

\[
\text{R}^* + \text{Cl}_2 \rightarrow \text{RCl} + \text{Cl}^* \quad (1.6)
\]

- where \( \text{Cl}^* \) and \( \text{R}^* \) represent highly reactive, unstable photo-excited chlorine atoms and alkyl molecules respectively.

Generally, the photochemical route allows lower reaction temperatures and consequently a low thermal budget.

1.4.9 Photo – resists

A coating applied to a surface to protect it against chemical or physical effects is a resist. A photoresist is one in which a photochemical reaction is required to alter the solubility of the resist material. The photoresist material may be coated over an entire surface and then selectively irradiated through a mask. The resist is then developed in a suitable solvent to remove the soluble material. Photoresists have applications in the production of printed circuit boards and integrated circuits in the electronics industry, processing of lithographic plates, etching of glass and in the printing industry. In dry film photoresists, the photoresist material is supplied as a dry thin film sandwiched between two thin plastic films, one of polyester, the other of polyethylene. The
polyethylene film is removed and the photoresist is laminated to the substrate prior to use. The polyester film protects the material until after the irradiation process. In deep UV lithography, wavelengths <300 nm are required for the resolution of submicrometre details. Sources of intense short wavelength radiation are required. The most widely used “deep UV” photoresist has been poly methyl methacrylate, which has peak absorption at 215 nm and is transparent above 260 nm [20].

1.4.10 Excimer Lamps and applications

Excimer lamps have been tested for applications that include the generation of ozone, oxidation of surfaces, water treatment, surface cleaning, treatment of inks, metallo-organic decomposition and deposition of materials. These are covered in detail in the next chapter.

1.5 Conclusion

A description has been made of the various UV sources and their applications. The sources include lasers and lamps. These are mainly used for low – temperature processing. Chapter 2 discusses the principles of excimer lamp operation, the various types of lamps available and their configurations. A detailed review of excimer lamp applications is given.
1.6 References


Chapter 2

Excimer lamps and their applications

This chapter discusses excimer lamps, their principles and applications. A review is made of materials deposited by metallo-organic decomposition (MOD).

A study of the background of these lamps traces back to 1857, when Siemens used an annular discharge gap between two coaxial external electrodes and an axial gas flow to produce ozone [1]. In 1955, Tanaka first used it for excitation of rare gases [2]. In 1987, the first industrial application of dielectric barrier discharges in ozone production was reported [3]. In 1989, Esrom et al achieved metallisation with excimer lamps [4]. In 1992, dielectric materials were deposited at UCL using excimer lamps [5]. To the present day, research in the area has burgeoned with the growth of high and low dielectric constant dielectric films, photo-oxidation of Si, UV curing, etching of polyimide and other applications.
2.1 Excimer lamps

When a voltage applied across a pair of parallel electrodes, separated by a gap distance $d$ and immersed in a gas of number density $n$, is slowly increased, then an electrical breakdown of the gas occurs at some critical breakdown voltage, $(V_{bd})$ [6]. By Paschen's law:

$$V_{bd} = f(nd)$$  \hspace{1cm} (2.1)

with Paschen voltage given by the smallest constant voltage needed to initiate breakdown in the gap.

When an alternating high voltage is applied to the gap, electron avalanches are propagated from the cathode towards the anode. In silent discharges, a field which is self-induced locally at the avalanche head enhances the field applied towards the anode by superposition. High-energy tail electrons of the avalanche are thus accelerated, leading to fast propagation of the electron charge towards the anode. On reaching the anode, the field due to the space charge is reflected towards the cathode, ionising atoms and molecules in its way. Some of the excited atoms and molecules emit UV photons during the passage of the electrons. Continuous discharge thus occurs, with each microdischarge spreading into surface discharges at the dielectric boundaries. An alternating high voltage of typically a few kV amplitude is adequate to sustain such microdischarges. The frequency of the applied voltage can vary over a wide range, from 50 Hz to 1 MHz, with the discharge operable at elevated pressures of between 0.1-10 bar [7]. The properties of these microdischarges have been extensively studied by using different rare-gases and halogens in...
dielectric barrier discharge (DBD) [3, 8-10]. Figure 2.1 shows a picture of microdischarges from an excimer lamp.

Figure 2.1 Photograph showing excimer microdischarges

A model of silent discharges proposed by Eliasson and Kogelschalz is shown in figure 2.2 [7]. In this model, four processes identified are:

a) the application of an electric field;

b) production of fast electrons and ions during a very small time;

c) excitation of atomic and molecular species by the electrons and

d) initiation of chemical reactions.
Figure 2.2 Schematic illustration of the interplay of discharge physics and plasma chemistry in the silent discharge [7].
An excimer (excited dimer) is a complex containing two molecules, and is stable only in an electronically excited state [11]. Excimers under normal conditions do not possess a stable ground state. Because of their instability, excimer complexes disintegrate within typically a few ns and their excitation energy is converted to spontaneous emission of UV photons. Upon decay, a large number of excimers, emit spontaneous radiation in the spectral range from 50 nm to 600 nm, thus covering the energy range most important for photoinduced bond breaking [12]. Such emissions are associated with a bandwidth of 10-20 nm.

An excimer lamp's operation relies on the radiative decomposition of excimer states created by a dielectric barrier discharge or silent discharge. This usually occurs in a rare gas or rare gas-halide complex. The silent discharge is a high-pressure non-equilibrium discharge in which the plasma parameters can be optimised for the excimer formation process [12]. Silent discharge excimer UV sources can provide much higher intensities than conventional lamps and a choice of different wavelengths in the desired VUV ranges. Practically, any known excimer can be formed in silent discharges if the gas mixture and the operating conditions are properly chosen [13]. Excimer lamps have the capability of producing high power radiation from the near UV (λ = 354 nm) to the VUV (λ = 108 nm) over large areas for continuous wave processing [8, 14 - 16]. The introduction of novel excimer lamps has made possible the emission of up to 22 wavelengths in dielectric barrier discharges from the vacuum ultraviolet (<200 nm) to the visible part of the spectrum [17, 18].
2.1.1 Rare gas excimers, halogen excimers and rare gas halide exciplexes

High density rare gases at around or above atmospheric pressure can convert electron kinetic energy to electron excitation energy and pass that excitation to a few low lying atom and excimer levels [19]. Theoretical predictions of the fluorescence efficiency of rare gas excimer radiation lie in the 45-80% range [13]. Rare-gases (Rg) emit bright continua and resonance lines across a range of wavelengths between 100 - 300 nm. Table 2.1 shows the different resonance lines and continua of rare-gases, created by discharge excitation [20, 21].

<table>
<thead>
<tr>
<th>rare-gas</th>
<th>I/II Resonance line (nm)</th>
<th>I Continuum (nm)</th>
<th>II Continuum (nm)</th>
<th>III Continuum (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>106.4/104.8</td>
<td>110</td>
<td>126</td>
<td>188</td>
</tr>
<tr>
<td>Kr</td>
<td>123.6/116.5</td>
<td>125</td>
<td>146</td>
<td>220..270</td>
</tr>
<tr>
<td>Xe</td>
<td>146.96/129.56</td>
<td>150</td>
<td>172</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 2.1 Resonance lines and continua of Ar, Kr, and Xe gas in high pressure discharge [20, 21]

The resonance lines (I/II) are attributed to the transitions from the $^3P_1 \rightarrow ^1S_0$ and the $^3P_2 \rightarrow ^1S_0$ states. Two "first continua" emitted at the shorter wavelengths result from the transitions of two lowest excited dimer states ($^1Σ_u^+, ^3Σ_u^+$) of the neutral molecule $R_g^* \leftrightarrow R_g^*$ to the repulsive ground state. The third continua corresponds to transitions between the $R_g^{2+} \leftrightarrow R_g$ states and this can usually only be initiated by rare-gas excitation with protons, a particles, and electron beams [21].
Figure 2.3 presents the potential energy diagram of xenon and its corresponding excimer emission [15]. The excimer continua and resonance line of xenon are visible in figure 2.4. It has been noted that the wavelength of the VUV peak intensity can be changed by adjusting the pressure in the discharge, and it was found that at a low pressure of 40 mbar the peak at 147 nm was due to the resonance line (1) of xenon, resulting from a transition $^3P_1 - ^1S_0$ [15]. Increase in pressure changes the wavelength generated from the resonance lines to higher continua.
The first continuum corresponding to transitions from vibrationally excited excimer states $(^1\Sigma_g^+, ^3\Sigma_u^+)$ to the shallow minimum of the ground state was found to appear at a pressure of 150 mbar. The dominant emission feature at pressures of 500 mbar and greater is the second excimer continuum peaking at 172 nm.

The formation of excited rare-gases and rare-gas halides from ions and electrons begins with dissociative attachment of electrons to the rare-gas/halogen [6, 13]. In the case of xenon and chlorine, the following route is taken:
with the formation of the rare-gas dimer $\text{Xe}_2^*$, occurring through the three-body reaction of excited $\text{Xe}^*$ with another $\text{Xe}$ atom or buffer gas.

\[
e^- + \text{Xe} \rightarrow \text{Xe}^* + e^- \quad (2.2)
\]

\[
e^- + \text{Xe} \rightarrow \text{Xe}^+ + 2e^- \quad (2.3)
\]

\[
e^- + \text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}^* \quad (2.4)
\]

where $M$ is a collisional third partner which in many cases can be an atom or molecule of the active species or even of the buffer gas.

For efficient excimer formation, electrons of a suitable energy distribution are needed to create the necessary precursors by electron impact. These precursors can be excited atomic or molecular species as well as ions; the pressure has to be high enough for the three body reactions to occur faster than any decay or quenching processes that can deactivate the excited precursors. In practice, electron energies of about 10eV and pressures of the order of 1 bar are required, and these can be met only in a non-equilibrium discharge.
Table 2.2 shows the main peak wavelengths of rare-gas (Rg) halide excimers at high pressures [8, 22]. Most XeCl* exciplexes (excited complexes) can be created by the recombination of positive xenon ions and negative chlorine ions (2.6) or the reaction (2.7) in which the excited Xe* species react directly with a chlorine molecule [13].

\[
\begin{align*}
Xe^+ + Cl^- + M &\rightarrow XeCl^* + M \quad (2.6) \\
Xe^* + Cl_2 &\rightarrow XeCl^* + Cl \quad (2.7)
\end{align*}
\]

Excimer molecules are not very stable and once formed decompose within a few nanoseconds giving up their excitation energy in the form of a VUV or UV photon.
\[ \text{Xe}^*_2 \rightarrow 2\text{Xe} + h\nu \text{ (172 nm, VUV radiation)} \quad (2.8) \]

\[ \text{XeCl}^* \rightarrow \text{Xe} + \text{Cl} + h\nu \text{ (308 nm, UV radiation)} \quad (2.9) \]

A large number of different emission spectra of excimers can be obtained from rare-gas excimers, rare-gas halide exciplexes and halogen dimers [3, 15]. A selection of excimers obtained in dielectric barrier discharges is shown in figure 2.5. Also shown is the binding energy of several common chemical covalent bonds [20]. Selective photochemical processes can be induced by matching excimers with the bond energies.

Figure 2.5 Wavelengths of excimer VUV and UV radiation and binding energy of chemical bonds [16]
Table 2.3  Peak wavelengths and photon energies of excimer emission bands obtained from various dielectric barrier discharges

<table>
<thead>
<tr>
<th>Excimer</th>
<th>Wavelength (nm)</th>
<th>Photon energy (eV)</th>
<th>UV range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NeF*</td>
<td>108</td>
<td>11.48</td>
<td></td>
</tr>
<tr>
<td>Ar₂*</td>
<td>126</td>
<td>9.84</td>
<td></td>
</tr>
<tr>
<td>Kr₂*</td>
<td>146</td>
<td>8.49</td>
<td></td>
</tr>
<tr>
<td>F₂*</td>
<td>158</td>
<td>7.85</td>
<td></td>
</tr>
<tr>
<td>ArBr*</td>
<td>165</td>
<td>7.52</td>
<td></td>
</tr>
<tr>
<td>Xe₂*</td>
<td>172</td>
<td>7.21</td>
<td></td>
</tr>
<tr>
<td>ArCl*</td>
<td>175</td>
<td>7.08</td>
<td></td>
</tr>
<tr>
<td>KrI*</td>
<td>190</td>
<td>6.49</td>
<td></td>
</tr>
<tr>
<td>ArF*</td>
<td>193</td>
<td>6.42</td>
<td></td>
</tr>
<tr>
<td>KrBr*</td>
<td>207</td>
<td>5.99</td>
<td></td>
</tr>
<tr>
<td>KrCl*</td>
<td>222</td>
<td>5.58</td>
<td></td>
</tr>
<tr>
<td>KrF*</td>
<td>248</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td>XeI*</td>
<td>253</td>
<td>4.91</td>
<td></td>
</tr>
<tr>
<td>Cl₂*</td>
<td>259</td>
<td>4.79</td>
<td></td>
</tr>
<tr>
<td>XeBr*</td>
<td>283</td>
<td>4.41</td>
<td></td>
</tr>
<tr>
<td>Br₂*</td>
<td>289</td>
<td>4.29</td>
<td></td>
</tr>
<tr>
<td>XeCl*</td>
<td>308</td>
<td>4.03</td>
<td></td>
</tr>
<tr>
<td>I₂*</td>
<td>342</td>
<td>3.63</td>
<td></td>
</tr>
</tbody>
</table>

The peak wavelengths and photon energies of excimer emission bands obtained from various dielectric barrier discharges are shown in table 2.3. As can be seen, the peak wavelengths are in the range 108 nm (NeF*) to 342 nm (I₂*). The most powerful commercial excimer lamp reported is a microwave driven XeCl*(308 nm) source with a UV output of 900W, and an efficiency of 15% [23]. It uses sealed cylindrical quartz bulbs of 25 cm length mounted in an elliptical microwave cavity, which also acts as an optical collection system. This excimer lamp is mainly used for UV curing processes [24-25].
2.1.2 Excimer lamp geometries

The common lamp geometries are the classical and dielectric barrier discharge (DBD). In a classical discharge, the electrodes are directly in contact with the discharge gas and plasma, whereas in a DBD an insulator separates the electrode and discharge. During discharge electrode etching and corrosion occur in the former, whereas, in the latter they are eliminated by the insulator. A schematic of both classical and DBDs is shown in figure 2.6.

![Schematic of classical and dielectric barrier discharges](image)

*Figure 2.6 Schematic of classical and dielectric barrier discharges*

A device for UV light generation based on the DBD principle requires two electrodes covered with a dielectric and a glass cell filled with the required gas at a pressure of a few hundred torr. The glass cell is pumped down to $10^6$ torr, filled with gas or gas and then sealed. To avoid
generation of lower energy radiation from contaminants, the gas must be enclosed in a very pure, clean chamber of material which does not degas even at high temperatures.

This work employs excimer lamps in a DBD. In many cases a third buffer gas (He, Ne) is added to the binary excimer forming mixture. This facilitates ignition and provides additional control over the electron energy distribution. The width of the discharge gap ranges from 0.1mm to several mm. Filling pressures range from $10^4$ to $5 \times 10^3$ Pa, operating frequencies from 50 Hz to 1MHz, applied voltages from a few hundred volts to several kilovolt. Different geometries of excimer lamps are possible, with cylindrical or planar configurations [26].
Figures 2.7 and 2.8 show the cylindrical and planar excimer lamp configurations. These have one or more insulating layers in the current path between metal electrodes. The cylindrical configuration used for this research has an inner electrode in the form of a spiral and the outer in a mesh. The inner electrode is located in circulating deionised water that acts as a cooling agent, and the outer electrode is connected to the ground. The high voltage high frequency ac generator is connected to the inner electrode and shares a ground connection with the outer electrode.

![Diagram of excimer lamp configurations](image)

*Figure 2.8 Common dielectric - barrier discharge electrode configurations*
2.1.3 Advantages of DBDs

UV excimer lamps operate over large areas. Due to the absence of a stable ground state, self-absorption of emitted excimer radiation is not likely to occur. Because of their modular structure, DBDs can easily be scaled up for industrial use. UV radiation can be transformed to visible light by adding phosphors to excimer lamps. The measured energy conversion efficiency of excimer lamps has been found to range from 7 to 15 % [22, 27]. With excimer lasers only a limited number of wavelengths are available at high power levels such as $\lambda = 193$ nm (ArF*), $\lambda = 248$ nm (KrF*), $\lambda = 308$ nm (XeCl*), $\lambda = 351$ nm (XeF*), whilst much lower powers can be obtained using F*$_2$ ($\lambda = 157$ nm) and KrCl* ($\lambda = 222$ nm).

In this work an annular discharge gap with a diameter of a few millimetres, filled with Xe*$_2$ ($\lambda = 172$ nm) and KrCl* ($\lambda = 222$ nm) gas is used, and the photons are emitted radially through a cylindrical quartz dielectric and outer electrode which is transparent to the radiation generated. These are employed for oxidation of Si and metallo-organic decomposition (MOD).

2.2 Excimer lamp applications

Excimer lamps have found applications for ozone generation, curing of polyimide (PI), MOD, deposition of metals, deposition of curing of inks and resins and surface cleaning. This section discusses these applications.
2.2.1 Ozone generation

Ozone can be formed by the dissociation of O₂ molecules by electrons of energy ranging from 6-9 eV. Generally, oxidation takes the route:

\[ R_g^* \rightarrow 2R_g + h\nu (\lambda) \]  (2.10)

where \( R_g \) is a rare gas

In the case of the rare gas xenon,

\[ Xe^* \rightarrow 2Xe + h\nu (\lambda) \]  (2.11)

\[ O_2 + h\nu (\lambda) \rightarrow O(^3p) + O(^1D) \]  (2.12)

\[ O_2 + O(^3p) + M \rightarrow O_3 + M \]  (2.13)

where \( M \) is a third body, which can be O₂ or O₃

\[ O_3 + h\nu (\lambda) \rightarrow O_2 + O(^1D) \]  (2.14)

O₂ molecules are dissociated to ground state radical O atoms, which subsequently react with excess O₂ to form ozone (O₃). This results in a mixture of O, O₂ and O₃. O₃ is useful for water purification since it kills most micro-organisms in water and also retards their growth. Its
oxidising properties also enable it to reduce the carbon content in water contaminated by organic chemicals.

However, if the microdischarge is too strong, undesired side reactions can occur, resulting in the decrease in $O_3$ atoms by the formation of $O_2$ as follows:

$$O + O + M \rightarrow O_2 + M \quad (2.15)$$

$$O + O_3 \rightarrow 2O_2 \quad (2.16)$$

### 2.2.2 Photo-oxidation

Photo-oxidation with UV in $O_2$ atmosphere involves the dissociation of $O_2$ with a bond energy of 5.1eV into a mixture of $O$, $O_2$ and $O_3$ by the exactly the same route as above. After the photo-dissociation of oxygen molecules to ground state radical $O$ atoms by irradiation, and the subsequent formation of ozone resulting in a mixture of $O$, $O_2$ and $O_3$ in the reaction chamber, these species attack the substrate surface and rapidly form an oxide film. For example, silicon dioxide can be grown on a Si surface by UV irradiation in an $O_2$ atmosphere. The photo-oxidation of Si, using xenon excimer lamp irradiation is covered in Chapter 6.

### 2.2.3 Photo-etching and microstructuring of polymer surfaces

Dry etching of photo-resists and various polymers is an important process step in the fabrication of microelectronic devices. It has several advantages over wet processes including the elimination
of fluid use and the problems associated with its handling and disposal. Though polymer surfaces are usually smooth and chemically unreactive, photo-induced etching can lead to physical and chemical alteration of their properties. Photoetching of various polymers such as polymethylmethacrylate, polyimide (PI), poly-ethyleneterephthalate, poly-tetrafluoroethylene has been demonstrated at low temperatures with excimer lamps [14, 28 - 30]. Photo-induced etching can be used to improve the adhesion of coatings as well as wettability, bondability and printability of polymers by changing the morphology and chemical surface properties [31]. Curing of PI for use in interlayer dielectrics is very promising for the low temperature required in microelectronics processing and consequently low thermal budget.

2.2.4 Curing of polyimides for interlayer dielectrics

In order to reduce RC time delay at the metal interconnects in ULSI devices, low permittivity (low-k) dielectric materials or high conductivity metals are under investigation. Polymeric films are promising as low-k materials to replace SiO₂ as an interlayer dielectric to shorten RC time delays, and decrease power consumption at high signal frequencies [32]. PI have interesting properties that include easy application and patterning and thermal stability [33]. Photo-induced curing of polyamic acid films has been successfully carried out at low temperatures [34] which are compatible with microelectronic processing. Compared with conventional furnace processing, polyamic acid film was completely transformed to PI by the UV curing step at 150°C, whilst the thermally cured sample is only partly transformed. Moreover, the photo-induced curing of the PI provided both reduced processing time and temperature, with the leakage current density of the irradiated polymer found to be smaller than was obtained in layers prepared by thermal processing [34].
2.2.5 **Excimer UV lamp - induced photo - metallo-organic decomposition (photo-MOD)**

Traditionally, lasers and Hg lamps have been used for photo – MOD. Initially, most of the work on excimer UV/VUV lamp induced metal deposition was concentrated on low temperature organo-metallic decomposition of precursors to deposit materials such as thin palladium acetate films [12, 35]. Pd layers several nm thick were reported which served as activators for subsequent electroless metal plating processes in which micrometer thick copper, nickel or gold layers could be selectively grown on top of them. These metallic overlayers were reported to have reached a level of electrical conductivity which was adequate for applications in printed circuit boards and microcircuits [34].

