

Capturing the Dynamics of Ti Diffusion Across $\text{Ti}_x\text{W}_{1-x}/\text{Cu}$ Heterostructures using X-Ray Photoelectron Spectroscopy

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Interdiffusion phenomena between adjacent materials are highly prevalent in semiconductor device architectures and can present a major reliability challenge for the industry. To fully capture these phenomena, experimental approaches must go beyond static and post-mortem studies to include in situ and in-operando setups. Here, soft and hard X-ray photoelectron spectroscopy (SXPS and HAXPES) is used to monitor diffusion in real-time across a proxy device. The device consists of a $\text{Si}/\text{SiO}_2/\text{Ti}_x\text{W}_{1-x}$ (300 nm)/Cu(25 nm) thin film material stack, with the $\text{Ti}_x\text{W}_{1-x}$ film ($x = 0.054, 0.115, 0.148$) acting as a diffusion barrier between Si and Cu. The interdiffusion is monitored through the continuous collection of spectra whilst in situ annealing to 673 K. Ti within the TiW is found to be highly mobile during annealing, diffusing out of the barrier and accumulating at the Cu surface. Increasing the Ti concentration within the $\text{Ti}_x\text{W}_{1-x}$ film increases the quantity of accumulated Ti, and Ti is first detected at the Cu surface at temperatures as low as 550 K. Surprisingly, at low Ti concentrations ($x = 0.054$), W is also mobile and diffuses alongside Ti. By monitoring the Ti 1s core level with HAXPES, the surface-accumulated Ti was observed to undergo oxidation even under ultra-high vacuum conditions, highlighting the reactivity of Ti in this system. These results provide crucial evidence for the importance of diffusion barrier composition on their efficacy during device application, delivering insights into the mechanisms underlying their effectiveness and limitations.

1. Introduction

The binary pseudo-alloy of titanium–tungsten ($\text{Ti}_x\text{W}_{1-x}$, $x \leq 0.3$) is a well-established, effective diffusion barrier, and adhesion enhancer within silicon-based semiconductor devices.^[1–3] The diffusion barrier has the primary function to prevent the interdiffusion between adjacent metallisations and the underlying dielectric and semiconductor materials. TiW is compatible with various metallisations (Al, Au, Ag, In, and Cu) and has remarkable thermal stability at elevated temperatures ($\leq 850^\circ\text{C}$).^[4–19] Consequently, TiW diffusion barriers are now being widely implemented in next-generation SiC-based power semiconductor technologies with copper metallisation schemes,^[20–22] and more recently within electrodes for GaAs photoconductive semiconductor switches (PCSSs),^[23] and gate metal stacks in GaN-based high electron mobility transistor (HEMT) devices.^[24]

Diffusion barriers are needed as Cu and Si readily react at relatively low temperatures to form intermetallic copper–silicide compounds at the interface. The presence of such compounds can induce a number of failure routes, including the degradation of the interlayer dielectric, resulting in the creation of short circuit pathways and thermal runaways, the generation of deep trap levels within the semiconductor, and volume expansion at the interface which can cause the delamination between adjacent layers.^[18,25–29] All of these seriously hamper the performance and reliability of devices. Studies have shown that TiW films are capable of retarding and limiting this interdiffusion and subsequent reaction.^[2,18] However, when subjected to a high thermal budget, a depletion of Ti within the TiW grains has been observed, leading to the accumulation of Ti at grain boundaries.^[30] The segregated Ti is then able to diffuse out of the barrier and through the metallisation via grain boundary diffusion.^[8] This depletion of Ti is thought to lead to a greater defect density within the TiW layer, consequently allowing for the potential of Cu and Si to bypass the barrier and react. Fugger et al. cite that this out-diffusion process is an “essential factor” in the failure of this barrier,^[16] and others have also documented the segregation of Ti during high-temperature annealing.^[12,19,20,30,31]

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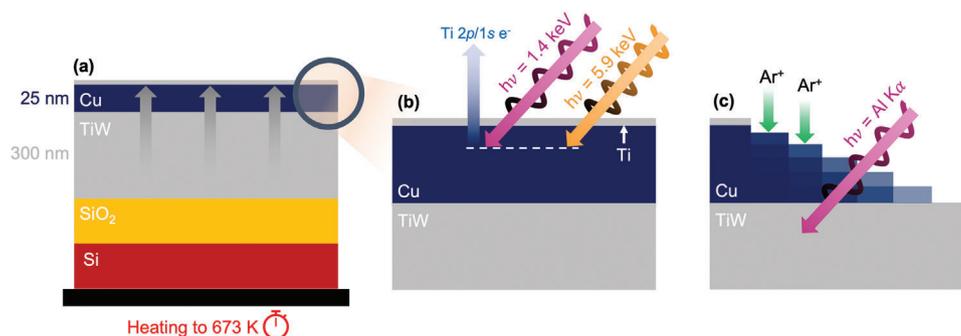


Figure 1. Schematic representation of the samples and experimental approach (not drawn to scale). a) Device stack on a sample holder being annealed in situ to 673 K and the expected Ti diffusion represented by grey vertical arrows. b) A magnified view of the copper surface showing the Ti accumulation and the two photon energies used for SXPS and HAXPES measurements to excite the Ti 2*p* and Ti 1*s* electrons from the same depth. c) SXPS laboratory-based Ar⁺ sputtering depth profile used to quantify the elemental distribution across the TiW/Cu bilayer after in situ annealing (i.e., post-mortem).