A number of other materials including metals and oxides have been deposited using metallo-organic precursors. Table 2.4 adapted from [20] and now expanded shows a summary of the materials deposited by photo-MOD using metallo-organic precursors and several UV sources. Also, the number of materials deposited using excimer lamps is increasing as more materials with good optical and electrical properties are being deposited. The table shows that some metals and compounds including dielectric materials can be deposited by the photo-MOD route at low temperatures. Moreover, wide area deposition, which was mainly carried out with Hg lamps, is possible with excimer lamps, providing UV light more efficiently.
### Table 2.4 Photo-induced metallo-organic decomposition (photo-MOD)

<table>
<thead>
<tr>
<th>Metal or compound</th>
<th>Substrate</th>
<th>Metallo-organic films</th>
<th>Radiation source</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Al₂O₃, glass-epoxy</td>
<td>dimethyl (1,3-diphenyl-1,3-propanedionato) gold</td>
<td>Hg/Xe deep UV lamp (254, 365 nm)</td>
<td>[36]</td>
</tr>
<tr>
<td>Au</td>
<td>Silicon</td>
<td>nitrocellulose/ammonium tetrachloroaurate</td>
<td>low pressure mercury lamp (185/254 nm)</td>
<td>[37]</td>
</tr>
<tr>
<td>Cu</td>
<td>glass, polymer (ULTEM™)</td>
<td>Cu(CH₃CN)₄BF₄-doped poly(N-vinylpyrrolidone) polymer</td>
<td>argon ion (532 nm)</td>
<td>[38]</td>
</tr>
<tr>
<td>Cu</td>
<td>silicon, quartz</td>
<td>copper formate</td>
<td>argon ion (515 nm)</td>
<td>[39]</td>
</tr>
<tr>
<td>Cu</td>
<td>glass, polymer, Silicon</td>
<td>copper formate</td>
<td>KrF* excimer laser (248 nm)</td>
<td>[40]</td>
</tr>
<tr>
<td>Cu</td>
<td>Al₂O₃</td>
<td>copper formate</td>
<td>Xe*₂ excimer lamp (172 nm)</td>
<td>[4]</td>
</tr>
<tr>
<td>Cu</td>
<td>Al₂O₃</td>
<td>copper acetate</td>
<td>Nd:YAG (1.06 μm)</td>
<td>[41]</td>
</tr>
<tr>
<td>Pd</td>
<td>Quartz</td>
<td>palladium acetate</td>
<td>Ar ion (515 nm)</td>
<td>[42,43]</td>
</tr>
<tr>
<td>Pd</td>
<td>Al₂O₃, quartz, AIN</td>
<td>palladium acetate</td>
<td>ArF*, KrF*, XeCl*, (193, 248, 308 nm)</td>
<td>[44]</td>
</tr>
<tr>
<td>Pd</td>
<td>Quartz</td>
<td>palladium acetate</td>
<td>KrCl* lamp (222 nm), ArF*, KrF*, XeCl*, Xe<em>F lasers(193, 248, 308,351 nm)Ar</em>₂, Kr<em>₂, Xe</em>₂ excimer lamps (126, 146, 172 nm)</td>
<td>[45]</td>
</tr>
<tr>
<td>Pd</td>
<td>Polyimide</td>
<td>palladium acetate</td>
<td>ArF*, KrF*, XeCl*, Xe<em>F lasers(193, 248, 308,351 nm)Ar</em>₂, Kr<em>₂, Xe</em>₂ excimer lamps (126, 146, 172 nm)</td>
<td>[46]</td>
</tr>
<tr>
<td>Pd</td>
<td>Al₂O₃, quartz,silica</td>
<td>palladium acetate</td>
<td>Xe<em>₂, KrCl</em>, XeCl*, lamps (172, 222, 308 nm)</td>
<td>[4,47,48]</td>
</tr>
<tr>
<td>Pd</td>
<td>Al₂O₃, quartz,silica</td>
<td>palladium acetate</td>
<td>ArF*, KrF* excimer lasers (193, 248 nm) synchrotron (40-300 nm)</td>
<td>[49,50]</td>
</tr>
<tr>
<td>Pd</td>
<td>Polyimide</td>
<td>palladium acetylacetonate</td>
<td>Ar ion laser (351 nm)</td>
<td>[51-53]</td>
</tr>
<tr>
<td>Pt</td>
<td>Polyimide</td>
<td>quartzmetalorganic platinum</td>
<td>Ar ion (515 nm)</td>
<td>[54,55]</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Quartz</td>
<td>Aluminium di(i-propoxide) acetoacetic ester chelate</td>
<td>KrCl* lamp (222 nm)</td>
<td>[56]</td>
</tr>
</tbody>
</table>

*Table continued on next page*
<table>
<thead>
<tr>
<th>Metal or compound</th>
<th>Substrate</th>
<th>Metallo-organic films</th>
<th>Radiation source</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO₃</td>
<td>Silicon, Sapphire</td>
<td>Lithium neodecanoate, niobium triethoxy -di-neodecanoate</td>
<td>tungsten lamp (250-1000 nm)</td>
<td>[57]</td>
</tr>
<tr>
<td>InₓGa₁₋ₓN (x=0, 1, 0.2)</td>
<td>Sapphire</td>
<td>triethylgallium (TEGa), NH₃ and trimethylindium (TMIn)</td>
<td>Hg lamp (254 nm)</td>
<td>[58]</td>
</tr>
<tr>
<td>ZnBeSe</td>
<td>n-GaAs (100)</td>
<td>Dimethylzinc (DMZn), dimethylselenide (DMSe) and diethylberyllium (DEBe) or bismethylcyclopentadienyl —beryllium (MeCp)₂Be.</td>
<td>ultrahigh-pressure Hg arc lamp</td>
<td>[59]</td>
</tr>
<tr>
<td>ZnTe</td>
<td>ZnTe (100)</td>
<td>Dimethylzinc (DMZn) and diethyltelluride (DTe)</td>
<td>xenon lamp 500W</td>
<td>[60]</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>Si (100)</td>
<td>tantalum tetraethoxy dimethylaminoethoxide TaDMae</td>
<td>KrCl (222 nm) excimer lamp</td>
<td>[61,62]</td>
</tr>
<tr>
<td>ZnSe epitaxy layers</td>
<td>GaAs (100)</td>
<td>DMZn and DMSe</td>
<td>high pressure Hg lamp (365 nm)</td>
<td>[63]</td>
</tr>
<tr>
<td>ZnSe/ Zn, Cd₁₋ₓSe heterostructures</td>
<td>GaAs (100)</td>
<td>diethylzincdimethylcadmium dimethylselenium diethyl sulphur</td>
<td>halogen lamp 100W</td>
<td>[64]</td>
</tr>
<tr>
<td>ZnSe</td>
<td>CrO-doped GaAs (100)</td>
<td>dimethylzinc, dimethylcadmium diethylsulfide, bismethylcyclopentadienyl-magnesium, and dimethylselenide</td>
<td>high-pressure Hg lamp 365 nm</td>
<td>[65]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Sapphire and quartz</td>
<td>Tetraethoxysiloxosilicate (TEOS)</td>
<td>Xe²⁺, excimer lamp (172 nm)</td>
<td>[66]</td>
</tr>
</tbody>
</table>
2.2.6 Deposition of dielectric materials

Low-temperature photo-MOD has been extensively used for the deposition of optical and dielectric materials for microelectronics. Experiment carried out on the photo-MOD by excimer lamps of respective precursors to form TiO\(_2\) and Ta\(_2\)O\(_5\) doped with TiO\(_2\) - using photo – CVD and the photo-induced sol-gel process, as well as the oxidation of Si to form films of ultrathin SiO\(_2\) are described over the next chapters.

2.3 Conclusions

A review has been carried out on excimer lamps and their construction and on films deposited by photo-MOD. It is clear that a lot of work involving different sources of radiation is ongoing, and that excimer lamps are also playing a great role in the low temperature deposition of thin films. This is also explored in the next chapters, with the deposition of TiO\(_2\) and composite TiO\(_2\)-Ta\(_2\)O\(_5\) with alkoxide precursors. The oxidation of Si will also be reported.
2.4 References

32. P. Singer, Semiconductor International, October (1994) 34


Chapter 3

Apparatus and measurements

This chapter discusses the apparatus used for the deposition of films and film characterisation. The two types of cold – wall reactors used are discussed. These are the windowless chamber incorporating 172 nm lamps and used in this research for large – area photo-induced decomposition of sol-gel materials, photo-assisted oxidation of silicon surfaces and annealing of samples and the 222 nm lamps contained in a chamber separated from the reaction chamber by a transparent magnesium fluoride (MgF₂) window. The latter is connected to a UV injection liquid source UV-ILS. Measurement methods used for the characterisation of films include ellipsometry, Fourier transform infrared spectroscopy, UV – VIS and CV-IV measurements.

Work on the design and construction of the 4 lamp windowless system was based on the initial one lamp system already constructed at UCL [1]. The demands for the system included low vacuum pumping system, gas backfill capabilities for oxygen, nitrogen and other gases, substrate holder, excimer lamp chamber, excimer lamp holder, heater, cooling water system and power supply.
The UV – ILS system combining an injection liquid source with an excimer lamp photo-CVD reactor had already been used for the deposition of Ta₂O₅ at the onset of this research [2]. However, chamber pressure was controlled manually, and the requirement was to incorporate a suitable automatic pressure controller.

3.1 Design and Construction of Large Area Lamp System

The large area system consisted of two stainless steel chambers: the lamp and reactor chambers. The lamp chamber was installed on top of the reactor chamber. The lamp chamber held the four lamps, to which the water cooling and power generation circuits were connected.

Figure 3.1 shows a detailed drawing of the excimer lamp tube envelope for the four lamp system. It was made of two concentric cylindrical quartz tubes. The inner and outer tube diameters were 18 and 30mm respectively. The outer tube had an elongation that was 10mm in diameter, leading to the narrow discharge gap between the two concentric cylindrical tubes through which the Xe excimer gas was introduced. An annular discharge gap where microdischarges occurred uniformly was about 5mm. The pressure of Xe gas in the gap was between 0.1 and 1bar. After the gas fill, the elongation was sealed. The outer lamp of the tube was made of suprasil, which was 1.5mm thick and had a transmission of about 80% at 172 nm. The length of the outer tube was 250mm. The inner tube was 310mm long.
Figure 3.1 Detailed drawing of the excimer lamp tube envelope for the four lamp system

Figure 3.2 shows the schematic diagram of an excimer lamp [1]. The voltage to the lamp was supplied using a copper wire, which was wound into a 250mm long coil of 16mm diameter and passing through the inner quartz tube. Alternating high voltage of a few kV amplitude was adequate to run the discharge. A supply voltage amplitude of 7.5kV was used. 0.75kW r.f. power was supplied to the lamps at 380kHz. The outer electrode passing through feedthroughs at the top of the chamber was connected to ground. The outer electrode, which was 30mm in diameter, was made of copper wire mesh wrapped around the length of the lamp.
Since the electrodes were located outside the xenon gas volume, no metal parts were in contact with plasma or corrosive gases, and this improved the lifespan and efficiency of the lamp. The sealed glass or quartz tubes have been demonstrated to operate over several hundred hours. Efficiency and lifespan of lamps is discussed later in this chapter.

The inner electrode and de-ionised water for controlling lamp temperature shared the inner quartz tube. De-ionised water was circulated from a reservoir through the lamp from a 12V dc pump circulating the de-ionised water at a flow rate of 5l/s and a head of about 1.2m.
The water circulation circuit is shown in figure 3.3. The water reservoir was made from a 20litre plastic container filled with about 15litres of de-ionised water.

Lamp holders consisted of two special flanges bolted on two of the side flanges of the vacuum lamp chamber. At the ends of the holders were housed two O-rings for the vacuum seal. The holder shape was designed to fit the shape of the lamp. The two flanges holding the lamp were inserted inside the chamber through the lateral flanges.
Figure 3.4 Diagram of the four lamp system with the lamp
Figure 3.4 shows a diagram of the four lamp system with the lamp and the reactor chamber sealed together. The bottom diagram shows a sectional view of the lamps from the top. As seen, the lamps were modular.

The lamp chamber was covered with an ISO flange type NW160, with a feedthrough for the lamp ground cable and an escape valve allowing the introduction of air into the chamber when opening under vacuum. There was also allowance for the connection of a vacuum gauge. Claw clamps were used to connect the flange to the lamp chamber. This allowed for easy access to the lamps during routine maintenance. Aluminium foil covered the top of the lamps below the flange in order to reflect any radiation moving upwards towards the reactor chamber. The chamber also held a KF50 quartz viewport through which lamps were visible. Using 4 x M6 bolts, the lamp and reactor chambers were fixed together.

The reactor chamber consisted of sample holder, heater, gas system and vacuum system. The walls of the reactor were made of stainless steel. The chamber was evacuated by a rotary and turbo vacuum pump system. The 250mm x 250mm four lamp array produced a constant power density on the sample at any level between 70 and 200mW/cm² and this was dependent upon sample - lamp distance.

Radiation was directed to the substrate and induced bond breaking in complex organometallic compounds or, in the oxidation case, produced ozone and free oxygen, which reacted with the silicon at the substrate surface to produce an oxide film. Gases could be introduced into the system via MFCs. The bond energy of O₂ was known to be close to 5.1eV, corresponding to a wavelength of 240 nm. Therefore, under 172 nm VUV irradiation, O₂ could be dissociated with
the subsequent formation of oxygen atoms and ozone, which could play an important role in the
photo-oxidation process. This is fully described in chapter 6.

A resistance heater was connected via electrical feedthroughs to the substrate holder. This was
held on an elevated jack. A MINCO® substrate heater, providing uniform heating ($\Delta < 10^\circ C$) up
to 500$^\circ C$ over the entire surface of sample holder was used. A thermocouple connected to the
holder's surface enabled automatic monitoring of temperature at pre-set by values by a
controller. The controller, thermocouple and heating circuitry was introduced to the chamber
through a CF34 flange at one side of the reactor chamber. The heater and substrate holder were
accessed through a CF250 quick access door.

The chamber was connected to the pumping system through a CF200 flange at the bottom. It was
evacuated by a two-stage mechanical pump to $10^{-2}$ mbar. A pirani gauge which could measure
between $1.33 - 1.33 \times 10^{-2}$ mbar pressure, and located on the top flange was connected to an
Edwards 1005 controller.

Two stainless steel pipes 80mm long were welded on the reactor. These were connected to $O_2$
and $N_2$ gas cylinders. During annealing, the system was filled to the desired pressure of 600mbar
with electronic grade oxygen (99.999%).

Due to the formation of ozone, organic and other gases, a possible escape route for these was
provided by a protective cubic glass stand serving as a “fume cupboard” and covering the system
reactor. The temperature controller, water pump, water container, vacuum gauges, generator,
were all located on the rack.
3.2 Photo – CVD system incorporating an injection liquid source

The UV - injection liquid source (UV – ILS) used for this research was provided by JIPELEC. The UV-ILS source is based on the principle of computer controlled injection of precursors in very small amounts. Droplets of liquid precursors were sequentially injected inside an evaporator where they were “flash” volatilised. A high-speed computer driven electrovalve ensured an accurate and reproducible injection of droplets into an evaporator, where flash evaporation occurred. The droplet size was controlled by the pressure of an inert gas applied to the hermetically closed vessel containing the precursor’s solution at room temperature, the injector’s opening time and the frequency of injection. The system had an accuracy better than 5% [3].

Many features of the photo-CVD apparatus were similar to those of the photoinduced processing reactor described above. The photo-CVD system comprised two stainless steel chambers: the lamp chamber and reactor cell. Handling of gas and vapour precursors required the lamp and reaction chambers to be separated by a window mainly to avoid deposition on the lamps resulting in their reduced efficiency. Since the KrCl* excimer lamps used emitted radiation of 222 nm, a MgF₂ window transparent to it separated the chambers. The lamp chamber required to be maintained at a pressure level, in this case about 10⁻² mbar, where turning on of lamps was fast. Figure 3.5 shows a schematic diagram of the photo-CVD system with an injector liquid source, used for this research.

Whereas, the photo – induced sol gel process required the breaking of bonds in the precursor already on the substrate, photo – CVD needed the transportation of the precursors to its surface.
The KrCl* excimer lamp was made of quartz. There was no need to coat the outer lamp surface with suprasil as with 172 nm lamps quartz is transparent to 222 nm radiation.

The evaporator was close to the deposition zone, making the transfer time very short, thus enabling high superheating, giving rise to very high precursor vapour pressure and high deposition rates. On the other hand, with the use of little droplet volume and slow injection frequency, very low deposition rates could be obtained, only by changing the computer’s data input [4]. This is very important for controlled growth of ultrathin film layers.

The precursors were maintained at room temperature and the precursor inputs were dependent only on the liquid injection rates and concentration of the solution. The precursor was contained
in a hermetically closed vessel, pressurised under Ar connected to the injector, a high-speed
electro valve. Liquid injection, which is currently used for fuel injection in thermal motors and
based on the principle of computer – controlled injection of micro amounts of liquid droplets was
used to introduce precursor droplets in the chamber. A vector gas flowing along the neck of the
injector drove the vapours towards an r.f. heated coil. The injected precursor and solvent droplets
were flash volatilised. The flash volatilisation of some microlitre droplets of liquid inside the
evaporator led to a pulsed variation of pressure, depending on the opening time, the frequency of
injection and also on the geometry of the reactor. Generally, at high injection frequency, the
system experiences an average pressure, and at a low injection frequency, it experiences pressure
pulses.

Two pressure gauges were connected to the reactor and lamp as compared to one on any side in
the four lamp system described above. Reactor chamber pressure was monitored by a control
valve, which was used in conjunction with a control unit for controlling gas streams to maintain a
desired pressure value. The same control valve was used for coarse gas flow regulation.

A 2 stage high vacuum rotary pump was used. An MF 30 mist filter was connected to the pump.
The mist filter prevents the emission of oil mist when pumping high gas thoroughputs. The pump
terminated in a KF 25 inlet adaptor. This was connected to the reactor and lamp chambers by
bellows through a KF 25 flange.

Figure 3.6 shows the complete photo-CVD evaporator, reactor and lamp chambers and their
configuration. A picture of the UV-ILS system is shown in figure 3.7.
Figure 3.6 The complete photo - CVD evaporator, reactor and lamp chambers
Figure 3.7 Photograph of new photo – CVD reactor with excimer lamp
3.3 Deposition of films - experimental procedures

Figure 3.8 shows a schematic diagram of the UV-ILS system showing the positions of the lamp, reactor, injector, pumping system and various valves. The de-ionised water circuit was the same as that for the 172 nm lamp described above. An ac pump circulated the de-ionised water through the lamps to cool them.

---

Figure 3.8 Schematic diagram of photo-CVD system with injector liquid source
The precursors were held in a hermetically sealed container labelled TT in the diagram. The injector source vaporised the precursor, and injects into the reactor chamber droplets of a pre-set size at a pre-set frequency. Injector source regions had different temperatures. Injector temperatures were set on the Eurotherm™ controllers as follows:

- Connection temperature: 80°C
- Injection temperature: 110°C
- Showerhead temperature: 110°C

\( \text{N}_2\text{O} \) and Ar gas flow to the reactor and injector source were read and controlled by Platon flow meters set at 20sccm and 50sccm respectively. An argon gas flow carried the precursor through the shower head to the wafer, whereas \( \text{N}_2\text{O} \) gas was used as an oxidant, due to the inorganic nature of the precursors.

The substrate heater was set at from room temperature to 350°C, with a thermocouple monitoring temperature. A cold trap held liquid N\(_2\) to avoid contamination of the reaction chamber. Valves labelled "chamber" and "source" controlled the flow of Ar gas into the reactor chamber and injector source respectively. Prior to this work, a manually controlled "chamber" valve was in use. A different automatically controlled "chamber" valve was installed during this research work for maintaining reactor pressure at a pre-set value during deposition. It could also be run in rough mode to introduce fast streams of Ar into the chamber, allowing pressure to rise to atmospheric when unloading substrates.

Before the first experiment, the injector jet was cleaned. This was done by disconnecting the evaporator cable connected above the hermetically sealed container and wiping the nozzle with hexane. The container was filled with anhydrous hexane, Ar gas supply was opened, with the cable reconnected and several drops of hexane were injected into a "waste" beaker. This also helped in pre testing the jet (nozzle) before experiments. A precursor container prebaked overnight at 250°C was used for the experiments. Hexane was used as a solvent, and the precursors constituted a tenth of the solution by volume. To get an even distribution of the precursor in the deposition chamber, the first deposition cycle results were not meaningful and
were therefore not taken into consideration. Caution was also taken to always clean the system with hexane only and always use baked out containers for the experiments.

The lamp power for the one lamp system was set at 70W at a frequency of 220kHz and a voltage of 3.6 kV. The injector source temperature parameters were set at 80°C and 110°C as described above. Frequency and time were respectively set at 1Hz and 2ms, with number of drops varying between 60 and 600. Platon flow meters for Ar and N₂O were set at the above values for all experiments.

Both reactor and lamp chambers were pumped down to about 10⁻² mbar and the lamp chamber valve was closed. Only the reaction chamber pressure was adjusted during the whole duration of experiments. Substrate temperature was pre-set and the heater was turned on. As the temperature approached the pre-set value, the cooling de-ionised water was turned on. The reactor pump valve was slightly closed and the pressure controller set at 2mbar was turned into pressure control mode. Gas flow controller valves were opened, the lamp was turned on, precursor container valves were opened and the injector was turned on. Table 3.1 below summarises the main deposition parameters used.

| Table 3.1 Main parameters used for the photo-CVD of TiO₂ and TiO₂ – Ta₂O₅. |
|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Injector frequency (Hz)       | Injector opening time (s)     | Number Of Drops               | N₂O flow (sccm)              | Ar flow (sccm)               | Reactor pressure (mbar)      | Substrate temperature (°C)   |
| 1                             | 2x10⁻³                        | 60 - 600                      | 20                           | 50                           | 2                            | 50 - 350                      |

As explained above, precursor droplet size is dependent on the frequency and opening time of the injector. The frequency and time settings were set at the same values for prior work on the deposition of Ta₂O₅ using the same reactor [2].

After deposition, the chamber was cooled to about 50 - 60°C (during experiments involving temperatures higher than these values) before samples were removed.
After the final experiment, to avoid blockage the injector was cleaned with hexane, which was flushed through at high speed and frequency.

Using actinometric measurements described below, and consistent with previous measurements it was found that the 222 nm excimer lamp emitted radiation with an optical power of approximately $10\text{mW/cm}^2$ at 6cm from the lamp outer surface [5]. A distance of 6cm was used for the photo-CVD experiments.

The precursor used for the sol-gel deposition of TiO$_2$ was titanium isopropoxide (TTIP). As discussed in Chapter 5, sol-gel processing requires alkoxides and TTIP was the most suitable. 0.1 mol/litre HCl in ethanol was used as the catalyst. 1 volume of the precursor was dissolved in 9 volumes of a solution of 0.5 mol/litre water in ethanol. The water initiated hydrolysis and condensation reactions. These are fully described in Chapter 5.

Precursors used for the sol-gel deposition of TiO$_2$ – Ta$_2$O$_5$ were titanium isopropoxide (TTIP) and tantalum ethoxide Ta(OEt)$_5$ an obvious choice for the photo-CVD of Ta$_2$O$_5$ films. 0.1 mol/litre HCl in ethanol was used as the catalyst. 1 volume of the precursor constituting several molar ratios was dissolved in 9 volumes of a solution of 0.5 mol/litre water in ethanol.

TTIP dissolved in hexane in a ratio of 1:9 was used as the precursor for the photo-CVD of TiO$_2$. TiO$_2$ – Ta$_2$O$_5$ composites were also deposited by the UV-ILS CVD. Ta(OEt)$_5$ has a high moisture sensitivity and low vapour pressure which lead to its difficult handling. An alternative to Ta(OEt)$_5$ was found in a new precursor, tantalum tetraethoxy dimethylaminoethoxide Ta(DMAE). Figure 3.9 shows the vapour pressure of Ta(OEt)$_5$ and Ta(DMAE) at different temperatures and the chemical formula of the latter.
This new precursor has advantages over Ta(OEt)$_5$, such as higher vapour pressure as shown in the diagram. It also has lower moisture sensitivity, thus it does not tend to produce unwanted deposits. Ta(DMAE) has previously been used in a thermal MOCVD process for Ta$_2$O$_5$ [6]. For the experimental work in this research, the injection liquid source was filled with a 10% cyclohexane solution of Ta(DMAE) and TTIP.

3.4 Characterisation of the deposited films

Characterisation of the films involved measurements of thickness and refractive index, and analysis of chemical bonds, the state of crystallinity, dielectric and electrical properties. Thickness and refractive indices were determined by a Rudolph Auto El II ellipsometer operating at a wavelength of 633 nm. The chemical bonding in the deposited thin films was analysed by Fourier
transform infrared spectroscopy. The optical properties of films prepared on quartz were investigated by a UV – visible infrared spectrophotometer. Dielectric and electrical properties were analysed by capacitance – voltage (C-V) and current – voltage (I-V) measurements. The crystallinity of the films was determined by X-Ray diffraction (XRD).

3.4.1 Ellipsometry

An ellipsometer measures changes in the polarisation state of a light beam caused by reflection. With this method, the surface of a sample is irradiated with a collimated beam of monochromatic light having a known, controllable state of polarisation at a known angle of incidence. The differences between the states of polarisation of the incident and reflected beams are then determined.

Figure 3.10 Schematic representation of ellipsometer principles

Figure 3.10 shows a schematic representation of an ellipsometer comprising two optical axes, an incident - beam axis and a reflected - beam axis, which are adjustable to desired angles of
incidence with respect to a sample located at the intersection of the two axes. Light produced by
a source at the far end of the incident - beam axis, strikes and is reflected from the surface of the
sample, and passes through any optical components that are mounted along the reflected - beam
axis, until it enters a photodetector at the far end of the reflected - beam axis. In the figure, $n_0$, $k_0$,
n$_1$, $k_1$, $n_2$, $k_2$ are the real and imaginary parts of the refractive indices of the ambient medium,
transparent film and substrate respectively, $E$ is the electric field and $E''$ its reflected component.

Differences can give either the real and imaginary parts for the refractive index of the substrate, or
the thickness and refractive index of a transparent film deposited on a substrate, provided the
optical constants of the substrate are known. From the representation of the instantaneous
amplitude of a single harmonic oscillation as:

$$E(t) = |E| e^{i(\omega t + \epsilon)} = |E| e^{\text{int}} \cdot |E| e^{i\epsilon}$$

(3.1)

where $E$ is the complex instantaneous amplitude of the electric field and $\epsilon$ is the time-independent
phase of the light wave, the basic equation of ellipsometry can be deduced as:

$$\rho = \tan \Psi e^{i\Delta}$$

(3.2)

$0^\circ \leq \Psi \leq 90^\circ$ - $0^\circ \leq \Delta \leq 360^\circ$

where $\Delta$ and $\Psi$ are angles and $\rho$ is the ratio $r_p/r_n$, with $r_p$ and $r_n$ the reflection coefficients having
their electric field vectors parallel and normal to the plane of incidence respectively.

Figure 3.11 shows a film - substrate model for ellipsometric measurements.
For single films on substrates, $\Delta$ and $\Psi$ depend on $n_0$ the refractive index of the ambient medium, $n_2$ and $n_3$ the refractive indices for film and substrate respectively, $k_2$ and $k_3$ the absorption coefficients for film and substrate respectively, $\varphi$ the angle of incidence, $\lambda$ the wavelength of the light and THK the film thickness:

\begin{align*}
\Delta &= f_2 (\varphi, \lambda, n_0, n_3, k_3, n_2, k_2, \text{THK}) \\
\Psi &= g_2 (\varphi, \lambda, n_0, n_3, k_3, n_2, k_2, \text{THK})
\end{align*}  

(3.3)  

(3.4)

The He–Ne laser used for this work operates at $\lambda = 633$ nm, $\varphi = 70^\circ$, and for Si, $n_3 = 3.858$ and $k_3 = 0.018$ [7]. Since the angles $\Delta$ and $\Psi$ are cyclic functions of film thickness, for measurement in air, cycle thickness (CYC) may be obtained from.
Advantages of ellipsometry over other methods include the measurement of thicknesses which are an order of magnitude smaller than can be measured by other methods like interferometry, the possibility of determining the index of refraction of thin films of unknown thickness, the possibility of making measurements in optically transparent environments such as liquids and the possibility of making measurements under normal conditions or in special conditions like vacuum. Thin films of thicknesses between 1 to 600 nm were measured within the boundaries of a 5% error attributed to instrument related and sample-related factors. The ellipsometer used, a Rudolf AutoEl II model was very reliable. Sample initial experiments were carried out on TiO$_2$ grown by the photo-induced sol-gel process, which is explained later. Measurements yielded results as seen in the sample figure 3.12 below.

![Figure 3.12 Thickness and refractive index of TiO$_2$ films formed by irradiating a number of spin-coated layers using 172 nm excimer lamps.](image)

Chapter 3 80
Figure 3.13 shows the thickness and refractive index of Ta$_2$O$_5$-TiO$_2$ thin films of 96% Ta$_2$O$_5$ content deposited by the photo-induced sol-gel process. Six different 1 cm$^2$ samples were used to check the reproducibility of the ellipsometry results.

Most results were found to be in the range ±5% of the average result.
3.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Spectroscopy studies the interaction of electromagnetic radiation with bonds in a chemical substance. The IR spectrum of a compound provides specific information about chemical bonding and molecular structure of a compound. Chemical bonds absorb infrared energy at specific wavelengths, leading to molecular vibrations. Absorbed wavelengths therefore, reveal the frequencies of vibration characteristic of the bonds during stretching or bending. Any absorption band is characterised by the wavelength at which the maximum absorption occurs and the intensity of absorption at this wavelength. The ratio of the intensity of transmitted radiation (I) to the intensity of incident radiation (I₀) is the transmittance (T) and is given by:

\[ T = \frac{I}{I_0} \quad (3.6) \]

The absorbance (A) is given by:

\[ A = \log \left( \frac{1}{T} \right) = \log \left( \frac{I_0}{I} \right) \quad (3.7) \]

Figure 3.14 shows a schematic representation of equipment for FTIR.

FTIR spectroscopy is a powerful analytical tool for characterising and identifying molecules. The main component of the FTIR spectrometer is an interferometer, which consists of two mirrors, and a beamsplitter positioned at an angle of 45 degrees to the mirrors. When incident light strikes the beamsplitter, half of it is transmitted through the beamsplitter and the other half is reflected to the mirrors. The two components are then reflected back and recombined at the beamsplitter. When the two halves of the beam recombine on the beamsplitter, they exhibit a pathlength difference or optical retardation. Half the light passes on toward the sampling areas and half travels back towards the source.
Figure 3.14  Simplified diagram of the optical system of Fourier transform infrared spectrometer [8]

With light of many frequencies, the output signal is the sum of all cosine waves, which is the Fourier transform of the spectrum or an interferogram. The interferogram is a function of time and the spectrum is a function of frequency. The signal at the detector is a cosine wave. A spectrum is obtained from the interferogram by computing the cosine Fourier transform of the interferogram.
The advantages of FTIR include the fact that thin films can be identified with a sensitivity that exceeds electron or ion beam-based surface analysis techniques. FTIR is non-destructive and offers speed and sensitivity impossible to achieve with other wavelength-dispersive instruments. FTIR can analyse non-conductive materials, provide molecular specific identification, provide detailed chemical bonding information, and analyse the organic molecular composition of polymers and plastics. Liquids, solids and gases can also analyse.

3.4.3 X-ray diffraction (XRD)

XRD constitutes a powerful non-destructive technique used to determine the structural arrangement of atoms in a substance.

![Figure 3.15 Primary and diffractive X-Ray beams](image-url)
The wavelength of x-rays is comparable to atomic spacings. XRD is based on the diffraction by the crystalline planes of a collimated beam of X-rays with wavelengths typically in the range of 0.07 – 0.2 nm. XRD can be used to identify the components of a thin film, or to distinguish between a single crystal or polycrystalline structure, between polycrystalline and amorphous structures and determining the texture (preferred orientation) in polycrystalline films. Figure 3.15 shows the primary and diffractive beams, passing through atomic spacings (d).

An XRD pattern consists of a series of intensity peaks plotted against angle, and each peak corresponds to specific atomic spacings (d). According to Bragg’s law:

\[ \theta_i = \theta_f = \theta \quad (3.8) \]

\[ n\lambda = 2d \sin \theta \quad (3.9) \]

\[ |\vec{k}_i| = |\vec{k}_f| = \frac{2\pi}{\lambda} \quad (3.10) \]

\[ \vec{q} = |\vec{k}_f - \vec{k}_i| \quad (3.11) \]

\[ = 2k_i \sin \theta = \frac{4\pi}{\lambda} \sin \theta = \frac{2\pi n}{d} \quad (3.12) \]

where \( n \) is an integer for constructive interference, \( \lambda \) is the wavelength of radiation, \( d \) is the spacing between adjacent planes in a crystal and \( \theta \), the angle which the primary and diffractive beam make with the plane, is called Bragg’s angle.
Different maxima corresponding to the contribution of the different crystalline planes in the crystal, are obtained when constructive interference of diffracted X-rays occurs according to the above law.

3.5 UV Power measurements

UV power measurement is essential for monitoring and controlling the absolute quantity of radiation in the various UV applications. UV, VUV and visible radiation can be measured physically or on the basis of chemical changes induced by the photons. Radiation is generally measured physically by photosensitive detectors and chemically by actinometers.

3.5.1 Photosensitive detectors

Radiant power (or flux) is given by:

$$\phi = \frac{dQ}{dt} \quad (3.13)$$

and irradiance, the flux per unit area by:

$$I = \frac{d\phi}{dA} \quad (3.14)$$

where $\phi$ is the radiant flux, $Q$ is the radiant energy.
When exposed to electromagnetic radiation, instrumental photosensitive detectors produce current or voltage signals, which can be measured quantitatively. The types of photosensitive detectors are thermal, photoemissive tubes and solid state photodiodes. Figure 3.16 shows a setup used to measure lamp irradiation. A filter ensures the required radiation only falls on the photodiode.

Figure 3.16 Diagram of a setup for measuring UV radiation

Most detectors provide a linear response over several orders of magnitude of input, then lose linearity at very high radiation levels. Spectral radiometry requires a uniform response over the wavelength region of interest, but zero response at other wavelengths. Thermal detectors, realise heating effects that can be measured by radiation thermocouples in which thermoelectric emf is
produced. Such detectors are usually painted black in order to absorb radiation falling on them. In photoemissive tubes, the cathode ejects electrons towards the anode, when struck by photons, which have energies greater than a certain threshold. In solid state photodetectors, photons excite electrons from the valence band to the conduction band. Electron-hole pairs are formed, which act as current carriers.

Problems such as surface damage due to high power radiation and ageing effects result in decreased sensitivity in physical detectors. Measurement of total radiant output of a lamp is difficult due to problems in collecting all radiation from a lamp and directing it to a measuring device, and due to difficulties posed by finding a measuring device which will respond to all wavelengths emitted.

UV power meters designed to measure absolute optical power in the UV to VUV region, without employing filters are also available commercially. However, they require specific sensor heads for specific UV and VUV line spectra. The sensor head employs a calibrated UV sensor (UV phototube), allowing UV measurement with a high degree of accuracy and stability over extended periods of use.

### 3.5.2 Actinometers

The term actinometry is applied to the process by which the concentration of the ground state species (chemical reactants) is derived from the optically detected species. Chemical actinometer systems are used to measure intensity on the basis of a light-induced chemical process for which the quantum yield is accurately known. Generally, the radiation-induced chemical reaction is irreversible. Chemical actinometers possess many advantages in comparison with physical
detectors, including simplicity and no requirement for specialised equipment, reduced systematic errors, reproducible results and no demand for recalibration. Chemical actinometers may be gaseous, liquid and solid. Fluid actinometers are widely used for measuring radiation fluxes in photochemical reactors. Gas phase actinometers are generally more difficult to use than solution actinometers and give less reliable results, but they can most usually be used for VUV measurements. The quantum yield for the actinometer reaction should be independent of reactant concentration, light intensity, temperature and wavelength over a reasonable range. Using actinometry, the intensity of excimer lamps has been measured using uridine [9].

---

Figure 3.17 Schematic diagram of actinometric measurement of 222 nm lamp UV intensity

Figure 3.17 above, shows the experimental set-up for the measurement of UV intensity emitted by a 222 nm lamp. Uridine (1-β-D-ribofuranosyluracil) contains one uracil and one β-D
ribofuranose molecule. Figure 3.18 shows the photochemical reaction of uridine after exposure to radiation.

\[
\begin{align*}
\text{Uridine} & \quad \begin{array}{c}
\text{hv} \\
\text{H}_2\text{O}
\end{array} \\
\text{Photohydrate of uridine}
\end{align*}
\]

Figure 3.18 Chemical reaction for the photohydration of uridine

Figure 3.19 shows the absorption spectra of uridine at with different lamp power supply values. The absorbance at \( \lambda = 260 \) nm decreases with power supplied due to the formation of the \( \alpha, \beta \)-saturated carbonyl groups in uridine. The uridine peak disappears above 800W power.

The absorption band of uridine at a wavelength of 260 nm is attributed to the \( \pi-\pi^* \) transition of the \( \alpha,\beta \) saturated carbonyl group.
3.5.2.1 222 nm UV intensity measurement using uridine

The reaction is completed according to first order kinetics and is described as follows [9]:

$$\frac{dc}{dt} = kc = \frac{I_0 \phi}{V} = (I_0 - I) \frac{\phi}{V}$$  \hspace{1cm} (3.15)

where $c$ is the concentration of uridine (mol/l), $k$ is the specific reaction rate constant, $t$ the exposure time $I_0$ is the intensity of incident radiation, $I$ the intensity of light through the actinometer, $\phi$ the quantum yield of the photohydrate of uridine and $V$ the volume of the irradiated uridine solution. For uridine, $\phi = 0.034$
Combined with the Beer Lambert Law which states that the intensity of radiation decreases exponentially as it passes through a medium:

\[
I_s = I_0 - I = I_0(1 - e^{-\varepsilon cd})
\]  \hspace{1cm} (3.16)

with \( \varepsilon \) the molar extinction coefficient \( (\varepsilon = 3.15 \text{m}^2/\text{mol} \text{ at } \lambda = 222 \text{ nm}) \),

A solution of this equation yields [9]:

\[
I_s = \frac{V \cdot \ln(c_0/c)}{\varepsilon d \phi}
\]  \hspace{1cm} (3.17)

where \( c_0 \) is the initial uridine concentration, \( d \) the path length inside the actinometer cell,

and with the actinometer concentration proportional to the absorbance,

\[
A = \log_{10} \frac{I_s}{I} = \varepsilon cd
\]  \hspace{1cm} (3.18)

the intensity of light can be calculated [9].

### 3.5.3 Spectral Radiometers

A spectral radiometer measures irradiance as a function of wavelength. It comprises of a photosensitive detector and a selective device, which may be a filter. Though absorption filters may be solid, of glass and plastic doped with materials having appropriate absorption characteristics, coloured glass filters are commonly used to absorb radiation of certain
wavelengths. Other selective devices include interference filters, monochromators, which separate different wavelengths by spreading them in space, and prisms that rely on the variation of refractive index with wavelength. Interference filters are often preferred for the isolation of very narrow wavebands.

3.5.4 Characterisation of the 172 nm lamp

A McPherson monochromator was used to measure the spectrum of the emitted radiation. The instrument volume was evacuated to pressure below $10^{-2}$ mbar for vacuum UV measurement. The output-measuring unit comprises a photomultiplier tube with a sodium salicylate fluorescent coating. Table 3.2 characterises 172 nm radiation. An intrinsic efficiency of 20-40% on a microwave driven Xe$_2^*$ excimer lamp has been reported [10].

<table>
<thead>
<tr>
<th>Voltage Output</th>
<th>3.6 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>150 - 250 kHz</td>
</tr>
<tr>
<td>Electrical Power</td>
<td>20 - 80 W</td>
</tr>
<tr>
<td>Radiated Geometry</td>
<td>cylinder</td>
</tr>
<tr>
<td>Lamp size</td>
<td>diameter: 30mm; length: 150 - 320 mm</td>
</tr>
<tr>
<td>Gap size</td>
<td>2 - 10 mm</td>
</tr>
<tr>
<td>Gas</td>
<td>Xenon</td>
</tr>
<tr>
<td>Emitted peak</td>
<td>172 nm</td>
</tr>
<tr>
<td>Half width of 172 nm</td>
<td>8 - 12 nm</td>
</tr>
</tbody>
</table>
3.5.5 Characterisation of Kr*Cl lamps

High purity krypton and chlorine gas were used to manufacture a Kr*Cl excimer lamp operating at 222 nm. Table 3.3 shows the specification of the Kr*Cl excimer lamps providing intense narrow radiation at 222 nm within the dielectric barrier discharge.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage Output</td>
<td>3.6 kV</td>
</tr>
<tr>
<td>Frequency</td>
<td>150 - 250 kHz</td>
</tr>
<tr>
<td>Electrical Power</td>
<td>20 - 80 W</td>
</tr>
<tr>
<td>Radiated Geometry</td>
<td>cylinder</td>
</tr>
<tr>
<td>Lamp size</td>
<td>diameter: 30 mm; length: 150 - 320 mm</td>
</tr>
<tr>
<td>Gap size</td>
<td>2 - 10 mm</td>
</tr>
<tr>
<td>Gases</td>
<td>krypton and chlorine</td>
</tr>
<tr>
<td>Emitted peak</td>
<td>222 nm</td>
</tr>
<tr>
<td>Half width of 172 nm</td>
<td>2 - 12 nm</td>
</tr>
</tbody>
</table>

The UV intensity of the lamp was measured physically by a photodiode and chemically by actinometry as described above. Figure 3.20 shows the intensity profile measured at various distances from the lamp.

3.5.6 Lamp lifetime

In a recent study [11], the UV intensity of 172 nm, 222 nm and 308 nm lamps was measured using photodiode with filters and photomultiplier while the absolute UV intensity generated was determined using chemical actinometry on the basis of light induced chemical reactions as described earlier in this chapter. With this approach, energy conversion efficiencies (UV output/electrical input) for the excimer lamps were measured. The lifetime, overall efficiency,
stability, switch-on and switch-off cycles, and output fluctuation of the excimer lamps were carried out at a temperature of 25°C.

During the study, it was found that efficiency increased as input power decreased. It was also, however, noted that colour centres due to irradiation with a photon energy less than the SiO₂ bandgap energy of 8.3 eV were formed within the first 60 hours of operation for 172 nm excimer lamps which reduced their output intensity during their time. By contrast, 100% of the original UV intensity output by the 222 nm and 308 nm lamps was still maintained after up to 4000 hours operating time. Figure 3.21 shows the UV intensity of the 222 nm lamp as a function of operating time [11].
Figure 3.21 UV intensity of 222 nm lamps vs operating time

It was observed lifetimes up to at least 4000h were possible with low fluctuation (less than 0.2%). A comparison was also made of these lamps with the lifetime of conventional mercury lamps. Immediate UV output after ignition can be achieved in excimer UV sources based on dielectric barrier discharge in a rare gas or a mixture of rare gas and halogen. It was also seen excimer lamps possessed greater stability and extended lamp life compared with conventional lamps.

Table 3.4 shows the lifetime of different industrial lamps obtained from a communication with Hamamatsu and Optical Radiation Corporation. The conversion efficiencies of these lamps were seen to vary with electrical power, with maximum values of around 22.5%. It was concluded that excimer UV sources could clearly provide a cost-effective, long lifetime, and high efficiency source of UV photons.
Table 3.4 Lifetime of different industrial lamps
(data source: Hamamatsu & Optical Radiation Corporation)

<table>
<thead>
<tr>
<th>Lamp type</th>
<th>Wavelength (nm)</th>
<th>Guaranteed Life(h)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-pressure mercury</td>
<td>185 and 254</td>
<td>2000</td>
</tr>
<tr>
<td>Medium pressure mercury</td>
<td>200 - 600</td>
<td>800 - 1000</td>
</tr>
<tr>
<td>High pressure mercury</td>
<td>300 - 600</td>
<td>600</td>
</tr>
<tr>
<td>Xenon</td>
<td>UV to IR continuous spectrum</td>
<td>600 - 1000</td>
</tr>
<tr>
<td></td>
<td>185-2000</td>
<td></td>
</tr>
<tr>
<td>Mercury-xenon (HgXe)</td>
<td>UV to IR continuous spectrum</td>
<td>400 - 1000</td>
</tr>
<tr>
<td></td>
<td>185-2000</td>
<td></td>
</tr>
<tr>
<td>Deuterium</td>
<td>UV continuous spectrum 160-400</td>
<td>1000</td>
</tr>
<tr>
<td>Directly-heated deuterium</td>
<td>UV continuous spectrum 115-400</td>
<td>300 - 500</td>
</tr>
</tbody>
</table>

* The end of life is defined as the time when the radiant intensity falls to 50% of its initial value.

Commercial excimer lamps now are available at the wavelengths 126 nm (Ar₂*), 146 nm (Kr₂*), 172 nm (Xe₂*), 222 nm (KrCl*) and 308 nm (XeCl*) [12]. For UV curing applications cylindrical XeCl* lamps up to 2m length are available. Most excimer lamps concentrate their emission in a narrow wavelength region. Even at high electrical input powers cooled versions can operate close to room temperature. Phosphors can be used to transform the UV radiation to visible light as discussed in Chapter 1. This is the basis of mercury-free fluorescent lamps and of flat plasma display panels with up to 1.5m picture diagonal.
3.6 Safety requirements

Great care was taken when using excimer lamps since they are a source of high-energy photons. Excimer lamps operate at high voltage and high frequency, and therefore connections needed to be checked often. Some deposition was carried out at high temperatures and therefore there was also a risk of burns. Some of the chemicals used like hexane and hydrofluoric acid can be toxic and corrosive, and great care was needed when handling. Ozone concentration also has to be checked when using 172 nm lamps [1].