Given the importance of the TiW barrier to the overall device performance, reliability and its application in future SiC technologies and beyond, this Ti diffusion degradation process must be better understood, including how it impacts the stability of the TiW/Cu structure. The common thread across the vast majority of past experimental studies on TiW and diffusion barriers in general, including the present authors' previous work,^[19,32] is that ex-situ samples are used to track the evolution of the diffusion process and to determine the temperature at which the barrier fails. Such studies also often focus on one Ti concentration and are therefore unable to address the effect of the titanium concentration of the film on the degradation mechanism.

Although ex-situ prepared samples give a good representation of the device after stress events, it is difficult to correlate the results directly with what a device is experiencing during the applied stress.^[8,20] Therefore, it is crucial to develop new characterisation strategies that can probe the degradation mechanism dynamically under realistic conditions while allowing for changes to the chemical states across the device stack to be monitored.

To the best of our knowledge, only Le Priol et al. and Siol et al. provide in situ monitoring measurements on TiW, both employing in situ X-ray diffraction (XRD). Le Priol et al. studied the efficiency of a TiW barrier deposited from a 70:30 at.% W:Ti alloy target against indium diffusion at temperatures between 573 and 673 K under vacuum.^[17] The authors could correlate the TiW barrier efficiency with its microstructure and determine the diffusion coefficient of In in TiW. Siol et al. were interested in understanding the oxidation of TiW alloy precursors and observed oxygen dissolution and the formation and decomposition of mixed (W,Ti)-oxide phases when ramping the temperature between 303 and 1073 K in air.^[33]

An explanation for the lack of in-situ/operando experiments in the field, which is in contrast to the importance of these material interfaces in both novel and commercial device applications, is the challenges associated with performing such experiments. These include extensive periods of time required to collect sufficient data, the availability of instruments with in situ capability, and difficulties in sample preparation and interfacing.

The present work combines soft and hard X-ray photoelectron spectroscopies (SXPS and HAXPES) with in situ anneal-

ing to study the effect of annealing temperature, annealing duration, and Ti:W ratio on the thermal stability of TiW/Cu bilayers in real-time, considerably expanding on the existing ex-situ work, including the present authors' previous studies.^[19,32] Si/SiO₂/Ti_xW_{1-x} (300 nm)/Cu(25 nm) device stacks (see Figure 1a for a schematic of the stack) are annealed up to a maximum temperature of 673 K (400°C) and held there for 5 h. At the same time, soft and hard X-ray photoelectron spectra are continuously recorded to capture the Ti diffusion process and changes to the chemical state across the copper surface (see Figure 1b for a schematic). The target temperature of 673 K is selected as it is in a common temperature regime employed during device fabrication to obtain desired grain growth and texture of the copper metallisation.^[31,34] Additionally, it is a temperature that can occur at short circuit events during the operation of potential devices.^[35]

A major benefit of combining the two variants of X-ray photoelectron spectroscopy (XPS) is that SXPS is more surface-sensitive, whereas HAXPES enables access to the Ti 1*s* core line. The Ti 1*s* offers an alternative to the commonly measured Ti 2*p* with soft X-ray sources. The Ti 1*s* compared to the Ti 2*p* has the added benefits of covering a smaller binding energy (BE) range and consequently necessitating a shorter collection time, the absence of spin-orbit splitting (SOS), no additional broadening to consider from the Coster–Kronig effect that influences the Ti 2*p*_{1/2} peak, and the absence of underlying satellites. For these reasons, the exploitation of the 1*s* core level over the 2*p* is becoming increasingly popular for transition metals, especially for the disentanglement of charge transfer satellite structures in the X-ray photoelectron spectra of metal oxides.^[36–40]

HAXPES is typically employed as it offers a larger probing depth than conventional SXPS.^[40] However, here, it is strategically used to obtain comparable probing depths of the Ti 2*p* and Ti 1*s* core lines, collected with SXPS and HAXPES, respectively. Using this combination, the more widely studied Ti 2*p* spectra can be used to understand the Ti 1*s* spectra better. In addition to the synchrotron-based XPS experiments, quantitative laboratory-based SXPS depth profiles were also conducted on the samples following the in situ experiment (i.e., post-mortem) to ascertain the quantitative distribution of Ti across the Cu metallisation (see Figure 1c for a schematic of the depth profiling).

2. Experimental Section

2.1. Samples

Three as-deposited Si/SiO₂/Ti_xW_{1-x}/Cu thin film stacks with varying Ti:W compositions were prepared through an established industrial route. The stack consists of a 50 nm SiO₂ layer on an un-patterned Si(100) substrate, above which a 300 nm thick TiW layer was deposited via magnetron sputtering. The TiW films were deposited from composite targets with a nominal atomic concentration of 30:70 Ti:W, determined by X-ray fluorescence spectroscopy (XRF). By varying the deposition parameters, three samples with an average Ti concentration, x across the entire film thickness of 5.4 ± 0.3 , 11.5 ± 0.3 , and 14.8 ± 0.6 at.% relative to W were realised (i.e., $(\text{Ti}/(\text{Ti}+\text{W})) \times 100$). These concentrations were determined using laboratory-based SXPS and depth profiling across the entire film thickness (further details regarding the quantification of the TiW films can be found in Content I, Supporting Information). These samples will be referred to as 5Ti, 10Ti, and 15Ti, respectively, for the remainder of the manuscript. Finally, a 25 nm Cu capping layer was deposited via magnetron sputtering on top of the TiW barrier. Deposition of both TiW and Cu was conducted in an argon discharge with no active substrate heating or vacuum break between successive depositions. The deposition chamber operated under a base pressure of 10^{-8} – 10^{-7} mbar. Further details regarding the deposition process have been reported in Refs.[31, 41].

2.2. Dynamic Synchrotron-Based SXPS/HAXPES

2.2.1. Beamline Optics and End Station Details

SXPS and HAXPES measurements were conducted at beamline I09 of the Diamond Light Source, UK,^[42] at photon energies of 1.415 and 5.927 keV, respectively (these will be abbreviated as 1.4 and 5.9 keV throughout the remaining manuscript). A 400 lines per mm plane grating monochromator was used to choose the energy range of 1.4 keV, resulting in a final energy resolution of 330 meV at ambient temperature. Using a post-monochromator Si(004) channel-cut crystal and a double-crystal Si(111) monochromator, 5.9 keV was used, yielding a final energy resolution of 290 meV at ambient temperature. The total energy resolution was determined by extracting the 16%–84% width of the Fermi edge of a clean polycrystalline gold foil (see Content II, Supporting Information, for further information on determining the resolution). The end station of beamline I09 was equipped with an EW4000 Scienta Omicron hemispherical analyser, which has a $\pm 28^\circ$ acceptance angle. The base pressure of the analysis chamber was 3.5×10^{-10} mbar. To maximise the efficiency in the collection of spectra, the measurements were conducted in grazing incidence and at near-normal emission geometry.

2.2.2. Annealing

Samples were individually annealed in situ to a sample target temperature of 673 K (400°C) using a tungsten filament heater, and held at the temperature for approximately 5 h. The sample

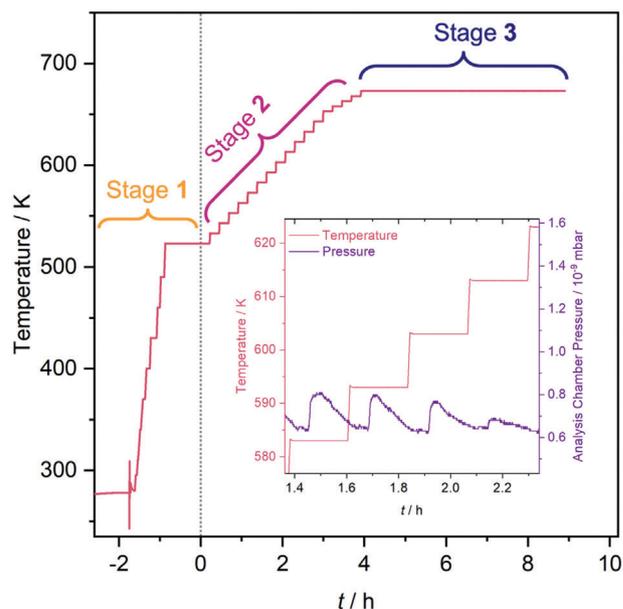


Figure 2. Representative temperature profile acquired from the Lakeshore temperature controller during the measurements on sample 5Ti. The temperature profile consists of three stages. Stage 1: a quick ramp to 523 K in a subsidiary chamber. Stage 2: a 10 K per (spectral cycle) ramp in the main analysis chamber, which was then decreased to a 5 K per (spectral cycle) ramp once 653 K was reached. The temperature was ramped step-wise in Stage 2 to allow the pressure in the analysis chamber to recover to $< 7 \times 10^{-10}$ mbar after each temperature step (see inset for the pressure profile). Stage 3: holding period at 673 K for 5 h. The dotted line at $t = 0$ h indicates the start of the measurement window.

plate used for the experiment consisted of a copper disk (3 mm thick, 8 mm diameter) fixed to the centre of a flat tantalum plate, on which the sample was placed and secured using clips. Good thermal contact was made between the copper disk and the sample using a thin silver foil. This allowed the sample temperature to be inferred by attaching an N-type thermocouple to the centre of the copper disc. The thermocouple was also connected to a Lakeshore temperature controller, which was programmed to ramp the sample temperature at a constant rate under a closed-loop control (see Content III, Supporting Information, for an image of the sample plate holder).

Prior to in situ annealing, all samples were gently sputter cleaned in situ for 10 min using a 0.5 keV de-focused argon ion (Ar⁺) source, operating with a 6 mA emission current and 5×10^{-5} mbar pressure. This was necessary to remove the native copper oxide that had formed on the sample surface during sample transport.

The process of in situ annealing encourages the purging of adsorbed gases and organic species within the sample and on the sample surface (i.e., degassing). Therefore, annealing in a UHV environment will increase the chamber pressure, which was undesired, especially during the collection of photoelectron spectra. To account for sample degassing, the annealing process was conducted step-wise to ensure a good analysis chamber pressure was maintained throughout the measurements. **Figure 2** displays a representative temperature profile acquired for sample 5Ti and the related pressure profile within the analysis chamber (see

Content IV, Supporting Information, for the temperature profiles collected for all three samples). The temperature profile consists of three stages. Additionally, as seen in the pressure profile in Figure 2, with every increasing step in temperature, a temporary increase in pressure resulted due to the degassing of the sample.