3.7 Conclusions

The large area lamp designed and used for this research has been described. The UV – ILS chamber and its operation have been discussed. UV generation and power measurement methods have been described. The UV intensity of the 172 nm and 222 nm lamps can be measured using photodiode with filters and photomultiplier while the absolute UV intensity generated by 222 nm lamps was determined using chemical actinometry on the basis of light induced chemical reactions. A brief outline of procedures used for processing thin films in this work has been made. Thin film characterisation methods have been described.
3.8 References

Chapter 4

The photo-CVD processing of titanium dioxide and tantalum pentoxide
doped with titanium dioxide

The photo-CVD technique was employed for the deposition of titanium dioxide \( (\text{TiO}_2) \) and tantalum pentoxide \( (\text{Ta}_2\text{O}_5) \) doped with \( \text{TiO}_2 \) or \( (\text{Ta}_2\text{O}_5)_{1-x}\text{TiO}_2_x \).

Generally, CVD processes offer the following advantages over competing deposition techniques:

a) high purity deposits are readily achievable,
b) deposition of materials of various chemical compositions is possible,
c) some films can be deposited with adequate film properties only by CVD and
d) good economy and process control are possible for many films.

Plasma enhanced CVD offers film deposition at low – temperature. However, deposited films are generally not stoichiometric because of complicated and varied deposition reactions. Moreover, by-products and incident species especially hydrogen, nitrogen and oxygen are incorporated into
the resultant films in addition to the desired products. Excessive contamination by these may lead to out-gassing accompanied by bubbling, cracking or peeling during later thermal cycling and to threshold shifts in metal oxide semiconductor (MOS) circuits.

As discussed in the preceding chapters, to date most photo-induced processing has been performed with lasers whose use is inherently limited by the total photon fluxes available, rendering them unsuitable for large area wafer processing. On the other hand, excimer lamps, which are capable of producing high power radiation in the 108 nm – 354 nm wavelength range can initiate a wide variety of large area – low temperature photo-induced reactions.

Photo-CVD uses high-energy, high intensity photons to either dissociate and excite reactant species in the gas phase or heat the substrate surface. In the latter case, the reactant gases are transparent to the photons and the potential for gas phase reaction is completely eliminated. In the case of reactant species' excitation, the energy of the photons can be chosen for efficient transfer of energy to either the reactant molecules themselves, or to a catalytic intermediary, such as mercury vapour. Photo-CVD enables deposition at extremely low substrate temperatures. Films deposited by this technique show good step coverage, but may however, suffer from low density and molecular contamination as a result of the low deposition temperatures.

4.1 The need for high dielectric constant materials

Presently, the target for ULSI is the production of very thin insulator films equivalent to nanometer scale SiO₂ films with a leakage current density less than 10⁻⁸A/cm² at the supply voltage. A required low current leakage of less than 10⁻⁹A/cm² for dielectric films is suggested
As the SiO₂ thickness is decreased, direct tunnelling currents increase exponentially. This physically limits the use of SiO₂ as a gate dielectric below 1.5 nm thickness. The need arises to continuously scale down chip sizes in DRAM products in order to improve circuit performance as the number of transistors per unit volume increases. However, as cell size is reduced, this conflicts with the requirement for maximised cell capacitance for charge storage, as shown in the expression for a parallel plate capacitor:

\[ C = k \varepsilon_0 A / t \quad (4.1) \]

where \( k \) is the dielectric constant, \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{F/cm}) \), \( A \) is the surface area of the capacitor and \( t \) the thickness of the dielectric. One solution as discussed above is the introduction of high-k dielectrics, in order to keep constant the effective capacitance as the dimensions are reduced. In such cases, expression (4.1) for SiO₂ with a dielectric constant of 3.9 leads to:

\[ t_{eq} = 3.9 \varepsilon_0 (A/C) \quad (4.2) \]

where \( t_{eq} \) is the equivalent thickness, \( C/A \) the capacitance density, with the physical thickness of an alternative dielectric employed to achieve the equivalent capacitance density of \( t_{eq} \) obtained from the expression [2]:

\[ t_{\text{high-k}} = k_{\text{high-k}} \cdot t_{eq} / 3.9 \quad (4.3) \]
though, however actual performance of a CMOS gate stack does not scale so simply with the dielectric due to possible quantum mechanical and depletion effects from the silicon substrate and gate [3].

As discussed above, in order to achieve lower leakage currents at the same equivalent oxide thickness, one approach is to replace the SiO$_2$ with a thicker dielectric, which has a higher permittivity. Alternatives include Si$_3$N$_4$ [4], Ta$_2$O$_5$ [1,5-6], TiO$_2$ [7,8,9], Pb(Zr,Ti)O$_3$ [10] and doped materials like TiO$_2$ in Ta$_2$O$_5$ [11] and others. In order to function as a successful gate dielectric, a high-k dielectric must meet criteria that include permittivity, barrier height, stability in direct contact with Si, interface quality, film morphology, gate compatibility, process compatibility and reliability [12].

Table 4.1 below shows a review of materials under consideration for high dielectric constants, and the values achieved [13]. Ta$_2$O$_5$ with a dielectric constant of 25 – 28 as shown in the table, is attracting much current interest as a potential high dielectric constant material in advanced microelectronic devices such as DRAMs. Recent work [11,14,15] has shown that the dielectric constant of Ta$_2$O$_5$ can be increased by doping the material with TiO$_2$ both in the bulk and thin film form. Thin films of Ta$_2$O$_5$ doped with TiO$_2$, deposited by the photo-CVD process are explored.
Table 4.1 Alternative gate dielectrics for use in silicon MOS transistors [13].

<table>
<thead>
<tr>
<th>Material</th>
<th>k</th>
<th>Material</th>
<th>k</th>
<th>Material</th>
<th>k</th>
<th>Material</th>
<th>k</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbZr\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} (PZT)</td>
<td>1000</td>
<td>Ta\textsubscript{2}O\textsubscript{3}</td>
<td>25-28</td>
<td>Nd\textsubscript{2}O\textsubscript{3}</td>
<td>16-20</td>
<td>MgO</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Ba\textsubscript{x}Sr\textsubscript{1-x}TiO\textsubscript{3} (BST)</td>
<td>500</td>
<td>LaAlO\textsubscript{3}</td>
<td>25</td>
<td>Y\textsubscript{2}O\textsubscript{3}</td>
<td>11-14</td>
<td>Li\textsubscript{2}O</td>
<td>8.1-8.8</td>
<td></td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>100</td>
<td>La\textsubscript{2}Be\textsubscript{2}O\textsubscript{5}</td>
<td>25</td>
<td>Er\textsubscript{2}O\textsubscript{3}</td>
<td>12.5-13</td>
<td>MgAl\textsubscript{2}O\textsubscript{4}</td>
<td>8.3-8.6</td>
<td></td>
</tr>
<tr>
<td>LaScO\textsubscript{3}</td>
<td>30</td>
<td>ZrO\textsubscript{2}</td>
<td>22</td>
<td>ZrSiO\textsubscript{2}</td>
<td>12-13</td>
<td>BeO</td>
<td>6.9-7.7</td>
<td></td>
</tr>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2}</td>
<td>29.7</td>
<td>La\textsubscript{2}O\textsubscript{3}</td>
<td>21</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>9-12</td>
<td>Ce\textsubscript{2}O\textsubscript{3}</td>
<td>7.0</td>
<td></td>
</tr>
</tbody>
</table>

In this work, TiO\textsubscript{2} and Ta\textsubscript{2}O\textsubscript{3} - TiO\textsubscript{2}, films were prepared by the photo-CVD method, with the latter prepared by using various precursor molar ratios. Advantages of photo-CVD have been explained above.

4.2. Deposition and characterisation of TiO\textsubscript{2}

Si substrates around 1cm\textsuperscript{2} in area were cleaved from a large wafer and cleaned in an ultrasonic bath with isopropanol, blown with nitrogen, and then transferred to a heater stage in the stainless steel UVILS-CVD described in chapter 2, together with similarly prepared quartz substrates.

Titanium isopropoxide (TTIP) precursor was mixed with anhydrous hexane in a hermetically sealed container. The mixture was introduced into the photochemical reaction chamber through a droplet injector vaporiser at 110°C by an Ar carrier gas flowing at a pressure of several mbar. N\textsubscript{2}O oxidising gas was also introduced into the chamber at several mbar. Substrate temperatures
for this work varied between 50 - 350°C, with deposition times of 60 - 600 seconds. After deposition, the samples were characterised ex-situ by the various methods described in chapter 2. These were ellipsometry, FTIR, XRD and UV-visible spectrophotometric measurements.

4.2.1 Results discussion of the photo-CVD processing of TiO₂

The thermal decomposition of TTIP is reported [16] to follow the route:

\[
\text{Ti(OC}_3\text{H}_7)_4 \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_6 + 2\text{H}_2\text{O} \quad (4.4)
\]

TTIP has also been shown to absorb UV light in the broad spectrum from 190 - 400 nm [17]. When TTIP vapour is irradiated with 222 nm excimer lamps, C-C, C-H and C-O bonds are dissociated. The N₂O supplied to the deposition chamber is also dissociated by the UV, yielding excited oxygen atoms O(^1D). These species attack the ligands to which the Ti atoms are attached, subsequently forming Ti-O-Ti bonds in the gas phase and on the substrate surface, leading to the growth of TiO₂ on the substrates. With the injector system, a precise number of droplets of identical size ensures accurate control of this process.

Figure 4.1 shows the dependence of thickness and refractive index on deposition time at a constant temperature of 350°C. The refractive index characteristics of TiO₂ films processed at various temperatures between 50 - 350°C are shown in figure 4.2. High refractive index values of between 2.2 - 2.54 were obtained. The increase in refractive index is attributed to an increase in film density and a decrease in the number of defects, with the higher values being achieved for the thickest films.
Figure 4.1 Thickness and refractive index of TiO$_2$ films grown at 350°C

The higher values compare favourably with the value of 2.58 recorded for the bulk material at a wavelength of 632 nm. The measured film thicknesses were between 20 – 510 nm, providing a high calculated deposition rate of approximately 50 nm/min at 350°C. Similar deposition rates have also been reportedly achieved by plasma enhanced CVD [18].
Figure 4.2 Refractive index characteristics of TiO$_2$ films grown at different temperatures

Figure 4.3 shows an Arrhenius plot of the deposition rate of films. Deposition time was 600s for all data shown. A linear relationship between $\ln R$ and the reciprocal of temperature was observed for temperatures between 150°C and 350°C, providing an activation energy of 0.382eV. Such kinetically controlled deposition is determined by surface decomposition of the precursor [19]. At temperatures below 150°C, the film growth rate appears to increase with decreasing temperature due to vapour condensation on the substrate, resulting in only partial decomposition of the precursor. This may be characterised by an activation energy of $-0.039$eV. The value of 0.382eV...
Figure 4.3 Arrhenius plot of the deposition rate of the TiO$_2$ films

is higher than 0.2073eV for TiO$_2$ films deposited by laser-induced CVD using a 308nm XeCl excimer laser at between 120 and 210°C [20] since lasers produce high beam energy and is lower than 0.8075eV obtained by metallo-organic CVD of TiO$_2$ [21].

Figure 4.4 shows the FTIR of films grown at 350°C for different time periods. A strong absorption peak generally attributed to TiO$_2$ is observed around 433cm$^{-1}$ [22]. The inset verifies the absence of OH absorption at 3300cm$^{-1}$ for these films. However, such absorption was found to be present in layers deposited at temperatures below 250°C.
Figure 4.4 FTIR of TiO$_2$ films deposited at 350°C. Inset shows the absence of OH bonds.

Figure 4.5 Transmittance and extinction coefficient of TiO$_2$ films as functions of wavelength.
Figure 6. XRD of TiO$_2$ films deposited at (a) 200°C and (b) 350°C.
Figure 4.5 shows the transmittance and extinction coefficient diagrams for films grown at 350°C. Transmittance values for the thinner films (~60 nm) was more than 90% above 500 nm. The average extinction coefficient calculated for all films on their respective thicknesses was found to be 3.5x10^{-2} at 500 nm, which is slightly higher than that obtained by radio frequency magnetron sputtering [23].

Figure 4.6 shows the XRD of TiO₂ films deposited at 200°C and 350°C. XRD measurements revealed that films deposited at 200°C and above were crystalline. All the peaks found in the films as-deposited at these temperatures were identified as crystalline anatase. No other peak types were observed. Films deposited at 200°C had the (101), (200) and (211) orientations as films deposited at 350°C had similar peaks and an additional (112) peak.

4.3 The photo-CVD processing of (Ta₂O₅)ₓ₋₆(TiO₂)₆

As with TiO₂ films, thin Ta₂O₅-TiO₂ films were deposited on quartz and crystalline p-type Si (100) at temperatures from 50 - 350°C by the UV - ILS CVD system described in chapter 2. The same experimental conditions as during the photo-CVD of TiO₂ were used. The alkoxide precursors TTIP and tantalum tetraethoxy dimethylaminoethoxide (TaDMAE) were mixed in various ratios, vaporised, and then driven into the reaction chamber by an Ar carrier gas, where they were exposed to the UV radiation. As with TiO₂, characterisation methods used were FTIR, ellipsometry, UV-VIS and XRD.

Since the liquid injection technique combined with excimer lamp processing provides low temperature growth of areas up to 4” diameter, films were grown on quadrants of 5cm radius for
CV measurements at National Microelectronics Research Centre. The electrical measurements were performed using a mercury probe gate electrode system. This allows samples to be examined immediately after deposition or subsequent thermal process step. The area of the mercury probe is 4.18x10^-7 m². The electrical testing performed was CV at 100kHz (using HP 4284A LCR meter) and IV (using HP 4156B Parameter analyser). In both cases the voltage was applied to the substrate as this minimises noise in the measurement process.

### 4.3.1 Results and Discussion

Figure 4.7 shows the refractive index characteristics of the Ta₂O₅-TiO₂ films of various compositions grown at 350°C, where refractive index values range from 1.6 to 2.8. It is clear that the refractive index can be fine-tuned in the films by tuning the Ta₂O₅-TiO₂ content. Films of 92% Ta₂O₅ content had the highest refractive index values.

Figure 4.8 shows the FTIR characteristics of Ta₂O₅-TiO₂ films of various composition deposited at 350°C for 10 minutes. The peak at 433cm⁻¹ associated with Ti-O decreases in intensity with a reduction in the TiO₂ content from 90% to 4% in the composite films. The broad peak at 650cm⁻¹ which is attributed to Ta-O-Ta and Ta-O stretching vibrational modes [24-25], clearly intensifies with increased Ta₂O₅ content. It is noted that no OH peak was observed at 3600cm⁻¹ in any of the films shown here, nor any grown at temperatures above 250°C.
Figure 4.7 Refractive index characteristics of Ta₂O₅-TiO₂ films of various compositions grown at different temperatures for 10 minutes.

Figure 4.9 shows the Tauc characteristics for Ta₂O₅-TiO₂ films of various composition grown at 350°C. Bandgap energies calculated from this plot [26] are seen to rise with increasing Ta₂O₅ content. This is readily understood since the bandgap energy of Ta₂O₅ is higher than that of TiO₂. The variation of bandgap energy with the composition of the films is shown in figure 4.10.
Figure 4.8 FTIR characteristics of Ta$_2$O$_5$-TiO$_2$ films deposited at 350°C for 10 minutes.

The energies range from 3.2eV which is near the TiO$_2$ value of 3.5 to 4.2eV, which is similar to the value for Ta$_2$O$_5$ obtained by pulsed laser deposition (4.2eV) [25] and was attained at the highest deposited Ta$_2$O$_5$ content of 96%.
Figure 4.9 $\Phi (\alpha h\nu)$ as a function of photon energy for Ta$_2$O$_5$-TiO$_2$ films of various compositions prepared on quartz at 350°C.

Figure 4.11 shows a TEM of composite Ta$_2$O$_5$ - TiO$_2$ consisting of 96% Ta$_2$O$_5$ content carried out at INPG. The films were grown at 350°C in the UV-ILS chamber and annealed in the four lamp chamber at 400°C in a 600mbar O$_2$ atmosphere for 10 minutes. Film thickness was 51.5 and 53 nm as measured by TEM and ellipsometry respectively, and indicating the closeness of values measured by the two methods. The TEM shows a 1.9 nm SiO$_2$ layer at the interface between the composite materials and the substrate.
Figure 4.10. Optical bandgap as a function of $\text{Ta}_2\text{O}_5$ content

Table 4.2 below shows the variation of thicknesses of 92%Ta$_2$O$_5$-8%TiO$_2$ and the SiO$_2$ at the interface with the number of drops injected into the deposition chamber.
Table 4.2 Variation of 92%Ta₂O₅-8%TiO₂ and SiO₂ interlayer thickness with number of precursor drops

<table>
<thead>
<tr>
<th>Number of drops</th>
<th>92%Ta₂O₅-8%TiO₂ thickness (nm)</th>
<th>SiO₂ thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ellipsometry</td>
<td>TEM</td>
</tr>
<tr>
<td>60</td>
<td>49</td>
<td>45</td>
</tr>
<tr>
<td>100</td>
<td>53</td>
<td>51.5</td>
</tr>
<tr>
<td>200</td>
<td>79.3</td>
<td>79.5</td>
</tr>
<tr>
<td>300</td>
<td>146.4</td>
<td>146</td>
</tr>
</tbody>
</table>

As seen in table 4.2 and in figure 4.12, SiO₂ interlayer thickness decreases with increased Ta₂O₅-TiO₂ film thickness. Dielectric film permittivity measurements were made only on annealed films.
The model in figure 4.13 below proposes a possible mechanism explaining the effect of annealing on deposited films [13]. An important role is played by O species formed by irradiation using 172 nm lamps, and according to the model, leads to:
Figure 4.13 Effect of annealing in an active $O_2$ species environment

a) Removal of defects and oxygen vacancies
b) Reduction of suboxides by reacting with them, leading to improved stoichiometry
c) Formation of silicon dioxide on the thin film surface and within the thin film at the interface between Si and the deposited film leading to improved interfacial quality.
d) Removal of any impurities present in the as-deposited films and densification of layers.

Figures 4.14 shows the C-V characteristics for films of 8%TiO$_2$ - 92%Ta$_2$O$_5$ content annealed for 10 minutes at a temperature of 400°C. The film test signal frequency was 1kHz.
Figure 4.14 CV tracing of 8%TiO$_2$-92%Ta$_2$O$_5$ film annealed at 400°C for 10 minutes.

Figure 4.15 shows variation of dielectric constant with Ta$_2$O$_5$ content. TaDMeE and TTIP mixed in their molar ratios were used as discussed above. Using the maximum capacitance values, calculated dielectric constants range from 17 to 51 for annealed films of from 91.8-92.2% Ta$_2$O$_5$ content and thickness between 27 and 100 nm. However, it was noticed that possibly, due to the high sensitivity of TaDMeE, microlitre volume changes yielded films of very different dielectric constant values. Since TaDMeE had a higher vapour pressure than TTIP, this could possibly have resulted in the composition of films formed not being representative of the precursor ratios, and having higher Ta$_2$O$_5$ content than expected.
An increased number of precursor drops was expected to yield higher dielectric constant values, due to the anticipated decrease in SiO₂ interlayer thickness. However, due to errors and precursor sensitivity, it was observed that the thinner films had higher dielectric constant than the thicker ones over most of the measurement range. Despite this, the highest dielectric constant values compare favourably with values of 23, 41 and 55 obtained respectively by electron beam evaporation, sol-gel processing followed by a rapid thermal annealing step and by r.f. magnetron sputtering [14-15, 27].
These values are however lower than the value obtained for bulk films of the same content by Cava et al at 1400°C [11]. This could be a direct result from the low processing temperatures, leading to different crystalline states. A comparison of films discussed is made in table 4.3.

Table 4.3 Comparison of dielectric constant $\text{Ta}_2\text{O}_5$-$\text{TiO}_2$ thin films obtained by various processes

<table>
<thead>
<tr>
<th>Method</th>
<th>Processing Temperature (°C)</th>
<th>Annealing Temperature (°C)</th>
<th>Thickness (nm)</th>
<th>Dielectric constant $\varepsilon_r$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.f magnetron sputtering</td>
<td>1000</td>
<td>800</td>
<td>110</td>
<td>55</td>
<td>[14]</td>
</tr>
<tr>
<td>Sol-gel processing</td>
<td>25</td>
<td>RTA 700</td>
<td>160</td>
<td>41</td>
<td>[15]</td>
</tr>
<tr>
<td>Electron beam evaporation</td>
<td>-</td>
<td>700</td>
<td>15</td>
<td>23 $a$</td>
<td>[27]</td>
</tr>
<tr>
<td>UV - ILS</td>
<td>350</td>
<td>400</td>
<td>82.9</td>
<td>51</td>
<td>This research</td>
</tr>
</tbody>
</table>

$a$ – as deposited           $b$ – annealed

4.4 Conclusions

The low temperature deposition of thin TiO$_2$ films on crystalline Si and quartz by photo-induced CVD using UV employing a dielectric barrier discharge excimer lamps at $\lambda$ =222 nm has been demonstrated. The growth of films with refractive indices from 2.20 - 2.54 has been achieved at temperatures between 50 and 350°C. Refractive index values coupled with an optical band gap of around 3.35 indicate the films deposited between 250 - 350°C were of the best quality. The relative permittivity of films had a highest value of 51. However, higher values of about 126 [11] were not achievable on thin films. Films grown at temperatures of 200°C and above were crystalline.
4.5 References.


Chapter 5

Sol-gel processing of titanium dioxide and tantalum pentoxide
doped with titanium dioxide

Here the novel UV assisted sol-gel technique used in this study is described. A background is
given on the sol-gel process, precursors employed and its advantages and disadvantages. The sol
gel processing of TiO₂ and Ta₂O₅-TiO₂ of various composition is then discussed. The sol-gel
process was chosen in favour of other methods for the growth and deposition of the selected thin
film materials because of various advantages. Sol-gel processing can occur at temperatures as low
as room temperature and, coupled with photo-processing, a minimal thermal budget is achievable.
Electron bombardment common during plasma processing is also avoided during these processes,
resulting in no surface damage.
5.1 The sol gel technique and sol-gel processing

The sol gel process involves the synthesis of an inorganic network by a chemical reaction in solution at low temperature. The process involves preparation of a homogeneous solution by the mixing of materials at a molecular level, converting the solution to a “sol” by treatment with suitable reagents, and bringing the materials out of solution either as colloidal gel or a polymerised macromolecular network whilst retaining the solvent. Colloids are stable molecules and atoms held together by intermolecular forces [1]. The colloidal suspension of a solid in a liquid is called a sol. Whilst a sol is a suspension of small particles of one phase in another, usually liquid phase, a solution is a single phase system. A sol does not gel as long as the very small size of the dispersed phase remains. Colloids can exist as systems comprised of any of the combinations, solid – solid or solid – gas or solid – liquid as shown in figure 5.1 below [1].