Prior to annealing in the analysis chamber, the samples were first heated in a subsidiary sample preparation chamber to remove the majority of adsorbed molecules. This stage of annealing involves a fast ramp from room temperature to 523 K and will be referred to as Stage 1 of the annealing process. The Ti diffusion process was assumed to be insignificant in this temperature range. Next, the sample was moved to the main analysis chamber, where the temperature was ramped step-wise from 523 K to the target temperature of 673 K while maintaining on average a pressure of 7×10^{-10} mbar (referred to as Stage 2). The temperature was then held at the 673 K target temperature for 5 h (referred to as Stage 3). The spectra were continuously collected using SXPS and HAXPES from the start of Stage 2 until the end of Stage 3 of the annealing process. The period where the spectra were collected will be referred to as the “measurement window”. Across the measurement window, the same group of spectra were collected iteratively, which will be referred to as the “spectral cycle”. Each spectral cycle took approximately 15 min to collect, and details on which spectra were selected will be discussed in the following section. During Stage 2, the temperature was increased once a spectral cycle was completed, which coincidentally allows sufficient time for the analysis chamber pressure to recover below 8×10^{-10} mbar.

For completeness, note that during the initial stages of annealing, sample 10Ti degassed more than samples 5Ti and 15Ti, and therefore the temperature ramp of Stage 2 for sample 10Ti was paused to allow the pressure to recuperate. This meant that sample 10Ti was held at 543 K for four spectral cycles rather than one. Therefore, the total annealing time of sample 10Ti was extended by approximately 1 h compared to the annealing time of samples 5Ti and 15Ti. This was not expected to affect the diffusion process significantly or the resultant accumulation profiles, as the Ti diffusion at this temperature was minimal.

2.2.3. Core Level Selection

The spectral cycle, which was run in an iterative loop during the experiment, included the following core level spectra: Cu $2p_{3/2}$, Ti $2p$, and W $4d$ collected with SXPS, and Ti $1s$ collected with HAXPES. The W $4d$ core level was selected over the commonly measured W $4f$ line as the former does not overlap with the core levels of Cu or Ti in this region, whereas the latter overlaps with the Ti $3p$ core level. The Cu Fermi edge was also included in the spectral cycle and was collected with both SXPS and HAXPES throughout the measurement window to (a) provide an intrinsic method of calibrating the BE scale and (b) monitor any change to the total energy resolution as a consequence of raising the sample temperature. Based on 16/84% fits of the collected Fermi edges across all measurements, the effect of thermal broadening was negligible under the experimental conditions used, and further information can be found in Content V (Supporting Information). All spectra were aligned to the intrinsic Cu Fermi energy

(E_F) and the spectral areas were obtained using the Thermo Advantage v5.9925 software package. The BE values quoted in this work were considered to have an estimated error of ± 0.1 eV.

The SXPS photon energy was set to 1.4 keV so that the kinetic energy (KE) of excited Ti $2p$ electrons at this photon energy matches the KE of Ti $1s$ electrons excited with the HAXPES photon energy ($KE_{Ti\ 1s} \approx KE_{Ti\ 2p_{3/2}} \approx 961$ eV). Using the QUASES software package,^[43] the inelastic mean free path (IMFP) of Ti $2p$ and Ti $1s$ electrons in Cu metal at the SXPS and HAXPES photon energies were calculated. The IMFP for the Ti $1s$ and Ti $2p_{3/2}$ was approximately 1.50 nm, and so the estimated probing depth (3λ) was 4.50 nm. Therefore, a direct comparison between the two Ti core levels will be possible as they originate from very similar probing depths.

2.3. Laboratory-Based SXPS

SXPS depth profile measurements were conducted on the samples annealed at 109 using a laboratory-based Thermo K-Alpha+ XPS spectrometer (i.e., the in situ annealed samples were removed and kept for a post-mortem analysis). The instrument operates with a monochromated Al $K\alpha$ photon source ($h\nu = 1.4867$ keV) and consists of a 180° double-focusing hemispherical analyser, a 2D detector that integrates intensity across the entire angular distribution range, and operates at a base pressure of 2×10^{-9} mbar. A $400\ \mu\text{m}$ spot size was used for all measurements, achieved using an X-ray anode emission current of 6 mA and a cathode voltage of 12 kV. A flood gun with an emission current of 100 μA was used to achieve the desired level of charge compensation. The total energy resolution of the spectrometer was determined to be 400 meV. Survey and core level (W $4f$, Ti $2p$, O $1s$, and Cu $2p_{3/2}$) spectra were collected with pass energies of 200 and 20 eV, respectively. Depth profiles were achieved by utilising a focused Ar^+ ion source, operating at 500 eV energy and 10 mA current, rastering over a $2 \times 2\ \text{mm}^2$ area with a 30° sputtering angle. A total of 17 sputter or etch cycles, each lasting 180 s, was carried out with survey and core level spectra collected after each etch cycle. The data were analysed using the Thermo Advantage v5.9925 software package. The error associated with the quantification values was estimated to be ± 0.3 at.% owing to the complexity of the W $4f$ core level and the low quantities of Cu and Ti/W in the TiW and Cu layers, respectively.

3. Results and Discussion

Reference room temperature survey and core level spectra (Ti $1s$, Cu $2p$, Ti $2p$, and W $4d$) were collected for the three samples after the in situ sputter cleaning process, and prior to annealing, with the results displayed in Content VI (Supporting Information). From the survey spectra, the sample surfaces appear clean and are dominated by signals from Cu. Virtually no carbon is detected, and only a trace quantity of oxygen is present when measured with SXPS. The Cu $2p_{3/2}$ core level spectra are near identical for the three samples, and the position and line shape are commensurate with metallic copper.^[44–46] A low-intensity satellite is observed between 943 and 948 eV in the Cu $2p_{3/2}$

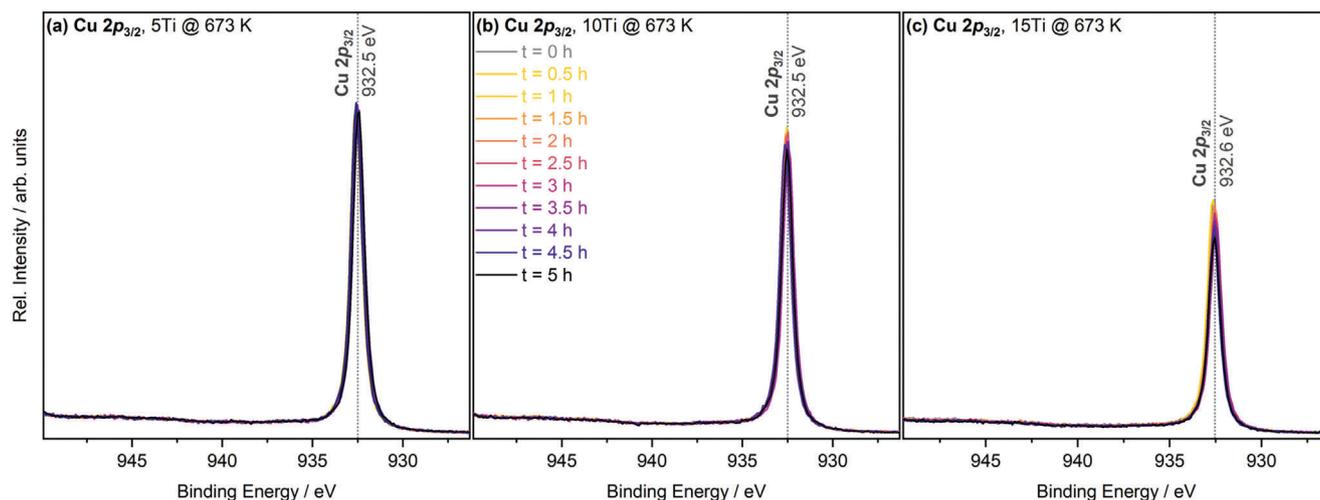


Figure 3. Cu $2p_{3/2}$ core level spectra collected during the 673 K holding period (Stage 3) for sample a) 5Ti, b) 10Ti, and c) 15Ti. Spectra for each sample are plotted over the same y-axis scale to show the differences in intensity across the three samples. The spectra have not been normalised, but a constant linear background has been removed. To avoid congestion of this figure, spectra collected every other spectral cycle are presented (i.e., ≈ 30 min) rather than at every spectral cycle (i.e., ≈ 15 min). The legend displayed in (b) also applies to (a) and (c). Here, $t = 0$ h refers to the start of the 5 h holding period.

core level spectra, but comparing the spectra to reference measurements of a polycrystalline Cu foil and an anhydrous Cu_2O powder, the satellite intensity is in agreement with the Cu foil. This confirms that the Cu surface of these samples can be considered metallic and the native oxide contribution is minimised after in situ sputtering.

Importantly no Ti or W is observed in these room temperature measurements. This confirms both that the Cu layer is sufficiently thick so that even with SXPS, the underlying TiW cannot be probed, and that the surfaces are consistent across all samples. The reference measurements show that the Cu $L_1M_1M_{4,5}$ Auger line overlaps with the Ti 1s core line, but its intensity is vanishingly small.^[47,48] Nevertheless, care was taken to remove this contribution when we quantified the Ti 1s region to accurately determine the relative change in Ti concentration at the surface.

The following sections present the Cu, Ti, and W core level spectra and associated accumulation profiles as a function of annealing duration/temperature across the three samples, with a focus on the initial stages of annealing and the 673 K holding period.

3.1. In Situ Annealing Profiles

3.1.1. Copper

Figure 3 displays the Cu $2p_{3/2}$ core level spectra collected over the 5 h holding period at 673 K for all three samples, that is, Stage 3 (with $t = 0$ h in **Figure 3** referring to the start of the 5 h holding period). The spectra across all samples confirm that Cu still remains in its metallic state during annealing, with a BE position of approximately 932.5 eV. Additionally, the narrow full width at half maximum (FWHM), found to be 0.8 eV, and the lack of significant satellite features in the 943–948 eV region give further

confirmation of the metallic nature of the Cu surface.^[44–46] From **Figure 3** it can be observed that after annealing and within the 673 K holding period, sample 5Ti has the highest Cu $2p_{3/2}$ signal intensity (**Figure 3a**), followed by samples 10Ti (**Figure 3b**) and 15Ti (**Figure 3c**). Moreover, within the 5 h holding period, the signal intensity is continually decreasing with annealing duration and this effect is most notable in **Figure 3c** for the sample with the highest Ti concentration.