![Figure 5.1 Combinations of Colloids](image)

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When particles in a sol combine and become heavier, they precipitate. If when they form a continuous network and interconnect, the sol is able to maintain the shape of the original container when removed, this means that the sol has formed gel. The basic possibilities for forming a gel from a sol are through alkoxide gels whereby molecules are formed capable of polymerisation or through particulate gels whereby particles in a liquid medium form a network through various mechanisms [2].

The resulting solvent can then be dessicated off, leaving a solid which possesses very high surface area and can be sintered and densified at much lower temperatures than expected in the normal processing of the final desired glass or other ceramic materials. [1, 3 - 4]. Thus, the transition from a liquid (solution or colloidal solution) into a solid (di- or multiphase gel) leads to the expression “sol-gel process” [5].

5.1.1 Precursors for the solgel process

Any precursor which is able to form reactive “inorganic” monomers or oligomers can be used for sol-gel techniques. [6]. Most work in the sol-gel field has been done by the use of alkoxides such as tetraethoxysilane, titanium tetraisopropoxide, zirconium tetraisopropoxide as precursors [7-11]. Alkoxides provide a convenient source for monomers which are soluble in common solvents. Hydrolysis and condensation reactions are controllable. The general reactions for alkoxides take the form:
\[ \equiv M - X + H_2O \rightarrow \equiv M - OH + HX \quad (5.1) \]

where \( M \) is a metal and \( X \) is a halogen or OR group in which \( R \) is an alkyl radical

\[ M - OH + X - M \rightarrow \equiv M - O - M= + HX \quad (5.2) \]

\[ M - OH + HO - M \rightarrow \equiv M - O - M= + H_2O \quad (5.3) \]

Scherer [12] describes polymerisation as the increase in connectivity of the network formed by condensation reactions such as in the case of Si:

\[ Si - OH + HO - Si \rightarrow \equiv Si - O - Si= + H_2O \quad (5.4) \]

Aging results in further hydrolysis as in equation (5.5):

\[ \equiv Si - OR + H_2O \rightarrow \equiv Si - OH + ROH \quad (5.5) \]

In the reverse reaction, re-esterification, occurs as in equation (5.6):

\[ Si - OH + R - OH \rightarrow \equiv Si - OR + H_2O \quad (5.6) \]

This reaction can be suppressed by introducing excess \( H_2O \).
Precursors should therefore be soluble in solvents especially alcohols and be reactive enough to participate in the gel forming processes. They could be alkoxides, halogenides or acylates [6]. The microstructure of a gelled product can be controlled by such parameters as precursor concentration, ratio of water to the precursor and the presence of an acidic or basic catalyst.

### 5.1.2 Sol gel deposition of films

Interesting liquid-phase mechanical techniques that are in use for depositing thin films from liquids include spinning, spraying, coating, brushing and dipping. [6]. Spin-on-deposition of organometallic precursors is employed in this work for the deposition of thin films of TiO₂ and Ta₂O₅ doped with TiO₂ with good optical and dielectric properties.

Figure 5.2 shows the typical stages during the spin coating process [13]. A stream of the precursor is dispensed onto the surface of the spinning Si substrate. The process goes through the stages deposition, spin-up, spin-off and solvent evaporation. Evaporation continues throughout the whole process. Uniformity and thickness of the final film is dependent on mass transfer and evaporation. Initially, convective outflow is the dominant thinning mechanism. However, towards the end, evaporation dominates.

An advantage of spin coating is that a film of liquid tends to become uniform in thickness during spin-off, and, once uniform, tends to remain so, provided that the viscosity is not shear dependant and does not vary over the substrate [14].
A process, such as thermal oxidation, hydrolysis, pyrolysis or irradiation with UV light of the matched wavelength for bond breaking induces production of the desired film.

5.1.3 Advantages and disadvantages of the sol gel process

Advantages of the sol gel method over conventional deposition methods such as CVD, evaporation or sputtering are listed [15, 16]. These include.
a) homogeneity,

b) lower cost due to less equipment and therefore need for complex vacuum equipment,

c) easier fabrication route,

d) better control over chemical composition as well as in multi-component systems,

e) low temperature processing, even at room temperature

f) possibility of depositing new noncrystalline solids outside the range of normal glass formation resulting in better glass products from special properties of gel

g) new crystalline phases from noncrystalline solids, and

h) the possibility to deposit complex thin films.

It is possible to achieve many technologically useful shapes and forms of materials and to control the composition much more easily than by conventional processing. The most important advantage over conventional coating methods is the ability to control precisely the microstructure the pore volume, pore size and surface area of the deposited film [16]. Low temperature processing avoids such problems as crucible contamination, expensive furnacing and difficult homogenisation of the melt. Coatings can be applied to almost any geometry of substrate. Fibres can be drawn from partially hydrolysed gels and subsequently densified by heat treatment [1, 17].
The sol gel process has its own disadvantages as compared to conventional processes. These are [6, 17] :

a) the high cost of raw materials,
b) large shrinkage during processing,
c) residual fine pores,
d) residual hydroxyl,
e) residual carbon,
f) health hazards of organic solutions and
g) long processing times.

5.2 Photo - induced sol - gel process

The sol - gel process can be divided into 3 parts - sol and gel formation, drying and densification [18]. Growing interest in the UV photochemistry of surfaces, gas - phase precursors and adsorbates has been stimulated by technical applications such as photo - induced surface cleaning, surface modification, material deposition as well as material removal [19]. Material growth can be carried out by using various radiation sources. These are described in the next section. A metallo-organic precursor, dissolved in an alcohol solution, is dispensed onto a substrate by spin coating. The film is then decomposed photochemically using a suitable atmosphere to convert the sol - gel precursors to their ceramic oxides or other compounds. Besides having all the above advantages, photo - induced sol - gel processing occurs without surface damage due to ion bombardment [20].
5.3 Deposition of single and multilayer films of TiO₂ by photo-induced sol-gel processing

Low temperature deposition of single and multilayer films of TiO₂ was carried out on Si (100) substrates at low temperature by the new photo-induced sol-gel process. The Si substrates were first cleaned in an ultrasonic bath with isopropanol. Polymeric sols were prepared by the hydrolysis and condensation of titanium isopropoxide Ti(OCH₃)₄ in C₂H₅OH in the presence of HCl as shown in figure 5.3, which has been adapted from [21].

Si and quartz substrates were cleaned in an isopropanol bath and then blown with N₂. The Ti(OCH₃)₄ precursor was left at room temperature in a container and continuously stirred magnetically for up to 100 hours. Small amounts of the precursor required for coating on the substrates were drawn at 24-hour intervals. A drop of the precursor was released onto the substrate, which was spinning at the required speed of 1000rpm, 2000rpm, 3000rpm, 4000rpm and 5000rpm. The spin time was set at 30 seconds, and all coating was carried out at room temperature. Substrates were subsequently loaded into the four lamp chamber described in Chapter 2, then UV-annealed with the excimer lamps. Initially, substrates were irradiated for different exposure times and at temperatures of 80, 120 and 200 and 300°C respectively. Subsequent irradiation was carried out at 300°C for 10 min.

TiO₂ multilayers were subsequently prepared on Si(100) in a step-wise process, as shown in figure 5.4, with thickness and refractive index determined for every step.
Figure 5.3 Flow chart for the preparation of TiO$_2$ films by photo-induced sol-gel processing.
5.3.1 Characterisation of single and multilayer films of TiO$_2$ deposited by photo induced sol-gel processing

Single and multiple layer TiO$_2$ films were prepared by a new photo-induced sol-gel process as described above, with FTIR spectra taken for various time periods at a constant temperature of deposition.
The synthesis of titanate polymers by the sol-gel process involves the hydrolysis and condensation of the starting alkoxide, in this case titanium isopropoxide in the following reactions:

**Hydrolysis**
\[
\text{Ti(OC}_3\text{H}_7)_4 + \text{H}_2\text{O} \rightarrow \text{Ti(OC}_3\text{H}_7)_3\text{OH} + \text{C}_3\text{H}_7\text{OH} \quad (5.7)
\]

**Condensation**
\[
\text{Ti(OC}_3\text{H}_7)_4 + \text{Ti(OC}_3\text{H}_7)_3\text{OH} \rightarrow \text{Ti}_2\text{O(OC}_3\text{H}_7)_6 + \text{C}_3\text{H}_7\text{OH} \quad (5.8)
\]

**Water Condensation**
\[
\text{Ti(OC}_3\text{H}_7)_3\text{OH} + \text{Ti(OC}_3\text{H}_7)_3\text{OH} \rightarrow \text{Ti}_2\text{O(OC}_3\text{H}_7)_6 + \text{H}_2\text{O} \quad (5.9)
\]
Figure 5.6 Thickness and refractive index dependence on spin coating speed of films grown by sol-gel processing after different gelation times
Figure 5.5 shows the FTIR spectra of as spin coated films and those irradiated at a temperature of 80°C. The broadband at 3100 – 3400cm\(^{-1}\) is attributed to the OH stretching vibrations of water and OH groups. Its intensity is visibly reduced first when films are irradiated, then with increased exposure time. The increase in temperature from 0 – 80°C, results in loss of weight through the evaporation of adsorbed water and the loss of hydroxyl groups. The Ti – O vibrations occur at 550cm\(^{-1}\).

Figure 5.6 shows the thickness and refractive index of films grown by sol-gel processing. Films with a greater gelation period are thicker and have higher refractive index values at the same coating speed. This can be explained by a stronger interconnection of precursor particles. Figure 5.7 shows the FTIR of TiO\(_2\) films irradiated at temperatures from 120°C to 300°C for a fixed UV exposure time of 10minutes. As seen, the OH peak disappears at 300°C, indicating the growth of OH free TiO\(_2\) at this low temperature. The films formed showed good optical properties with transmittance values between 85% and 90% in the visible range of the spectrum, as shown in figure 5.8. The thickness and refractive index of the films formed can readily be controlled by the spin – coating speed and by the number of sequential layers deposited.

Figures 5.9 and 5.10 show the respective dependence on the number of layers of thickness and refractive index of films grown, before and after exposure to excimer lamps. After the irradiation step, the films grown exhibited linear growth in thickness with increased number of layers.
Figure 5.7 FTIR of TiO₂ films irradiated at different temperatures for a fixed UV exposure time of 10min.

Figure 5.8 Spectral transmittance of a TiO₂ single-layer film grown by UV lamp.
Figure 5.9 Dependence of the thickness of TiO$_2$ before and after irradiation at 172 nm for 10 min on spin deposition speed and number of layers.

The decrease in film thickness from the spin deposition and irradiation steps is due to densification of films after organic components and the OH group are dissociated and driven away from the substrate. The thickness of films grown varied from 20 – 125 nm. Furthermore, high refractive indices of between 2.1 and 2.4 were measured on films exposed to the UV irradiation. The higher refractive index value of 2.4 compares favourably with 2.58 recorded for bulk TiO$_2$ [22].
Figure 5.10  Dependence of refractive index of TiO$_2$ before and after irradiation at 172 nm for 10 min on spin deposition speed and number of layers.

5.4 Photo-induced preparation of Ta$_2$O$_5$ - TiO$_2$ dielectric thin films using sol-gel processing with xenon excimer lamps

As discussed above, SiO$_2$ is perceived to be approaching its useful and practical limit in ULSI as a consequence of miniaturisation of microelectronic devices, and is predicted by the Semiconductor Industry Association roadmap to reach atomic dimensions by 2012. The required device capacitance can be maintained by continued reduction in the thickness of the SiO$_2$ layer or by using three-dimensional structures or new materials with higher dielectric constants [23].
However, below thicknesses of 2 nm, direct tunnelling currents will limit the functionality of devices that incorporate such layers of SiO₂. Materials with high dielectric constant, low leakage current and higher dielectric strengths will therefore be required to produce the same devices possessing the same effective capacitance but using thicker layers. High dielectric constant materials have potential applications as charge storage capacitors for memory cells in ULSI DRAMs and low inductance decoupling capacitors for the control of simultaneous switching noise in high speed switching ULSI chips.

Of the many available, tantalum pentoxide (Ta₂O₅) appears to be one of several promising materials for such applications due to its thermal and chemical stability and especially because of its compatibility with ULSI processing [24,25]. Ta₂O₅ has also been doped with many materials including ZrO₂, SiO₂, and TiO₂ resulting in a significant increase in its dielectric constant [26-31]. Of particular interest is the doping of bulk Ta₂O₅ with TiO₂ at high deposition temperatures of 1400°C to produce a four-fold increase in dielectric constant [27]. However, much lower preparation temperatures are more desirable, and photochemical processing which has a low thermal budget, offers a novel approach. Pure Ta₂O₅ has also been produced by photo-CVD [7, 25, 28-31]. As discussed, low temperature photo-induced processing combined with the sol-gel method, offers a range of advantages including the deposition of complex thin films [6, 14, 17, 32]. The application of excimer lamps to the growth of good quality single and multilayer films of TiO₂ by the photo-induced sol-gel process has been investigated above.

The growth of Ta₂O₅ using excimer lamps has been investigated and it was noted that leakage current densities for films annealed at 400°C using excimer lamps were comparable to those of films annealed at 700-800°C using plasma CVD as shown in table 5.1 [33].
Table 5.1 Comparison of leakage current densities at 0.5 MV/cm (A/cm²) in Ta₂O₅ films obtained by different methods [33]

<table>
<thead>
<tr>
<th></th>
<th>Plasma CVD</th>
<th>Excimer Lamp photo-CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>10⁻⁶</td>
<td>9 x 10⁻⁸</td>
</tr>
<tr>
<td>Annealed at 700-800°C</td>
<td>10⁻⁸ – 10⁻⁹</td>
<td>2.0 x 10⁻⁹</td>
</tr>
</tbody>
</table>

In the following section, research now looks into the deposition of Ta₂O₅ doped with TiO₂.

5.4.1 Experimental Details

Polymeric sols were prepared by mixing tantalum ethoxide Ta(OC₂H₅)₅ and titanium isopropoxide Ti(OC₃H₇)₄ in a range of molar ratios in ethanol in the presence of hydrochloric acid. As above, the resulting transparent sols were magnetically stirred continuously at room temperature over several hours. The same Si (100) and quartz substrates were used. The sols were then spin-coated onto the substrates at room temperature. The thickness and refractive index of the films were measured while FTIR transmittance spectra in the range 4000 to 400 cm⁻¹ were taken. The substrates were then transferred to the four lamp system and irradiated for 10 minutes at 300°C. The above measurements were repeated after irradiation. Multilayered Ta₂O₅-TiO₂ thin films were subsequently prepared on Si(100) in a step-wise process. The surface morphology of the films was characterised by Topometrix atomic force microscopy (AFM). I-V measurement was carried out at 1 MHz on MOS capacitors constructed by aluminium evaporation on as-grown films.
5.4.2 Results and Discussion

As already discussed above, polymerisation is the increase in connectivity of the network formed by condensation reactions [12]. Here, a network is formed within the Ta(O\textsubscript{3}C\textsubscript{2}H\textsubscript{5})\textsubscript{3} and Ti(O\textsubscript{3}C\textsubscript{2}H\textsubscript{5})\textsubscript{4} in the presence of ethanol. The complex network is broken down to constituent metal oxides in the appropriate ratios by 172 nm excimer lamp irradiation. Figure 5.11 shows the FTIR spectra of the films before and after UV irradiation at a temperature of 300°C for 10 minutes.

Figure 5.11 FTIR spectra of films before and after irradiation. The inset shows (a) films before irradiation (b) films after exposure to 172 nm radiation at 300°C for 10 minutes.
The absorption peaks at $600\text{cm}^{-1}$ and $529\text{cm}^{-1}$ are attributed to Ta–O–Ta and Ta–O stretching [9]. A broad band observed in the $800–1000\text{cm}^{-1}$ range for films after spin–on coating, is due to suboxides TaO and TaO$_2$ [29]. After irradiation, this peak is dispersed. The broad band in the $3100-3400\text{cm}^{-1}$ range shows the dehydration and dehydroxylation of the polymers within the film before and after the irradiation step.

Figure 5.12 shows an AFM of the as–deposited Ta$_2$O$_5$–TiO$_2$ sol–gel film.

![AFM of TiO$_2$–Ta$_2$O$_5$ films prepared by UV exposure](image)

Although homogeneous films were deposited, pin holes were observed on films before and after irradiation. The pin holes were possibly the result of small particles, which were suspended in the solution.
The refractive index was as low 1.7 before irradiation due to the presence of organic compounds in the films. After irradiation, these organic compounds decomposed and denser films were formed. The refractive index and thickness of the Ta$_2$O$_5$-TiO$_2$ thin films reach maximum values at a TiO$_2$ composition of 8% both for single and multilayer films grown under the same conditions, as shown in Figures 5.13 and 5.14.

![Graph showing refractive index vs. Ta$_2$O$_5$ content for single and multilayer films](image)

**Figure 5.13 Refractive index of Ta$_2$O$_5$ - TiO$_2$ films of different composition**

*after UV irradiation at 300°C for 10 minutes.*

After irradiation, the refractive index $n$ values were 1.86, 1.98 and 1.97 for single layer films of 96%, 92% and 90% Ta$_2$O$_5$ content respectively and 2.04, 2.05 and 2.04 for 7 layer films. These values are similar to those obtained for CVD Ta$_2$O$_5$ at 350°C [29]. Multilayers exhibited a higher refractive index than monolayers as was also observed in work on TiO$_2$ described above. Film thicknesses of up to 140 nm were achieved for our multilayered structures.
Figure 5.14 Thickness of thin films of different composition before and after UV irradiation at 300°C for 10 minutes.

The main objective was to grow ultra-thin films to replace SiO₂ of dimensions below 20nm. However, a phenomenon was observed whereby with an increase in thickness refractive index was also observed to increase.
Figure 5.15 shows leakage current characteristics of capacitors built on as deposited thin films of 96\% \( \text{Ta}_2\text{O}_5 \) content. A value of \( 6 \times 10^{-7} \text{A/cm}^2 \) is obtained at a field of 0.5MV/cm. This is less than the value for films obtained by electron beam evaporation where the current was reported to be \( 2 \times 10^{-6} \text{A/cm}^2 \) at the same applied field [34].

Table 5.2 shows a comparison of films grown by different methods. The leakage current value for as deposited sol–gel films of \( (\text{Ta}_2\text{O}_5)_{0.96}(\text{TiO}_2)_{0.04} \) is in the same range as for films deposited by plasma CVD though it is higher than the value for films deposited by excimer lamp photo–CVD at UCL.
Table 5.2 Comparison of leakage current densities at 0.5 MV/cm (A/cm²) in as-deposited films obtained by different methods

<table>
<thead>
<tr>
<th>Plasma CVD</th>
<th>Excimer lamp photo-CVD</th>
<th>UV sol-gel method</th>
<th>Electron beam evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta₂O₅</td>
<td>Ta₂O₅</td>
<td>Ta₂O₅-TiO₂</td>
<td>Ta₂O₅-TiO₂</td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>9×10⁻⁸</td>
<td>4×10⁻⁶</td>
<td>2×10⁻⁶</td>
</tr>
</tbody>
</table>

5.5 Conclusions

The photo-CVD growth of Ta₂O₅-TiO₂ films of various compositions and thickness at different temperatures between 50-350°C has been demonstrated on Si and quartz. OH peaks were not present in films grown at 350°C. Refractive index values of between 1.6 and 2.8 can be fine-tuned by altering precursor ratios and temperature. Optical bandgap values within the range of 3.2 – 4.2 were attained, as expected by varying the ratio of Ta₂O₅ - TiO₂.

A new technique for preparing TiO₂ and Ta₂O₅ doped with TiO₂ at low temperature using a photo-induced sol-gel process has been demonstrated. (Ta₂O₅)₁₋ₓ(TiO₂)ₓ films were prepared on Si (100) substrates with maximum refractive index and thickness values at a TiO₂ content of x = 0.08. FTIR confirmed the presence of Ta-O bonds which were more pronounced after UV irradiation. AFM showed a uniform surface structure though pin-holes were also observed.
5.6 References


5. H. Schmidt - ibid, p 61.


Chapter 6

Low-temperature photo-oxidation of Si

This chapter explores the oxidation of Si to produce ultra-thin SiO₂, discusses its properties and limitations. Factors underlying the scaling down of features in miniaturisation are discussed. A background is given on Moore’s Law, and its significance to the microelectronics industry.

6.1 The need for ultrathin SiO₂

SiO₂ has been the gate dielectric of choice over other dielectrics because of its physical and electrical properties on Si substrates in metal oxide semiconductor field effect transistors (MOSFETs). SiO₂ possesses properties such as low defect density and high thermal stability. It is ideally suited to its role, meeting demands for high performance (speed) low static (off-state) power and a wide range of power supply and output voltages [1]. SiO₂ also enables defect charge densities on the order of $10^{10}/\text{cm}^2$, mid bandgap interface state densities of $\sim10^{10}/\text{cm}^2\text{eV}$ and breakdown fields in excess of 10mV/cm [1, 2].
With a growing demand for miniaturisation, a need has arisen for the deposition of ultra-thin SiO₂. Development of high density MOS dynamic random access memory (DRAM) devices with small cell areas is being accomplished by reducing the thickness of the SiO₂ storage capacitors to maintain the required charge storage level. Recently reported work on the direct photo-oxidation of Si with excimer lamps at a temperature of 250°C yielded an oxidation rate more than three times greater than that for photo-induced Si oxidation using a typical low-pressure Hg lamp at 350°C [3, 4]. With excimer lamps, a fixed oxide charge number density (Q/q) of 4.5 x 10¹⁰cm⁻², which is comparable to some of the best reported values for thermally grown oxides on Si at a high temperature of 1030°C [2] was obtained [5], indicating an ideal reaction between oxygen and SiO₂ species.