To determine the change in concentration of Cu at the sample surface across the measurement window, peak fit analysis of the Cu $2p_{3/2}$ core level was conducted to determine the change in area, with the resultant profile displayed in **Figure 4a**. In **Figure 4**, time, $t = 0$ h is redefined as the first measurement point of the measurement window (i.e., at the start of Stage 2 at a temperature of 523 K (250°C)). Note, $t = 0$ h in the context of **Figure 4** is not the same as $t = 0$ h in **Figure 3**. The same is also true for **Figures 5** and **7**, which present the equivalent spectra to **Figure 3** for the Ti 1s and W 4d core levels, respectively.

The Cu $2p_{3/2}$ intensity profile in **Figure 4a** reflects what is observed in the core level spectra collected across the 673 K holding period shown in **Figure 3**, in that the Cu $2p_{3/2}$ signal intensity decreases as a function of time and annealing temperature across both Stages 2 and 3 of the annealing process. The decrease in intensity of the Cu $2p_{3/2}$ signal with time is a consequence of the diffusion of Ti out of the TiW layer during annealing. The accumulation of Ti leads to a displacement of Cu atoms and the formation of a Ti-rich surface layer, consequently attenuating the Cu signal. Additionally, when the TiW is more Ti-rich, **Figure 4a** shows that the Cu signal diminishes more extensively, suggesting a greater out-diffusion of Ti. As expected based on this interpretation, sample 15Ti shows the largest decay rate in the Cu $2p_{3/2}$ signal, followed by sample 10Ti and then 5Ti. At the end of the measurement window, the Cu $2p_{3/2}$ signal intensity has depreciated by approximately 2.8, 8.8, and 32.3 %, for sample 5Ti, 10Ti, and 15Ti, respectively.

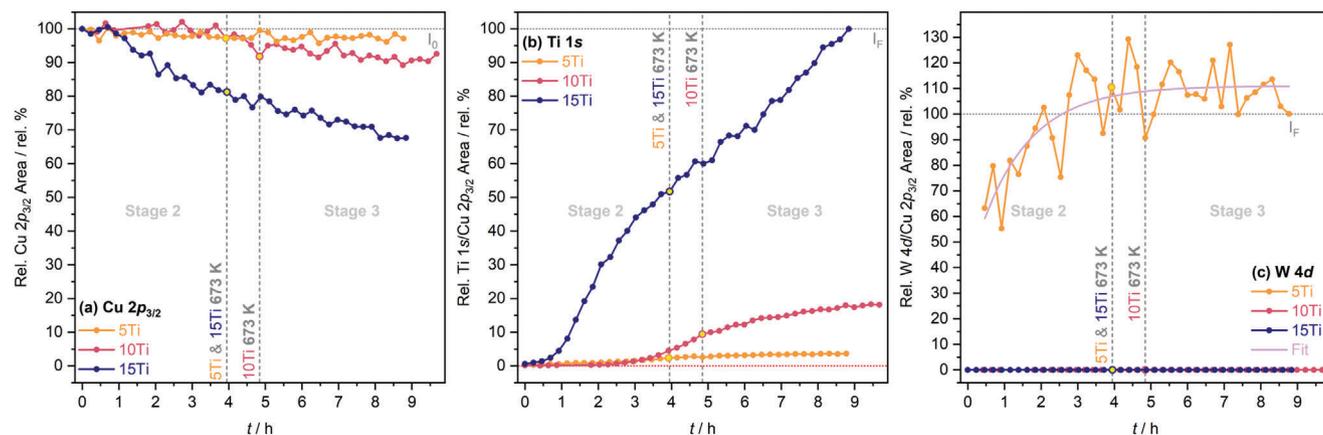


Figure 4. Relative area intensities measured as a function of time, t collected across the measurement window for all three samples, including a) Cu, b) Ti, and c) W profiles, determined from peak fitting the Cu $2p_{3/2}$, Ti $1s$ and W $4d$ core level spectra, respectively, at each spectral cycle. Here, $t = 0$ h refers to the start of the measurement window. The yellow-filled marker for each dataset refers to the time when the 673 K holding period commences (i.e., data points before and after the marker refer to Stage 2 and 3 of the annealing process). Vertical guidelines are also in place to mark this point for each sample. For Cu, the measured total Cu $2p_{3/2}$ areas are normalised relative to the initial raw area (I_0) of their respective sample (i.e., I/I_0). For Ti, the measured total raw Ti $1s$ signal area for each sample is first normalised relative to the raw area of the Cu $2p_{3/2}$ core level measured during the same spectral cycle, and then, the resultant Ti $1s$ /Cu $2p_{3/2}$ area is normalised relative to the final raw intensity of sample 15Ti (i.e., I/I_F). The W accumulation profile was determined by normalising the measured total raw W $4d$ spectral areas following the method used for the Ti $1s$ normalization (i.e., I/I_F).