6.2 Moore's Law

Moore's Law states that the power and speed of computers will double every 18 – 24 months [6]. Gordon Moore also observed a doubling every 18 months of microprocessor performance, which is given by:

\[
\text{Clock frequency (MHz)} \times \text{Instructions per clock} = \text{MIPS} \quad (6.1)
\]

where MIPS is millions of instructions per second.

The semiconductor industry has been seen to improve the productivity of integrated circuits by about 30% annually since the invention of the integrated circuit in 1959. Microprocessors should maximise performance which is dominated by the length of the transistor gate and by the number
of interconnect layers as costs decrease, and in agreement with Moore’s Law, the great demand in microelectronics has led to devices with feature sizes below 180 nm [7]. Figure 6.1 shows a logarithmic increase in the number of transistors with year of introduction since 1971 [8].

![Graph showing the number of transistors vs year of introduction]

*Figure 6.1 Number of transistors vs year of introduction [8]*

As shown in the diagram, transistor numbers have doubled every 24 months. Transistor numbers required for a continued trend in Moore’s Law are shown for the period 2002 to 2010.
In computers, the scaling down of features has seen a trend in rapidly falling prices of computer equipment as computers become obsolete within a few years of purchase. As existing materials and technologies approach their physical limits, technology breakthroughs in materials and processes are required as device sizes decrease significantly below 100 nm. It has been demonstrated at laboratory research level that transistors with gate oxides as thin as 1.3 – 1.5 nm operate satisfactorily [9, 10]. It has further been proven that CMOS structures with SiO₂ gate oxides thinner than ~1.2-1.3 nm exhibit no further gains in transistor drive current and may serve as the practical SiO₂ scaling down limit [9]. Table 6.1 shows a summary of the projected gate oxide thicknesses for CMOS integrated circuits for 1997 – 2012 [11, 12].

Table 6.1 Projected gate oxide thickness for CMOS integrated circuits for 1997 – 2012

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Design rule (µm)</td>
<td>0.25</td>
<td>0.18</td>
<td>0.15</td>
<td>0.13</td>
<td>0.10</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>Wafer Diameter (mm)</td>
<td>200</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>Gate Dielectric (nm, k=3.9) Equivalent SiO₂ thickness</td>
<td>4-5</td>
<td>3-4</td>
<td>2-3</td>
<td>2-3</td>
<td>1.5-2</td>
<td>&lt;1.5</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

The Semiconductor Industries Association Roadmap for Semiconductors [7, 12] predicts that the projected SiO₂ thickness will reach atomic dimensions of about five silicon atom layers, or less than 1 nm by 2012. As seen from table 6.1, and from figure 6.2, the SiO₂ gate thickness must be scaled below a thickness of 1.5 nm by 2009. However, at such thicknesses, reliability and leakage currents limit the functionality of ULSI devices.
As electric devices are scaled down to build ULSI circuits, thickness and reliability of ultrathin gate oxides become the most important factors of MOSFETS. The additional issue of boron penetration through the oxide into the channel in downscaling of devices, a concern for threshold voltage shifts [13] led to an interest in oxynitrides and oxide/nitride stacks (SiOxNy and Si6N5/SiO2) with slightly higher dielectric constant (k=7 for Si3N4) for near-term gate dielectric alternatives yielding $t_{eq} \sim 1.2$-1.3 nm [14]. As also discussed in the previous chapters, high dielectric constant materials are under consideration.
At present, SiO$_2$ still remains the material of choice for gate dielectrics. The scaling down of dimensions requires controllable low-temperature processes. Thermal reactions are too fast for controlled growth of ultrathin gate oxides, making photo-assisted deposition techniques more favourable. The oxidation of Si surfaces is a key process in the fabrication of Si based devices. SiO$_2$ has been successfully deposited at low temperature assisted by UV irradiation in dry O$_2$ ambient [15,16].

6.3 The oxidation of Si

As discussed above, SiO$_2$ is projected to reach its limit in size by 2012, and in the interim period, it will still be used due to the excellent properties mentioned above. Since its growth at ultrathin dimensions requires control over wide areas at low temperatures, photo-oxidation is proposed as one of the methods for such growth. The photo-oxidation of Si with UV in an O$_2$ atmosphere follows the model in which the oxidation of Si by Xe$^*$ excimer lamps operating at 172 nm is assumed to take the route:

\[
\begin{align*}
\text{Xe}^* & \rightarrow \text{Xe} + h\nu (172 \text{ nm}) \\
\text{O}_2 + h\nu (172 \text{ nm}) & \rightarrow \text{O}^3(p) + \text{O}(^1\text{D}) \\
\text{O}_2 + \text{O}(^3\text{p}) + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

where M is a third body that can be O$_2$ or O$_3$. 

Chapter 6
\[ O_3 + h\nu (172 \text{ nm}) \rightarrow O_2 + O(^1\text{D}) \] (6.5)

The radiation photo dissociates oxygen molecules to ground state radical O atoms and subsequently, ozone is formed, resulting in a mixture of \( O, O_2 \) and \( O_3 \) in the reaction chamber. These species attack the substrate surface and rapidly form an oxide film. During oxidation, oxygen can be dissociated by UV irradiation to form active oxygen species, which react with the substrate to form an oxide at its surface. Photo-oxidation has been used to grow \( \text{GeO}_2 \) at low temperatures [17].

![Figure 6.3 Oxide thickness as a function of exposure time for different photon, particle and thermal sources [18]](image)

Direct photo-oxidation of Si using excimer lamps was also carried out at UCL prior to this research and it was seen that these lamps provided a higher oxidation rate than Hg lamps and thermal processes [18]. It was further seen that whereas films were grown at 250°C with these lamps, no significant growth was observed for thermal processes at higher temperatures of 450°C. Figure 6.3 from the same report shows a comparison of results obtained by various
methods. This work is extended here to produce ultra-thin films of SiO₂ using 172 nm excimer lamps. This is achievable by increasing the sample–lamp distance from 1 cm to 4 cm and reducing the UV-exposure time from 120 minutes to 30 minutes.

6.3.1 Experimental details for the deposition of ultrathin SiO₂

Here, experimental details of work on the growth of SiO₂ by photo-oxidation, at temperatures lower than 400°C using excimer lamps and its characterisation are discussed.

Low temperature growth of ultrathin SiO₂ films on crystalline Si was carried out by photo-oxidation using the four lamp system described in Chapter 2. Crystalline Si substrates were dipped in dilute HF (1%) for native oxide etching, rinsed in deionised water and cleaned in an isopropanol ultrasonic bath at room temperature. They were then blown dry using high purity N₂ and immediately transferred to the reactor chamber. The substrates were placed on a mica heater under the lamps, where temperatures of up to 400°C could be induced. Temperature was measured by a MINCO process controller, which also kept the maximum temperature at a pre-set value. The chamber was evacuated then filled with electronic grade O₂ (99.999%) to a pressure of 1000 mbar prior to VUV irradiation at exposure times of 5–30 minutes and temperatures of 100°C – 400°C. After irradiating the various samples at different exposure times, the oxide thickness was measured by ellipsometry assuming a fixed refractive index of 1.45. This is because at such very low thicknesses, ellipsometry cannot calculate both refractive index and thickness, and prior knowledge of one of the two parameters is required. Chemical bonding of the ultrathin films was analysed. MOS structures of surface area 5.02 x 10⁻³ cm² were fabricated in a clean
room environment by aluminium evaporation to form the contacts as shown in figure 6.4. These were then characterised by I-V tracing at a frequency of 1MHz.

---

Figure 6.4 Structure of the MOS test devices used

---

6.3.2 Experimental results and discussion

Figure 6.5 shows oxide thickness of ultrathin SiO$_2$ films as a function of temperature. Films of thickness from 0.7 – 3.0 nm were grown between room temperature and 400°C at a constant time period of 10minutes. Taft, however, required 360 minutes to grow only about 0.2nm of oxide by thermally in a dry oxygen at 612°C [19].
Figure 6.5 Oxide thickness SiO$_2$ films grown at different temperatures for 10 minutes

Figure 6.6 shows the Arrhenius plot of the deposition rate of the photolytically enhanced growth of SiO$_2$. With many thin film reactions characterised by interface bond breaking kinetics or by a diffusion controlled reaction, the rate limited process is given by:

\[ d(t) = B t \exp \left( -\frac{E_a}{kT} \right) \]  \hspace{1cm} (6.1)

where \( d(t) \) is the reacted thickness at time \( t \), \( B \) is a constant, \( E_a \) the activation Energy, \( k \) the Boltzmann constant (\( k=8.617 \times 10^{-5} \text{eV/K} \)) and \( T \) is the absolute temperature (K).
Figure 6.6  Arrhenius plot of the deposition rate of the photolytically enhanced growth of $\text{SiO}_2$.

The plot of $\ln (R)$ against $1/T$ gives activation energies $E_a$ of 0.015eV and 0.005eV respectively between temperatures of 200 – 400°C and 100 to 200°C. These are far lower than the value of 1.5eV obtained for thermal oxidation in an $\text{O}_2$ ambient [20]. These are also lower than the values for plasma oxidation of Si, where reported values for O-field – enhanced diffusion through $\text{SiO}_2$ are between 0.14eV and 0.7eV [21 - 23].

Figure 6.7 shows thickness of films grown vs exposure time. Growth rates of 0.2 nm/min, which are not achievable with thermal processing, were attained at 400°C. It is noted that though HF etching was carried out on the films, there remained a residual native oxide, hence the thickness
characteristics at the onset of exposure already is about 0.7 nm. As can be seen, the thickness of the films grown rapidly increased in the first 5 minutes then tended to saturate after 30 minutes. Here, it is assumed that the possibility exists for both $O^-$ and $O_2^-$ formed at $E_{\text{photon}} > 3.15 \text{eV}$ to enhance the reaction by drifting rapidly towards the Si-$\text{SiO}_2$ interface until the field totally restricts the photogenerated current and ceases to ionise sufficient species [15]. It is also assumed that UV radiation could also be influential in limiting the photolytic oxidation process.
Figure 6.8 FTIR of SiO\textsubscript{2} ultra thin films grown at different exposure times and temperatures

Figure 6.8 shows the FTIR peak at 1075 cm\textsuperscript{-1} of films of different thicknesses grown at different exposure times and temperatures. This is assigned to the Si-O-Si asymmetric stretching vibration [24, 25]. The stretching mode is more distinctive for films of thickness above 2.7 nm. Two components to the 1075 cm\textsuperscript{-1} absorption indicate that films of thickness below 2.7 nm might not be stoichiometric SiO\textsubscript{2} but most likely suboxide [26].
Figure 6.9 shows the I-V characteristics of a MOS device fabricated using a 3.3 nm ultrathin SiO$_2$ grown at 400°C for 30 minutes, with a leakage current below $10^{-7}$ A/cm$^2$ at an applied field of 1 MV/cm. These characteristics are close to values of about $2 \times 10^{-7}$ A/cm$^2$ obtained on 3.4 nm SiO$_2$ grown by dry oxidation [27]. Compared to RTO processing, this low temperature method has a much reduced thermal budget, and unlike plasma processing, there is no surface damage due to ion bombardment.
6.4 Conclusions

Ultrathin SiO$_2$ photo-oxidation has been discussed. The films grown under controlled conditions exhibited low leakage currents below $10^{-7}$ A/cm$^2$ at 1MV/cm and were close to values of about $2 \times 10^{-7}$ obtained on SiO$_2$ of the same thickness grown by dry oxidation. Activation energies $E_a$ of 0.015eV and 0.005eV, which are lower than the value of 1.5eV, obtained for thermal oxidation in an O$_2$ ambient were obtained on our films.

Though the discussion in this chapter was mainly on the deposition and applications of ultrathin SiO$_2$, the reader is reminded that the material's applications are not limited to its role as a capacitor and gate dielectric in the insulated gate field effect device technology. SiO$_2$ will still maintain its other uses such as an insulator between conductors and an etching mask.
6.5 References

   http://public.itrs.net/
12. The National Technology Roadmap for Semiconductors, Semiconductor Industries
Chapter 7

Summary of Results and achievements

7.1 Overview

In this research programme, the design and construction of a 4 lamp system has been successfully carried out. The use of UV radiation provided by excimer lamps to process various materials over wide areas was achieved. The 4 lamp system was then applied towards new photo-induced sol-gel and oxidation techniques. Photo-CVD was also carried out using the UV - ILS chamber.

Excimer sources have been noted to have several advantages. The lamps provide:

a) UV radiation at more than 22 wavelengths since they are quasi – monochromatic high output incoherent sources
b) "cold lamps" suitable for use with heat sensitive materials,
c) immediate UV output allowing instant strike,
d) continuous operation
e) designs in different geometries,
f) large area application, fewer processing steps requiring less equipment at lower cost
g) environmental benefits such as reduction in the use of chemicals for processing, materials and less waste
h) ozone free design when required and
i) no electrodes in discharge gap leading to long life, no self absorption and high efficiency
The objectives of the research were achieved. Films were successfully grown by various methods using the four lamp chamber designed and constructed for this research. Ultrathin SiO₂ was grown by the photo-oxidation using 172 nm lamps. TiO₂ – Ta₂O₅ was first grown by the photo-CVD process then by the photo-induced sol gel technique. However, it has been proved that the highest dielectric constant of 51 obtained on 82.9 nm films by UV – ILS at 350°C is more than twice lower than the value (εᵣ = 126) obtained on thick films obtained by ceramic processing at temperatures up to 1400°C.

All deposition was repeatable within a ± 5% variation in thickness and refractive index as measured by ellipsometry. Furthermore, film uniformity across the wafers showed a variation within ± 5% in thickness and refractive index for films deposited by photo-CVD, photoinduced sol-gel and photo oxidation. Favourable results were obtained in all deposited films. Experimental error in such measurements was within ± 3%. As already seen, the films exhibited good optical and electrical properties.

However, some disadvantages were also noted with the deposition. These were:

a) Maintenance of the UV-ILS system was laborious. Cleaning of the window separating the lamp chamber from the reactor chamber required disconnecting the lamp chamber – pump line, pressure gauge connections, cooling water system, generator cables and moving the lamp chamber to a working desk. A thin film and fine white dust often accumulated on the window, and this was removed by cleaning with HF and then immediately wiping with isopropanol. This was done after on average 14 depositions. Reconnecting the water system was time consuming. Also, when a heater broke down, about 6 hours was needed to pre-heat the new heater outside the chamber and allow organic components in the heater components to disperse to avoid chamber contamination.

b) All wafer cutting and processing was carried out in the laboratory, and cleaner processing under strict clean-room conditions would have produced better results. It is planned to move the systems to the clean room, to minimise the risk of contamination and ensure that all processes can be taken out in a cleaner environment.
c) Thickness measurements using the Auto El Ellipsometer are accurate at macroscopic levels and above. However, for systems with molecular dimensions, such measurements require prior knowledge of the refractive index. A refractive index value of SiO₂ was therefore assumed for the measurements. Ellipsometry also poses difficulties in measurement especially when values being measured fall within the far and steep edges of the Δ and ψ vs refractive index plot.

d) Films grown by the photo-induced sol-gel process were homogeneous and exhibited good I-V characteristics and low leakage currents. However, dielectric constant values on these as-grown films were inconclusive. These were carried out on as-grown films, with aluminium contacts fabricated on them.

e) Initially, there were difficulties with locating a heater that would give uniform heat over 4” substrates. Therefore, the chamber was improved to incorporate a MINCO® heater, which could provide uniform heating (Δ< 10°C) up to 500°C over the entire surface of sample holder.

f) Also at the initial stages, manual checking of pressure required monitoring and adjusting of the pump – chamber valve continually, especially at the beginning of deposition. The incorporation of a new automatic pressure controller made the deposition task easier.

Since dielectric barrier discharges can easily be scaled up for industrial use due to their simple construction, such deposition is possible at an industrial scale.

7.2 Recommendations

It has been proven that this low temperature, large area, photochemical processing approach offers great promise for reduced thermal budget fabrication of advanced devices. Earlier research [1] established that the lamps had long lifetimes of at least 4000 hours at conversion efficiencies of up to 22.5%. Lamp lifetime measurements could therefore be of very great interest. Further
research in this area is recommended in order to establish the real lifetime of various wavelength lamps.

A further study of the dielectric constant of composite TiO$_2$ – Ta$_2$O$_5$ is recommended since the dielectric constant of 51 obtained at a TiO$_2$ content of 8%, though higher than the value of 28 for Ta$_2$O$_5$ grown by the same method, is lower than the value obtained on other thin films and bulk materials. As explained, reasons for this may include contamination due to working in a laboratory and not a clean room environment. In depth studies of film stoichiometry such as XPS would be beneficial in determining the level of other components such as carbon in the material. It is not also conclusive as to whether TiO$_2$ – Ta$_2$O$_5$ the films grown were of the exact content required though these were mixed at their molar ratios. The reason underlying this might be in the different vapour pressures of the different precursors resulting in different transport speeds to the shower. The same films have attracted the attention of some semiconductor industry companies. A study of TiO$_2$ – Ta$_2$O$_5$ deposited using either UV lamp wavelengths of 222 nm and 172 nm would be beneficial.

The study of ultrathin SiO$_2$ growth and characterisation was limited, since there were requirements to study surface roughness as well as the stoichiometry by other methods. Nevertheless, the characterisation methods used, proved very similar properties to SiO$_2$. Due to time constraints, this study also was not extensive in as far as kinetic studies of the ultrathin SiO$_2$ could have been conducted.
7.3 Conclusions

The application of excimer UV lamps to large-area low temperature deposition of thin films has successfully been demonstrated from spin-on coatings of metallo-organic compounds, and the oxidation of silicon to form silicon dioxide at the surface. Excimer VUV and UV sources providing narrow-band radiation over large surface areas at tuneable wavelengths in the UV and VUV range number of different wavelengths are an interesting alternative to excimer lasers. The principles and the properties of excimer lamps have been discussed. Such new excimer VUV and UV sources are well suited to the efficient generation of high-power wavelength-selective ultraviolet radiation. All deposition has been done at the substrate temperature of 300°C and below. Up scaling of excimer lamps for industrial use over wide areas in materials processing is an achievable task, hence, their great potential for photo-induced processing.

7.4 References

Annexes

Publications

a. **Characterisation of TiO\textsubscript{2} deposited by photo-induced chemical vapour deposition.**

b. **(Ta\textsubscript{2}O\textsubscript{5})\textsubscript{1-x}(TiO\textsubscript{2})\textsubscript{x} deposited by photo-induced CVD using 222 nm excimer lamps.**

c. **Effects of active surface nitridation on the properties of high permittivity films deposited by UV-assisted CVD**

d. **Photo-induced preparation of (Ta\textsubscript{2}O\textsubscript{5})\textsubscript{1-x}(TiO\textsubscript{2})\textsubscript{x} dielectric thin films using sol-gel processing with xenon excimer lamps.** Applied Surface Science 168 (2000) 13-16. Never Kaliwoh, Jun-Ying Zhang and Ian W Boyd.


Characterisation of TiO$_2$ deposited by photo-induced chemical vapour deposition

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Abstract

We report the deposition of thin TiO$_2$ films on crystalline Si and quartz by photo-induced chemical vapour deposition (CVD) using UV excimer lamps employing a dielectric barrier discharge in krypton chloride (KrCl*) to provide intense narrow band radiation at $\lambda = 222$ nm. The precursor used was titanium isopropoxide (TTIP). Films from around 20–510 nm in thickness with refractive indices from 2.20 to 2.54 were grown at temperatures between 50 and 350 °C. The higher refractive index values compare favourably with the value of 2.58 recorded for the bulk material. The measured deposition rate was around 50 nm/min at 350 °C. Fourier transform infrared spectroscopy (FTIR) revealed the presence of TiO$_2$ through the observation of a Ti-O absorption peak and the absence of OH in films deposited at 250–350 °C indicated relatively good quality films. The phase of films deposited at 200–350 °C was anatase as determined by X-ray diffraction. © 2002 Published by Elsevier Science B.V.

Keywords: Excimer lamps; Photo-CVD; TiO$_2$ films

1. Introduction

Titanium dioxide (TiO$_2$) has many interesting physical properties that make it suitable for a variety of applications. Its high dielectric constant, due to its large lattice polarisability, gives it potential as a capacitor for charge storage insulators in dynamic random access memories (DRAMs), and as a potential replacement material for silicon dioxide (SiO$_2$) as tunnelling leakage currents limit a further downscaling of microelectronic dimensions below approximately 1.5 nm. TiO$_2$ is chemically stable, has excellent optical transparency in the visible and near-infrared regions and a high refractive index, which makes it useful for anti-reflection coatings in optical devices. Dielectric constant values between 30 and 100 have been reported [1–4] for a range of such films prepared by methods including photo-induced sol–gel processing [5], metal-organic chemical vapour deposition (MOCVD), [6], CVD [7], r.f. sputtering [3], photo-induced CVD using excimer lasers [8] amongst other methods. Photo-CVD is appealing for the deposition of TiO$_2$ for microelectronic devices because deposition conditions are controllable. Moreover, excimer lamps can be selectively used to deposit materials over wide areas. Combined with an injection liquid source, which has previously been used to grow other high dielectric constant materials including Ta$_2$O$_5$, precise properties can be achieved at low temperatures that are compatible with microelectronic processing over wide areas [9,10]. In this paper, we report the growth and characterisation of TiO$_2$ thin films on Si substrates and on quartz at temperatures in the range 50–350 °C by photo-CVD using KrCl excimer lamps.
applied to the deposition chamber, is also dissociated by the UV, yielding excited oxygen atoms O(^D). These species attack the ligands to which the Ti atoms are attached, subsequently forming Ti-O-Ti bonds in the gas phase and on the substrate surface, leading to the growth of TiO_2 on the substrates. With the injector system, a precise number of droplets of identical size ensures accurate control of this process.

Fig. 1 shows the dependence of thickness and refractive index on deposition time at a constant temperature of 350 °C. High refractive index values between 2.2 and 2.54 were obtained. The increase in refractive index is attributed to an increase in film density with the higher values being achieved for the thickest films. The higher values compare favourably with the value of 2.58 recorded for the bulk material at a wavelength of 632 nm [13]. The measured film thicknesses were between 20 and 510 nm, providing a calculated deposition rate of approximately 50 nm/min at 350 °C. Similar deposition rates have also been achieved by plasma-enhanced CVD [14].

Fig. 2 shows an Arrhenius plot of the deposition rate of films. Deposition time was 600 s for all data shown. A linear relationship between \( \ln R \) and the reciprocal of temperature was observed for temperatures between 150 and 350 °C, providing an activation energy of 0.382 eV. Such kinetically controlled deposition is determined by surface decomposition of the precursor [15]. At temperatures below 150 °C, the film growth rate appears to increase with decreasing temperature due to vapour condensation on the substrate, resulting in only partial decomposition of the precursor. This may be characterised by an activation energy of \(-0.039\) eV. These compare favourably with values for TiO_2 films deposited by laser-induced chemical vapour deposition (LICVD) [8] and are lower than the values obtained by MOCVD [6].