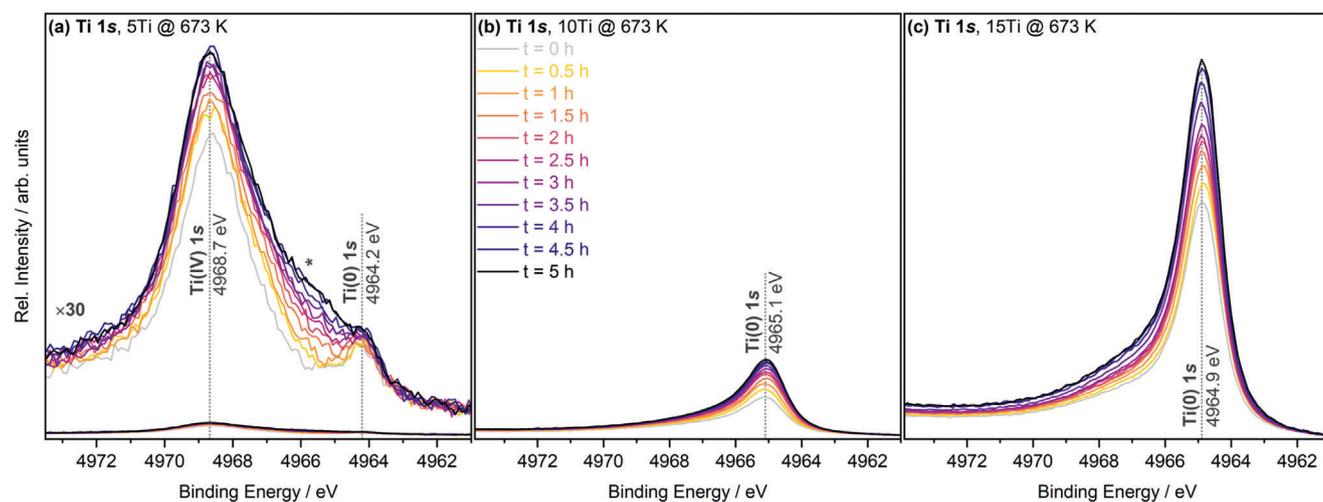


Figure 5. Ti $1s$ core level spectra collected during the 673 K holding period (Stage 3) for samples a) 5Ti, b) 10Ti, and c) 15Ti. Spectra for each core level are plotted over the same y-axis scale to show the differences in intensity across the three samples. The spectra have not been normalised, but a constant linear background has been removed. Additionally, spectra recorded every other spectral cycle are displayed to aid in interpreting the data. For sample 5Ti, the spectra are also shown magnified by $\times 30$ to aid with viewing. The legend displayed in (b) also applies to (a) and (c). Here, $t = 0$ h refers to the start of the 5 h holding period.

3.1.2. Titanium

The Ti $1s$ core level spectra collected across the 5 h 673 K holding period (Stage 3) are displayed in Figure 5, with the BE positions of the main signals annotated (see Contents VII and VIII, Supporting Information, for the equivalent Ti $2p$ core level spectra and heat maps of the Ti $1s$ spectra collected across the measurement window, respectively).

Figure 5 shows that by the time the 673 K holding period starts, a Ti $1s$ peak is observed across all three samples and the intensity continually increases during the 5 h holding period. This con-

firms that the onset of diffusion occurs prior to Stage 3 of the annealing process, as assumed during the discussion of the Cu profile. Significant differences in intensity of the Ti $1s$ spectra as a function of Ti concentration are observed, with sample 15Ti showing a considerably more intense peak than sample 10Ti and 5Ti (note the $\times 30$ magnification of the 5Ti spectra). Notably, the spectral line shape also appears different across the samples indicating a change in the chemical state of the accumulated Ti.

All spectra exhibit a lower BE feature at 4964.2–4965.1 eV, corresponding to metallic Ti in varying environments (labeled as Ti(0)). As the Ti $1s$ core level is not as widely studied as Ti $2p$ due to

the need for hard X-ray sources, only a handful of publications exist, with reported BEs varying considerably.^[36,49–56] The BE positions of the Ti(0) 1s peak observed in the present work fall within the literature range of metallic Ti, and the asymmetric line shape of the peak, which can be clearly observed in Figure 5b,c, is commensurate with this assignment. An asymmetric line shape is a hallmark of the core level spectra of many transition metals.^[57]

The 10Ti and 15Ti samples show a small BE difference of 0.2 eV, which could be attributed to the differences in the Ti:Cu and/or Ti:O ratio at the evolving surface. In contrast, the BE position in the 5Ti spectra is considerably lower, with a -0.9 eV shift relative to the BE position observed in the spectra of sample 10Ti. This shift can be attributed to the distinctly different surface configuration of this sample due to the dominance of Ti-O environments and the co-diffusion of tungsten, both of which will be discussed later. Moreover, the quantity of Ti diffused to the surface is incredibly small for sample 5Ti, and therefore, the shift could be due to strong surface effects, with far fewer nearest neighbors being Ti leading to a negative shift in BE position.^[58,59]

During the 673 K holding period, the nature of the accumulated Ti for samples 10Ti and 15Ti is predominately metallic, given that a single asymmetric peak is visible (see Figure 5b,c). The accumulated Ti for sample 5Ti, shown in Figure 5a, is strikingly different as the intensity of the lower BE metallic peak is overshadowed by a large, fairly symmetric peak at approximately +4.5 eV from the Ti(0) 1s peak. This peak, labeled as Ti(IV) 1s, is attributed to Ti-O environments in the Ti +4 oxidation state (i.e., TiO₂ like). Renault et al. report the Ti 1s BE position of the TiO₂ environment on a TiN film at 4968.8 eV,^[54] which agrees well with the value reported here. Therefore, unlike samples 10Ti and 15Ti, the Ti accumulated at the surface of sample 5Ti is not predominately metallic but oxidic. Additionally, there is a shoulder on the lower BE side of this Ti(IV) 1s peak (marked with an asterisk, *), which is attributed to lower valence states of Ti (i.e., +2, +3) that may also form due to the limited quantity of oxygen expected to be present (see Content IX, Supporting Information, for a peak fit analysis of the spectra highlighting the presence of such environments). This shoulder increases in intensity with increasing annealing duration, and at the end of the 5 h period, a distinct Ti(0) 1s peak is difficult to observe.