Fig. 3 shows the FTIR of films grown at 350 °C for different time periods. A strong absorption peak generally attributed to TiO_2 is observed around 433 cm\(^{-1}\) [16]. The inset verifies the absence of OH absorption at 3300 cm\(^{-1}\) for these films. However, such
absorption was found to be present in layers deposited at temperatures below 250 °C.

Fig. 4 shows the transmittance (top) and extinction (bottom) coefficient diagrams for films grown at 350 °C. Transmittance values for the thinner films (~600 Å) was more than 90% above 500 nm. The average extinction coefficient, calculated for all films on their respective thicknesses was found to be $3.5 \times 10^{-3}$ K at 500 nm, which is slightly higher than that obtained by r.f. magnetron sputtering [17].

XRD showed that films deposited below 200 °C were amorphous, whereas those deposited at higher temperatures were anatase. Fig. 5a and b shows the XRD of TiO$_2$ films deposited at 200 and 350 °C, respectively. Several peaks found in the as-deposited films were identified as crystalline anatase peaks. Films deposited at 200 °C had the (1 0 1), (2 0 0) and (2 1 1) orientations as films deposited at 350 °C had similar peaks and an additional (1 1 2) peak.

4. Conclusions

The low-temperature deposition of thin TiO$_2$ films on crystalline Si and quartz by photo-induced CVD using UV employing a dielectric barrier discharge
excimer lamps at $\lambda = 222$ nm has been demonstrated. The growth of films from 20 to 510 nm in thickness with refractive indices from 2.20 to 2.54 has been achieved at temperatures between 50 and 350°C. Refractive index values indicate the films deposited between 250 and 350°C were of the best quality. Films grown at temperatures of 200°C and above were crystalline. The measured deposition rate of around 50 nm/min at 350°C is higher than values achieved by most methods.

References


(Ta2O5)1−x(TiO2)x deposited by photo-induced CVD using 222 nm excimer lamps

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Abstract

We report the deposition of thin (Ta2O5)1−x(TiO2)x films on quartz and crystalline p-type Si (1 0 0) by photo-induced CVD using 222 nm excimer lamps at temperatures from 50 to 350 °C. The alkoxide precursors titanium isopropoxide and tantalum tetraethoxy dimethylamenoethoxide were mixed in various ratios, vaporised, and then driven into the reaction chamber by an Ar carrier gas, where they were exposed to the UV radiation. Films greater than 500 nm in thickness were grown at a pressure of several millibars and at a deposition rate of approximately 60 nm/min at 350 °C. The chemical bonding of the films has been analysed by Fourier transform infrared spectroscopy, and indicated that both Ta2O5 and TiO2 stretching absorption peaks were present. The optical properties of the layers were analysed by UV–Vis spectroscopy between wavelengths of 195–1100 nm. Band gap energies ranging between 3.2 and 4.2 eV were obtained for films of various compositions. © 2002 Published by Elsevier Science B.V.

Keywords: Dielectric; Excimer lamp; Photo-CVD; Ta2O5–TiO2

1. Introduction

The Semiconductor Industry Association roadmap predicts that SiO2 thickness will reach atomic dimensions by 2012 [1]. Below thicknesses of 2 nm, direct tunnelling currents will limit the functionality of devices that incorporate such layers of SiO2. Materials with high dielectric constant, low leakage current and higher dielectric strengths will, therefore, be required to produce the same devices possessing the same effective capacitance but using thicker layers. High dielectric constant materials have potential applications as charge storage capacitors for memory cells in ULSI DRAMs [2] and low inductance decoupling capacitors for the control of simultaneous switching noise in high speed switching ULSI chips [3]. Because of its thermal and chemical stability Ta2O5 appears to be one of several promising materials for such applications especially because of its compatibility with ULSI processing [4]. A significant increase in dielectric constant has been observed when Ta2O5 has been doped with other oxides including Al2O3 [5], ZrO2 [6] and TiO2 [7]. Of particular interest is the doping of Ta2O5 with TiO2 to produce a fourfold increase in dielectric constant [7]. Desirable low-temperature processes can be provided by excimer lamps whose potential has already been shown in areas that include photo-deposition of dielectric thin films [8,9]. In our previous work, Ta2O5–TiO2 has been grown by the photo-induced sol–gel process [10]. In the present work, we report the growth of the same materials by photo-CVD, which is faster and more precise in controlling thickness of films than the photo-induced sol–gel process. During photo-CVD, an injection...
liquid source enables precise thicknesses to be achieved by controlling such factors as droplet size, frequency of introduction into the reaction chamber, and pressure of the carrier gas. Liquid injection photo-CVD involves the dissolution of precursors in suitable solvents and the injection of the liquid directly into a hot vapouriser before entering the growth reactor. The photo-CVD system for this work comprises two stainless steel chambers separated by a MgF₂ window, a 222 nm (KrCl') excimer lamp chamber and reactor cell. A one-stage mechanical pumping system evacuates both chambers to about 10⁻¹ mbar while a sealed container carrying the precursors is connected to the liquid injection system, which feeds the reactor chamber. The precursors are maintained at room temperature and the precursor inputs are dependent only on the liquid injection rates and concentration of the solution. Details of the liquid injection source are described elsewhere [11]. This liquid injection technique combined with excimer lamp processing provides low-temperature growth of areas up to 4" diameter.

2. Experimental details

Tantalum tetraethoxydimethylethoxoide (TaDMae) and titanium isopropoxide (TTIP) were mixed in a range of molar ratios in anhydrous hexane in a sealed container to avoid contact with air. Quartz and Si (1 0 0) substrates were cleaned separately in an isopropanol bath, blown dry with N₂ and then loaded on to a heater stage located directly under the lamps. The fixed temperature used was measured and maintained by a Eurotherm temperature controller, and a Pfeiffer automatic controller regulated pressure at a pre-set value during processing. Ar was the carrier gas used to transport the precursors into the reaction chamber and N₂O was employed as the oxidising agent. Ar and N₂O flowed simultaneously into the chamber as the samples began to be irradiated with the lamps. FTIR transmittance spectra in the range 4000–400 cm⁻¹ of the films grown were taken by a Perkin Elmer Paragon 1000 spectrometer while a Rudolph Auto El II (λ = 633 nm) measured their thickness and refractive index. UV–Vis spectra were recorded for films deposited on quartz substrates. The band gap energy values of the mixed Ta₂O₅–TiO₂ layers were deduced from these characteristics.

3. Results and discussion

Fig. 1 shows the Arrhenius plots of the deposition rates of Ta₂O₅–TiO₂ films of various compositions. There are clearly two growth regimes, which depend upon the TiO₂ concentration. For films of TiO₂ content of 80% or more, the growth rate was found to be 50 nm/min, and the activation energy 0.263 eV. For layers with a TiO₂ content less than 30%, the growth rate was higher, at 60 nm/min, although the average activation energy was reduced to around 0.112 eV. Below 100 °C, the mechanism controlling the growth of films containing above 80% TiO₂ clearly changed, as has also been noted for layers grown by laser CVD [12], with condensation-controlled kinetics dominating as the precursors more easily adsorbed on the substrate surface at such low temperatures [13]. These activation energies are low as compared to TiO₂ film growth on Si by MOCVD where values of approximately 77.9 kJ/mol (0.8075 eV) have been reported [14], which are comparable to those for layers deposited by LICVD [12]. Lower activation energy values for films of higher Ta₂O₅ content than for films of high TiO₂ content suggests that Ta₂O₅ deposition is less dependent on temperature than TiO₂.

Fig. 2 shows the refractive index characteristics of the Ta₂O₅–TiO₂ films of various composition grown at 350 °C, where refractive index values range from 1.6 to 2.8. It is clear that the refractive index can be
Fig. 2. Refractive index characteristics of Ta$_2$O$_5$–TiO$_2$ films of various compositions grown at different temperatures. Fine-tuned in the films by tuning the Ta$_2$O$_5$–TiO$_2$ content. Films of 92% Ta$_2$O$_5$ content had high refractive indices as also observed in our previous work [10].

Fig. 3 shows the FTIR characteristics of Ta$_2$O$_5$–TiO$_2$ films of various composition deposited at 350 °C. The peak at 433 cm$^{-1}$ associated with Ti–O decreases in intensity with a reduction in the TiO$_2$ content from 90 to 10%.
4% in the composite films. The broad peak at 650 cm$^{-1}$ which is attributed to Ta–O–Ta and Ta–O stretching vibrational modes [15,16], clearly intensifies with increased Ta$_2$O$_5$ content. It is noted that no OH peak was observed at 3600 cm$^{-1}$ in any of the films shown here, nor any grown at temperatures above 250 °C.

Fig. 4 shows the Tauc characteristics for Ta$_2$O$_5$–TiO$_2$ films of various composition grown at 350 °C.
Bandgap energies calculated from this plot [17] are seen to rise with increasing Ta$_2$O$_5$ content. This is readily understood since the bandgap energy of Ta$_2$O$_5$ is higher than that of TiO$_2$. The variation of bandgap energy with the composition of the films is shown in Fig. 5. The energies range from 3.2 eV which is near the TiO$_2$ value of 3.5–4.2 eV, which is similar to the value for Ta$_2$O$_5$ obtained by pulsed laser deposition (4.2 eV) [16], and was attained at the highest deposited Ta$_2$O$_5$ content of 96%.

4. Conclusion

The growth of Ta$_2$O$_5$–TiO$_2$ films of various compositions and thickness at different temperatures between 50 and 350 °C has been demonstrated on Si and quartz. OH peaks were not present in films grown at 350 °C. Refractive index values of between 1.6 and 2.8 can be fine-tuned by altering precursor ratios and temperature. The activation energies of 0.263 and 0.112 eV obtained for films grown at temperatures up to 350 °C are low as compared to TiO$_2$ films grown on Si by MOCVD with an activation energy is approximately 0.8075 eV. Optical bandgap values within the range 3.2–4.2 were attained, as expected by varying the ratio of Ta$_2$O$_5$/TiO$_2$.

References

Effects of active surface nitridation on the properties of high permittivity films deposited by UV-assisted CVD


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An in situ low temperature chemical vapour deposition (CVD) system, featuring surface nitridation, dielectric layer deposition and post deposition anneal is presented. Processing is performed under the influence of ultra-violet radiation. After a range of nitridation treatments, Ta2O5 films are deposited and the effects of the N2O step on the dielectric films are analysed. From the electrical analysis performed, the nitridation step reduces the SiO2 equivalent thickness and leakage currents flowing, while also increasing the effective breakdown field of the films. Transmission electron microscopy (TEM) analysis reveals a thinner interface layer between substrate and dielectric, with increasing nitridation time.

1. INTRODUCTION

With the continuing reduction of CMOS and memory device dimensions, and the resulting scaling of dielectric layers, SiO2, which has been the linchpin of semiconductor processing since the industry’s inception, is approaching its limits on further thickness scaling for MOSFET and DRAM applications. As a result, higher permittivity (κ) materials are being investigated and will need to be implemented for continued reductions in device dimensions. Most dielectric layers that are deposited directly on the silicon substrate do not form an interface of comparable quality to thermally grown SiO2. This results in an interfacial silicate layer grown due to thermodynamic instability of the metal oxide in contact with silicon [1]. The thickness of this interfacial silicate layer is dependent on the level of thermodynamic instability between the silicon substrate and the dielectric metal oxide. This layer reduces the effective capacitance of the gate stack, thereby negating some of the benefits of the high κ material. This presents a serious problem that must be resolved before high κ dielectrics will be adopted in place of silicon dioxide. All treatments performed before the dielectric is deposited can alter the physical, chemical and electrical properties of the films deposited subsequently.

A wide range of techniques have been used to deposit these high κ dielectric on silicon substrates, including r.f. sputtering [2], metal organic CVD (MOCVD) [3] and atomic layer epitaxy [4]. Recently, ultra-violet assisted, injection liquid source (UVILS) CVD has emerged as an alternative technique for low temperature deposition of dielectric layers [5]. In this work, we extend on the previous reports of UVILS-CVD, by performing the pre-deposition surface preparation step, the high κ film deposition and also the post deposition anneal step in the same chamber. The nitridation, CVD, and post-deposition oxygen-rich anneal steps are all performed, under the influence of UV irradiation at 222 nm (KrCl* excimer lamp), thereby allowing low temperatures processing. The substrate temperature for these steps is 350°C.
In this work, Ta$_2$O$_5$ dielectrics are used to demonstrate the multi-functional and in situ capacity of the UVILS-CVD technique for the manufacture of the gate stack. The effects of the surface nitridation on physical and electrical properties of high $k$ films formed using various N$_2$O anneal processes, followed by Ta$_2$O$_5$ deposition are examined, using a range of measurement techniques.

2. EXPERIMENTAL

The starting substrates were 100 mm 2-4 $\Omega$cm n-Si wafers, which received a standard F5IB clean. Following the 1000 mbar UV N$_2$O step at 350°C for 0, 10 or 20 minutes, Ta$_2$O$_5$ films were deposited by injecting 20 or 60 drops (precursor Ta(OC$_2$H$_5$)$_5$(OCH$_2$CH$_2$N(CH$_3$)$_2$) dissolved in cyclohexane) from the liquid injection system (using a JIPelec INJECT system). The injector frequency was 1 Hz, and the open time of the injector per cycle was 2 ms. For these conditions, the mass injected per cycle was approximately 3 mg. The deposition temperature was 350°C, for each of the surface preparation steps, in the presence of UV irradiation. A post deposition UV O$_2$ anneal step was carried out at 350°C at 1000 mbar on all samples for 10 minutes. No final forming gas anneal was performed.

The measurement techniques used on these samples were transmission electron microscopy (TEM), capacitance-voltage (CV) and current-voltage (IV). The IV measurements were performed with a mercury probe gate electrode system ($A=4.2\times10^{-7}$ cm$^2$), using an HP4156B parameter analyser. Aluminium was e-beam evaporated through shadow masks to form MIS capacitors ($A=2.5\times10^{-5}$ cm$^2$) for capacitance-voltage (CV) measurements to be carried out with an HP4284A LCR meter, operating at 10 kHz, with an a.c. signal level of 40 mV.

3. RESULTS

3.1 Electrical results

The CV profiles for samples which received 0, 10 and 20 mins N$_2$O steps are plotted in Figure 1a and b for the 20 and 60 precursor injection cycle samples, respectively. From the plots, it is clear that the maximum capacitance measured increases with the length of the N$_2$O step. There are peaks/glitches in the depletion regions of the curves, most noticeably for the 20 injector cycle samples. These defect-related phenomena are induced by X-ray damage of the dielectric during Al gate e-beam evaporation. CV’s were performed with an Hg gate also (i.e. measured immediately after O$_2$ post deposition anneal step), and these peaks were not observed. The maximum capacitance values are extracted from the Al gate data, as the area of the Hg gate was larger by several orders of magnitude, which resulted in calibration issues with the data recorded with the Hg probe. Therefore, no valid information about charge density levels could be extracted from the CV data. The leakage currents flowing as a function of effective SiO$_2$ fields ($t_{ eff}$ calculated from CV) are plotted in figure 2(a) and (b), for 20 and 60 precursor drop injections, respectively. From the figures, it is noticeable that the presence of the nitridation step increases the effective breakdown field of the samples.

3.2 TEM results

Figure 3a, b and c show the TEM micrographs for the samples that received 0, 10 and 20 mins N$_2$O anneals respectively. The subsequent processing was identical for the three samples; 20 Ta precursor injection cycles into the chamber, followed by a 10
min post-deposition $O_2$ anneal at 350°C. These figures focus on the interfacial layer between the silicon substrate and the $Ta_2O_5$ dielectric layer, and there are noticeable effects of the length of the UV $N_2O$ step. From the figures, the interface layers are 39, 19 and 14 Å thick for the 0, 10 and 20 minute UV $N_2O$ steps, respectively. The presence of the $N_2O$ anneal step is preventing the growth of the interfacial layer during the post deposition $O_2$ anneal. It has also been observed, in the case of no pre-deposition nitridation step (0 mins $N_2O$), that the thickness of the interface layer increases from 10 to 39 Å, during a post-deposition $O_2$ anneal for 20 injector cycle samples. In the case of a 20 min $N_2O$ pre-deposition nitridation, the interface layer thickness reduces from 18 to 14 Å during the post-deposition anneal (TEM’s not available).

4. DISCUSSION

From the figures shown above, the electrical properties of the films are improve by performing a pre-deposition UV $N_2O$ step. In a bid to understand how this happens, the electrical and TEM results are summarised in table 1. The presence of the nitridation step reduces the equivalent oxide thickness, interface layer thickness and the leakage current densities flowing at a specified field (10 MV cm$^{-1}$), while also increasing the effective breakdown field. It is also clear that the properties of the samples with 20 minutes $N_2O$ step are superior to the 10 mins $N_2O$ samples. These values compare favourably to values previously published on substrate nitridation prior to $Ta_2O_5$ deposition. In the work of Sun et. al. [6], the nitridation is performed by RTN at 900°C, the post deposition is also a high temperature step (800°C) and the effective oxide thicknesses are in the range 34-38 Å. The leakage currents flowing though these samples are approximately two orders of magnitude higher, at 10 MV cm$^{-1}$, than those in this work, which had 60 injection cycles after both 10 and 20 mins $N_2O$ anneal. In the work by Kamiyama et. al. [7], following a nitridation (RTN) in the range 900-1100°C, temperatures of 700-800°C have to be used in a post deposition oxygen anneal, to achieve similar effective oxide thicknesses as are obtained at 350°C in this work. Finally, it should be pointed out, that in comparison to pure $SiO_2$ of the same (effective) thickness, the samples of 20 injection cycles and both 10 and 20 mins $N_2O$ anneal, display leakage currents approximately six orders of magnitude lower at a gate voltage of 2V [8].

Table 1. Summary of electrical and TEM results from samples which received 0, 10 and 20 mins UV $N_2O$ steps prior to dielectric layer deposition. $T_{eff}$ is the effective oxide thickness (from CV), $T_{IL}$ is the thickness of the interface layer (from TEM), $C_{max}$ the maximum capacitance measured, $E_{bd eff}$ is the effective breakdown field and $J$ is the leakage current density flowing at a specified effective electric field (10 MV cm$^{-1}$).

<table>
<thead>
<tr>
<th>UV $N_2O$ time [mins]</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>0</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of precursor injection cycles</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>UV $O_2$ time [mins]</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>$T_{eff}$ [Å]</td>
<td>43</td>
<td>23</td>
<td>21</td>
<td>35</td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td>$T_{IL}$ [Å]</td>
<td>39</td>
<td>19</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$C_{max}$ [$10^{-9}$ F]</td>
<td>2.01</td>
<td>3.35</td>
<td>4.16</td>
<td>2.50</td>
<td>2.68</td>
<td>3.51</td>
</tr>
<tr>
<td>$E_{bd eff}$ [MV cm$^{-1}$]</td>
<td>10</td>
<td>11.5</td>
<td>-</td>
<td>10.6</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>$J_{bd eff}$ [10 MV cm$^{-1}$] [$10^{-5}$ A cm$^{-2}$]</td>
<td>5.4</td>
<td>3.4</td>
<td>0.35</td>
<td>6.6</td>
<td>6.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The small difference in maximum capacitance (and hence effective thickness) values measured for the 20 and 60 injector cycle samples, without the $N_2O$ anneal, emphasises the significance of the interface layer on the overall gate stack capacitance.
for thin dielectric layers. The increase in $C_{\text{max}}$ is approximately 20%, even though the Ta$_2$O$_5$ dielectric layer is approximately three times thicker in the 60 than the 20 precursor injection samples. As the interface layer and the dielectric layer are capacitors connected in series, the layer with the lower capacitance (i.e. the interface layer) dominates collective capacitive properties. This is highlighted by the 43 Å effective oxide thickness of the sample with 0 mins N$_2$O anneal, 39 Å of which is attributed for by the interfacial layer (assuming this is SiO$_2$ i.e. $\epsilon_r = 3.9$).

It has been shown that the UV N$_2$O anneal is very effective at reducing the effective oxide thickness of thin films. This is achieved without degradation of the $\text{JEff}$ characteristics of the gate stack, as can clearly be seen from table 1. It should be emphasised that the N$_2$O deposition and O$_2$ anneal are all low thermal budget processes, which are all performed at 350°C.

5. CONCLUSIONS

The results presented in this work have demonstrated the ability of the UVILS-CVD technique to perform pre-deposition surface nitridation, high $\kappa$ dielectric deposition and post deposition O$_2$ annealing in a single chamber in situ reactor. From the results presented in this work, the UV N$_2$O anneal minimises the growth of an interface layer during the CVD and post-deposition anneal steps. The effective oxide thickness of the films are decreased by the N$_2$O anneal steps and the effective breakdown fields increase. The longer anneal time (20 mins) of the nitridation films further increase the film properties, as demonstrated from TEM, CV and JE measurements. Finally, given that many dry of silicon substrates cleans (prior to surface nitridation, or dielectric layer deposition) in an UV ambient [9, 10] are being investigated, it is clear this technique could also be utilised to perform this step, by modifying the gases flowing into the chamber. Therefore the entire gate stack, from pre-clean to post-deposition anneal can be performed in this single chamber apparatus at low temperatures.

6. REFERENCES


7. ACKNOWLEDGEMENT

This work was supported by the European Commission under the IST programme (Project IST-1999-10541 TOPS).
Figure 1. CV plots for 0, 10 and 20 mins N₂O samples, which were formed with (a) 20 and (b) 60 precursor injection cycles. All samples received a 10 min O₂ anneal after Ta₂O₅ deposition. In the figure, the maximum capacitance increases with the length of the N₂O step.

Figure 2. Jₑₑₑₑэфф plots for 0, 10 and 20 mins N₂O samples, which were formed with (a) 20 and (b) 60 precursor injection cycles. All samples received a 10 min O₂ anneal after Ta₂O₅ deposition. From the diagrams, the effective breakdown field increases with the length of the N₂O step.

Figure 3. TEM micrographs, focusing in the interface layer between the substrate and dielectric layer for (a) 0, (b) 10 and (c) 20 mins N₂O samples, which were formed with 20 precursor injection cycles. All samples received a 10 min O₂ anneal after Ta₂O₅ deposition. From the figure, the interface layer thickness reduces with increasing the length of the N₂O step.
Photo-induced preparation of \((\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x\) dielectric thin films using sol-gel processing with xenon excimer lamps

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Abstract

We report the growth of thin films of \(\text{Ta}_2\text{O}_5\) doped with \(\text{TiO}_2\) on \(\text{Si}(1\,0\,0)\) substrates at low temperatures by a new photo-induced sol–gel process. Polymeric sols were formed through hydrolysis and condensation of tantalum ethoxide mixed with titanium isopropoxide. These were then spin-coated on the substrates and irradiated by \(\text{Xe}_2^+\) excimer lamps operating at a wavelength of 172 nm. The chemical bonding changes in the thin films were analysed by Fourier transform infrared spectroscopy (FTIR), which confirmed densification of the films and the removal of \(\text{H}_2\text{O}\) and \(\text{OH}\) groups after some 10 min irradiation at 300°C. Layer thicknesses between 18–140 nm were readily achievable by this technique whose refractive index, \(n\), increased from 1.6 after spin on to 2 after irradiation. Film thickness and refractive index were found to be dependent on exposure time, substrate temperature and film composition. Maximum values of \(n\) were recorded at a \(\text{TiO}_2\) content of 8%.

Keywords: Excimer lamp; FTIR; Sol–gel; \((\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x\) thin films

1. Introduction

\(\text{SiO}_2\) is perceived to be approaching its useful and practical limit as a consequence of miniaturisation of microelectronic devices. The required device capacitance can be maintained by continued reduction in the thickness the \(\text{SiO}_2\) layer or by using three-dimensional structures or new materials with higher dielectric constants [1]. The use of materials with higher permittivities as a replacement for \(\text{SiO}_2\) is most appealing. Of the many available, tantalum pentoxide \((\text{Ta}_2\text{O}_5)\) is attracting much current interest [2,3]. \(\text{Ta}_2\text{O}_5\) has also been doped with many materials including \(\text{ZrO}_2\), \(\text{SiO}_2\), and \(\text{TiO}_2\) resulting in a significant increase in its dielectric constant [4–9]. In bulk form, deposition temperatures can be as high as 1400°C [5]. However, much lower preparation temperatures are more desirable, and photochemical processing which has a low thermal budget, offers a novel approach. Many materials have already been deposited by photo-induced processing using ultraviolet (UV) radiation from excimer lamps including \(\text{Si}_3\text{N}_4\) [10], \(\text{a-SiC:H}\) [11], \(\text{Pd}\) [12], \(\text{TiO}_2\) [13], \(\text{PZT}\) [14] and ultrathin \(\text{SiO}_2\) [15]. Pure \(\text{Ta}_2\text{O}_5\) has also been produced using this approach, [3,16–20]. Combined with the sol–gel method, low temperature photo-induced processing offers a range of advantages including good compositional control [21,22], lower cost, higher purity, homogeneity, easier fabrication, control of the microstructure and the deposition of complex thin films. [14,21–26]. Most work in the sol–gel field has used alkoxides as precursors [19–21,27–29]. Alkoxides provide a convenient source for monomers, which are soluble in common solvents while the
hydrolysis and condensation reactions are controllable. In recent work, we reported the application of excimer lamps to the growth of good quality single and multilayer films of TiO_2 by the photo-induced sol-gel process [13]. This work now is extended to the deposition of Ta_2O_5 doped with TiO_2, and reported here.

2. Experimental details

Polymeric sols were prepared by mixing tantalum ethoxide Ta(OC(CH_3)_3) and titanium isopropoxide Ti(OCH(CH_3)_2) in a range of molar ratios in ethanol in the presence of hydrochloric acid. The resulting transparent sols were magnetically stirred continuously at room temperature over several hours. Si (1 0 0) substrates were cleaned with isopropanol in an ultrasonic bath, then dried by blowing with N_2. The sols were then spin-coated on to the substrates at room temperature. The thickness and refractive index of films were measured by ellipsometry (Rudolph Auto El II) while Fourier transform infrared (FTIR) transmittance spectra in the range 4000 to 400 cm\(^{-1}\) were taken by a Perkin-Elmer Paragon 1000 spectrometer. The substrates were then transferred to a processing chamber containing a bank of XCI* excimer VUV lamps and irradiated for 10 min at 300°C. The windowless excimer lamp system used in this work comprises four lamps and is explained elsewhere in the literature [20]. The above measurements were repeated after irradiation. Multilayered (Ta_2O_5)_{1-n}(TiO_2)_n thin films were subsequently prepared on Si(1 0 0) in a step-wise process. The surface morphology of the films was characterised by Topometrix atomic force microscopy (AFM). I-V measurement was carried out at 1 MHz on MOS capacitors constructed on as-grown films.

3. Results and discussion

Polymerisation is the increase in connectivity of the network formed by condensation reactions [30]. In the present work, a network is formed within the Ta(OC(CH_3)_3) and Ti(OCH(CH_3)_2) in the presence of ethanol. The complex network is broken down to constituent metal oxides in the appropriate ratios by excimer lamp irradiation at 172 nm. Fig. 1 shows the FTIR spectra of the films before and after UV irradiation at a temperature of 300°C for 10 min.

The absorption peaks at 600 cm\(^{-1}\) and 529 cm\(^{-1}\) are attributed to Ta-O-Ta and Ta-O stretching [27]. Both of these shift to higher wavenumbers after irradiation as a result of densification of the films. Fig. 2 shows a typical AFM image of a film. A broad band observed in the 800–1000 cm\(^{-1}\) range for films before exposure shifted to higher wavenumbers after exposure to 172 nm radiation at 300°C for 10 min.

![Fig. 1. FTIR spectra of films before and after irradiation. The inset shows, (a) films before irradiation (b) films after exposure to 172 nm radiation at 300°C for 10 min.](image-url)
after spin-coating is due to suboxides TaO and TaO$_2$ [17]. After irradiation, this peak is dispersed. The broad band in the 3100–3400 cm$^{-1}$ range shows the dehydration and dehydroxylation of the polymers within the film before and after the irradiation step. Although homogeneous films were deposited, pin holes were observed on films before and after irradiation. The pin holes were possibly the result of small particles which were suspended in the solution or the formation of porous films. Refractive index is as low as 1.7 before irradiation due to the presence of organic compounds in the films. After irradiation, these organic compounds decomposed and denser films were formed. Refractive index and thickness of the (Ta$_2$O$_5$)$_{1-x}$(TiO$_2$)$_x$ thin films reach maximum values at a TiO$_2$ composition of 8% both for single and multilayer films grown under the same conditions, as shown in Figs. 3 and 4.

After irradiation, the refractive index $n$ values were 1.86, 1.98 and 1.97 for single layer films of 96, 92 and 90% Ta$_2$O$_5$ content, respectively and 2.04, 2.05 and 2.04 for 7 layer films. These values are similar to those obtained for CVD Ta$_2$O$_5$ at 35°C [17]. Thus the films become denser at the 8% composition. Multilayers exhibited a higher refractive index than monolayers as was also observed in work on TiO$_2$ [13]. Film thicknesses of up to 140 nm were achieved for our multilayered structures. Fig. 5 shows leakage current characteristics of capacitors built on as deposited thin films. This compares favourably with films obtained by CVD at 390°C and annealed at 800°C by RTO [8].
Characterization of the dielectric properties of these films is underway and will be reported later.

4. Conclusion

A new technique for preparing Ta$_2$O$_5$ doped with TiO$_2$ at low temperature using a photo-induced sol–gel process has been demonstrated. (Ta$_2$O$_5$)$_{1-x}$(TiO$_2$)$_x$ films were prepared on Si (100) substrates with maximum refractive index and thickness values at a TiO$_2$ content of $x = 0.08$. FTIR confirmed the presence of Ta–O bonds which were more pronounced after UV irradiation. AFM showed a uniform surface structure though pin holes were also observed.

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Ultrathin silicon dioxide films grown by photo-oxidation of silicon using 172 nm excimer lamps

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Abstract

We report the low temperature growth of ultrathin SiO₂ films on crystalline Si by photo-oxidation with an array of Xe₅ excimer vacuum ultraviolet (VUV) lamps operating at a wavelength of 172 nm. Ultrathin layers from 1.2 to 3.3 nm thickness were grown at time intervals from 5 to 40 min at 100-400°C at an O₂ pressure of 1000 mbar. Growth rates of up to 0.2 nm min⁻¹ have been achieved at 400°C, while the chemical bonding of the films has been analysed by Fourier transform infrared (FTIR) spectroscopy and found to be SiO₂. The as-grown 3.3 nm films exhibited good dielectric properties, comparable to SiO₂ films of identical thickness, grown by RTP at 800°C. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Dielectric materials; Excimer lamp; Photo-induced oxidation; Ultrathin SiO₂

1. Introduction

SiO₂ has historically been the most commonly used material for diffusion barriers and insulating layers in microelectronic devices due to its properties such as low defect density, high thermal stability, high resistivity and reasonable dielectric constant. Although alternatives are continually being sought, it remains a very important material in developing submicron (<100 nm) integrated circuits (ICs) such as Ta₂O₅. Maintenance of the required charge storage level during the development of high density metal-oxide-semiconductor (MOS) dynamic random access memory (DRAM) devices of smaller cell areas has been achieved by reducing the thickness of storage capacitors. A scaling down of thickness is also required as the operation speed of ICs and the current drive capability of MOSFETs are increased. These dielectric films which are 30–40 Å for 0.18 μm devices are projected to be 15–20 Å for the 0.1 μm technology scheduled for 2006 [1]. The reliability of such ultrathin layers for gate oxides is one of the most important factors during this scaling down of device sizes [2,3]. The continued miniaturisation of integrated circuit devices is even predicted to reach atomic dimensions by 2012 [1,4]. At this level, however, direct tunnelling current imposes a scaling limit on leakage current [5]. Since a practical alternative to SiO₂ has not yet emerged, the ultimate practical limits of extremely thin SiO₂ gate oxide have been studied [6–8]. A fundamental physical limit has been suggested to be a thickness of less than four layers of Si atoms [4]. Although thermal Si oxidation for the production of current gate dielectrics typically occurs at 1050°C, controllable, low temperature techniques are more desirable for these future ultrathin layers. Reduced temperature photo-oxidation of semiconductors has received considerable attention for low
temperature thin-film growth [9–14] for many reasons, not least because of the very controllable reaction rates available. In recent work, the dependence of oxidation rate upon oxygen pressure was studied and 11 nm thick layers were characterised for electrical properties [13]. In this paper, we report the growth of ultrathin silicon dioxide layers with an array of vacuum ultraviolet (VUV) lamps, whose electrical properties are comparable with oxides grown by rapid thermal oxidation (RTO).

2. Experimental details

The crystalline Si substrates used in this study were dipped in dilute HF (1%), rinsed in deionised water and cleaned in an isopropanol ultrasonic bath at room temperature. They were then blown dry using high purity N₂ and immediately transferred to a stainless steel chamber containing an array of four Xe* excimer VUV lamps operating over an area of 200 × 200 mm² and at a wavelength of 172 nm. Xe excimer molecules readily dissociate and there is no self-absorption of the emitted radiation. The excimer lamp system is more completely described elsewhere in the literature [15,16]. The substrates were placed on a mica heater under the lamps, where temperatures of up to 400°C could be induced. Temperature was measured by a MINCO process controller, which also kept the maximum temperature at a pre-set value. The chamber was evacuated then filled with electronic grade O₂ prior to VUV irradiation at exposure times of 5–40 min and temperatures of 100–400°C. The thickness of the as-grown oxide layers was measured at a fixed incident angle of 70° by a Rudolph Auto El II ellipsometer, and assuming a constant refractive index of 1.45. A Paragon 1000 Fourier transform infrared (FTIR) spectrometer was used to analyse the chemical bonding of the ultrathin films. MOS structures of area 5.02 × 10⁻² cm² were fabricated by aluminum evaporation to form the contacts. These were then characterised using I–V tracing at a frequency of 1 MHz.

3. Results and discussion

Photo-oxidation with Xe* excimer VUV lamps operating at a wavelength of 172 nm in an O₂ atmosphere involves the dissociation of oxygen into radicals and the subsequent formation of ozone, resulting in a mixture of O, O₂ and O₃ in the reaction chamber.

These species attack the Si surface rapidly to form a film of SiO₂. Figs. 1 and 2 show oxide thickness of ultrathin SiO₂ films as a function of exposure time and temperature, respectively. Growth rates of 0.2 nm min⁻¹ were achieved at 400°C. As can be seen, the thickness of the films grown could be controlled by varying exposure time and temperature.

Fig. 3 shows the FTIR peak at 1075 cm⁻¹, of films of different thickness grown at different exposure times and temperatures, assigned to the Si–O–Si asymmetric stretching vibration [17]. The stretching
mode has a full-width half maximum (FWHM) value for these films of 80 cm\(^{-1}\) which is similar to that of 70 cm\(^{-1}\) recorded for thermally grown oxides [18]. Structural analysis of the oxides by XPS is underway. Fig. 4 shows the I-V characteristics of a MOS device fabricated using a 3.3 nm ultrathin SiO\(_2\) grown at 400 °C for 30 min. These characteristics are close to those obtained on 3.0 nm SiO\(_2\) grown by thermal oxidation at 800 °C [8] and to simulated results [19]. Compared to RTO processing, this low temperature method has a much reduced thermal budget, and unlike plasma processing, there is no surface damage due to ion bombardment.

4. Conclusion

Ultrathin SiO\(_2\) films have been grown by photo-oxidation of silicon using large area 172 nm VUV excimer lamps. Growth of ultrathin SiO\(_2\) films from 1.2 to 3.3 nm at temperatures as low as 100–400°C has been demonstrated at an O\(_2\) pressure of 1000 mbar. Growth rates of 0.2 nm min\(^{-1}\) have been achieved at 400°C. Growth rates are dependent on exposure time and temperature. MOS structures fabricated on as-grown films without an annealing step exhibited good dielectric properties. Large area photo-oxidation offers great potential for low-temperature ultrathin film growth for advanced devices.

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References

Titanium dioxide films prepared by photo-induced sol-gel processing using 172 nm excimer lamps

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Abstract

We report the growth of single- and multilayer films of titanium dioxide (TiO\textsubscript{2}) on Si(100) substrates at low temperature by a new photo-induced sol-gel process. Polymeric TiO\textsubscript{2} sols prepared by the hydrolysis and condensation of titanium isopropoxide were spin-coated on the silicon substrate and then irradiated by an Xe\textsuperscript{2+} excimer vacuum ultraviolet (VUV) lamp operating at a wavelength of 172 nm. Films with thicknesses between 10 and 200 nm were achieved by this technique. The effects of spin speed, irradiation time and substrate temperature on the films formed have been studied. The chemical bonding changes in the thin films were analysed by Fourier transform infrared spectroscopy (FTIR), while thickness and refractive indices were determined by ellipsometry. FTIR confirmed the removal of H\textsubscript{2}O and OH groups after VUV irradiation for 10 min at 300°C. The refractive index reached a value of 2.4, which compares favourably with the value of 2.58 recorded for the bulk material, while optical transmittance values in the visible region of the spectrum between 85 and 95% were obtained on quartz substrates. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ellipsometry; Excimer lamp; FTIR; Photo-induced processing; Sol-gel; Titanium dioxide thin films

1. Introduction

TiO\textsubscript{2} is currently attracting much interest as a nanocrystalline material for a range of potential applications, such as in dye-sensitised solar cells [1,2], as an anti-reflective coating for solar cells [3,4], as an insulator for memory devices [5], as a catalyst [6], and as a humidity and fibre-optic chemical sensor [7].

TiO\textsubscript{2} has been deposited by many techniques including pyrolysis [8], electron-beam evaporation of TiO\textsubscript{2} [9], pulsed laser deposition [10], metal–organic chemical vapour deposition (MOCVD) [11,12], molecular-beam epitaxy [13], atomic-layer deposition (ALD) [14,15], hydrothermal techniques [16,17], plasma-enhanced chemical vapour deposition (PECVD) [18], reactive sputtering [19,20] and sol–gel processes [21–23].

Sol–gel processing involves the polymerisation of metal–organic compounds to form ceramic synthesis by the hydrolysis of metal alkoxides, resulting in metal oxides or hydrated oxides [21]. A gel with a continuous network is thus formed. Thin, transparent, multi-component oxide layers can be readily deposited on various substrates by this process. A firing step is required to displace organic (in this case propyl) compounds, and the hydroxyl groups. The method has been widely used to fabricate high-quality ceramics and glasses [24]. Advantages of this technique as compared with other processes include low cost, relative simplicity, and easier control of the composition of the deposited films [7,24].

In this work, TiO\textsubscript{2} produced from titanium isopropoxide [Ti(OC\textsubscript{3}H\textsubscript{7})\textsubscript{4}] by an excimer-lamp based photo-induced sol–gel process has been studied. The interest in ultraviolet (UV) processing and studies of the dynamics of photochemical reactions have burgeoned in recent years [25]. Photochemical processing by excimer lamps has an added advantage of a low thermal budget due to the ability of processing at low temperatures.

2. Experimental details

The excimer lamp system used comprises four lamps, employs the dielectric barrier discharge principle and is described more completely elsewhere in the literature [26]. Polymeric sols were prepared by the hydrolysis
and condensation of Ti(OC₃H₇)₄ in C₂H₅OH in the presence of HCl as shown in Fig. 1. The resulting transparent mixture was sealed in a container and stirred continuously at room temperature. The solution was spin-coated on to silicon wafers at various speeds, first after 2 h, then at 24 h intervals, and was analysed with an ultraviolet-visible (UV-VIS) spectrophotometer (Lambda 14), where the polymerisation process was monitored by observing changes in the absorbance spectra. Thickness and refractive index were measured by ellipsometry (Rudolph Auto El II) and Fourier transform infrared spectroscopy (FTIR) was used to monitor the absorption of OH and CH₃ groups to provide information on the presence and removal of H₂O and propyl radicals. Initially, substrates were irradiated with 172 nm radiation from an Xe⁵⁺ excimer lamp for different times and at temperatures of 80, 120 and 200 and 300°C. Subsequent irradiation was carried out at 300°C for 10 min. The optical properties of the films prepared on quartz and irradiated by the 172 nm radiation were investigated using a UV–VIS spectrophotometer. TiO₂ multilayers were subsequently prepared on Si(100) in a step-wise process, with thickness and refractive index determined for every step.

3. Results and discussion

The synthesis of titanate polymers by the sol–gel process involves the hydrolysis and condensation of the starting alkoxide, in this case titanium isopropoxide, in
the following reactions:

\[
\begin{align*}
\text{Hydrolysis} & \\
\text{Condensation} & \\
\text{Water condensation} & 
\end{align*}
\]

\[
\begin{align*}
\text{Ti(OCH}_3)_4 + H_2O & \rightarrow \text{Ti(OCH}_3)_3\text{OH} + \text{C}_2\text{H}_5\text{OH} \\
\text{Ti(OCH}_3)_4 + \text{Ti(OCH}_3)_3\text{OH} & \rightarrow \text{Ti}_2\text{O(OCH}_3)_3\text{H}_6 + \text{C}_2\text{H}_5\text{OH} \\
\text{Ti(OCH}_3)_3\text{OH} + \text{Ti(OCH}_3)_3\text{OH} & \rightarrow \text{Ti}_2\text{O(OCH}_3)_3\text{H}_6 + \text{H}_2\text{O}.
\end{align*}
\]

Fig. 2 shows the FTIR spectra of films irradiated at a temperature of 80 °C. Changes taking place within the gel under the influence of irradiation can be observed by considering the spectral range 3100–3400 cm\(^{-1}\) where the OH stretching vibrations of water and OH groups appear, at 550 cm\(^{-1}\) where Ti–O vibrations occur and 1300–1500 cm\(^{-1}\) (due to CH\(_2\)). As the irradiation time is increased from 0 to 20 min, the intensity of these bands decreases. The spectra in the 3100–3400 cm\(^{-1}\) range show the dehydration and dehydroxylation of the polymer. The increase in temperature between 0 and 80 °C results in loss of weight through the evaporation of adsorbed water and the loss of hydroxyl groups. The appearance and growth of new absorption features below 730 cm\(^{-1}\) indicate the presence of Ti–O bonds [27]. No significant changes were observed upon raising the temperature to 200 °C. At 300 °C, the OH peak disappeared, and the Ti–O peak shifted to shorter wavenumbers due to densification of the films. Fig. 3 shows the FTIR spectra of these films irradiated at different temperatures for a fixed exposure time of 10 min. The spectra show that conversion of the gel into a complex TiO\(_2\) film takes place after irradiation for 10 min at 300 °C, with the removal of OH and CH\(_3\) groups being achieved.

TiO\(_2\) multilayers were deposited at 2000 and 3000 rev min\(^{-1}\) from the same solution with a 24 h time difference. These coating speeds were chosen as homogeneous films are formed at these spin-on speeds. Refractive index values ranging from 2 to 2.4 were measured for multilayers coated at 2000 and 3000 rev min\(^{-1}\), after each irradiation step, as seen in Fig. 4. These values compare well with those for bulk material in rutile single crystals, which is reported to be 2.58 at 633 nm [28].

The multilayers deposited at the same speed exhibited a higher refractive index than the monolayers. Rao and Mohan [9] also observed an increase in refractive index with an increase in thickness of their TiO\(_2\) films. Thicknesses of up to 200 nm were achieved for our multilayers, indicating that a predetermined thickness of film can therefore be achieved readily by employing this deposition technique to produce layers in stack form. The thin film deposited on quartz crystals showed good optical properties in the 250–1100 nm wavelength

![Fig. 4](image-url) (Dependence of the thickness (d) and refractive index (n) of TiO\(_2\) after irradiation at 172 nm for 10 min on spin deposition speed and number of layers.)

![Fig. 5](image-url) (Spectral transmittance of TiO\(_2\) films deposited on quartz after irradiation at 172 nm for 10 min.)
range as seen in Fig. 5. In the range 350 to 1100 nm, optical transmittance between 85 and 95% was obtained. This compares very well with films produced by other techniques.

4. Conclusion

Single- and multilayer TiO$_2$ films have been prepared by a new photo-induced sol–gel process using a 172 nm VUV excimer lamp. Low-temperature deposition of TiO$_2$ films at 300 C has been demonstrated. The refractive index of the deposited films (2.4) compares favourably with that for bulk TiO$_2$ (2.58). The OH groups were dispersed at 300 C and the films formed showed good optical properties with transmittance values between 85% in the visible range of the spectrum. The thickness of the films formed can readily be controlled by the spin-coating speed and the number of sequential layers deposited.

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