To aid with the interpretation of the Ti 1s spectra, as well as validate the chemical state assignments made so far, the Ti 2p spectra are used in parallel (see Content VII, Supporting Information). The Ti 2p spectra for samples 10Ti and 15Ti show a doublet peak with an asymmetric line shape at 454.5 and 460.6 eV (SOS = 6.1 eV), in agreement with metallic Ti.^[60,61] For sample 5Ti, three peaks are identified at 453.8, 459.0, and 464.8 eV. The lowest BE peak corresponds to Ti 2p_{3/2} of Ti(0), whereas the other two correspond to the doublet of Ti oxide in the +4 oxidation state (SOS = 5.8 eV), labeled as Ti(IV) (with the Ti(IV) 2p_{3/2} peak overlapping the Ti(0) 2p_{1/2} peak). These BE positions and the SOS of the Ti(IV) oxide doublet match well with literature values.^[62,63]

A shift of the lower BE Ti(0) 2p_{3/2} peak between the three samples is observed, with the peak positioned at 453.8, 454.7, and 454.4 eV for samples 5Ti, 10Ti and 15Ti, respectively. The relative shifts are similar to those observed in the Ti 1s spectra. Moreover, the Ti 2p spectra recorded for sample 5Ti also display a shoulder on the lower BE side of the main Ti(IV) 2p_{3/2}, again reflecting what has been observed in the Ti 1s spectra, suggesting the pres-

ence of lower valence oxidation states that may form during the reaction between Ti and oxygen.^[64,65] Overall, this confirms the peak assignments made using the Ti 1s core level and shows the importance of using multiple core levels to have confidence in the assignment of chemical states.

The observation of almost completely oxidised Ti on the surface of sample 5Ti is of interest, given that these measurements were conducted under ultra-high vacuum (UHV) conditions and annealed in situ. The level of observed oxidation cannot be explained by Ti gettering residual oxygen from the analysis chamber as the quantity present in the chamber is insufficient to promote oxidation of Ti to the extent observed. Furthermore, as the sample is heated during the measurement, the sticking coefficients for adsorbed gases are greatly reduced. An alternative source of oxygen is residual oxygen within the Cu film, whether that be intrinsic to the film (i.e., incorporated during deposition) or that the sputtering process prior to annealing did not fully remove the native oxide layer that formed during the exposure of the samples to the atmosphere. From the room temperature reference survey spectra found in Content VI (Supporting Information), a small intensity O 1s signal is present. Laboratory-based SXPS depth profiling on the as-deposited samples was conducted to determine the oxygen level within the starting (i.e., pre-annealed) films and to validate this assumption further. Three sputter cycles (or etch steps) were completed before the underlying TiW signal became strong (see Content X, Supporting Information, for the collected spectra). The profiles showed that within the Cu bulk, less than 2 rel. at.% of O is present, that is, <2 at.% O, >98 at.% Cu. Within the errors of the performed quantification, this amount is enough to facilitate the observed Ti oxidation.

Overall it is apparent that the oxidation of Ti is dependent on both the quantity and rate of accumulation of Ti metal at the surface. Given the significant Ti oxidation observed for sample 5Ti, owing to the low concentration of accumulated Ti, it is expected that during the early stages of annealing for the higher concentration samples (10Ti and 15Ti), when an equally low concentration of Ti is expected to accumulate, oxidation will occur. To confirm this and explore the oxidation of accumulated Ti further, Figure 6 displays the Ti 1s core level spectra collected across the measurement window for sample 10Ti (equivalent figures for sample 5Ti and 15Ti can be viewed in Contents XI and XII, Supporting Information, respectively). Figure 6a shows that during the initial stages of annealing sample 10Ti (≤603 K), the intensity first increases within the region of 4966–4970 eV. After 603 K the intensity increases below 4966 eV, where the metallic Ti(0) 1s peak is located, and this peak quickly becomes the dominant contribution to the total line shape and consequently masks the intensity of the environments seen on the higher BE side.

From Figure 5a, we know that the 4966–4970 eV region corresponds to Ti-O environments, namely the Ti(IV) oxidation environment, suggesting that even for sample 10Ti, during the initial stages of annealing when the accumulated Ti concentration is low, oxidation of Ti metal occurs. This region will be referred to as Ti-O environments in the following discussion. Figure 6b further emphasises the development of Ti-O environments by focusing on the spectra collected between 523 and 623 K. From this, it is clear that Ti-O environments evolve first and then after 603 K, the Ti(0) 1s peak appears due to the continuing diffusion of Ti metal from the TiW layer. It should be noted that the Cu LMM

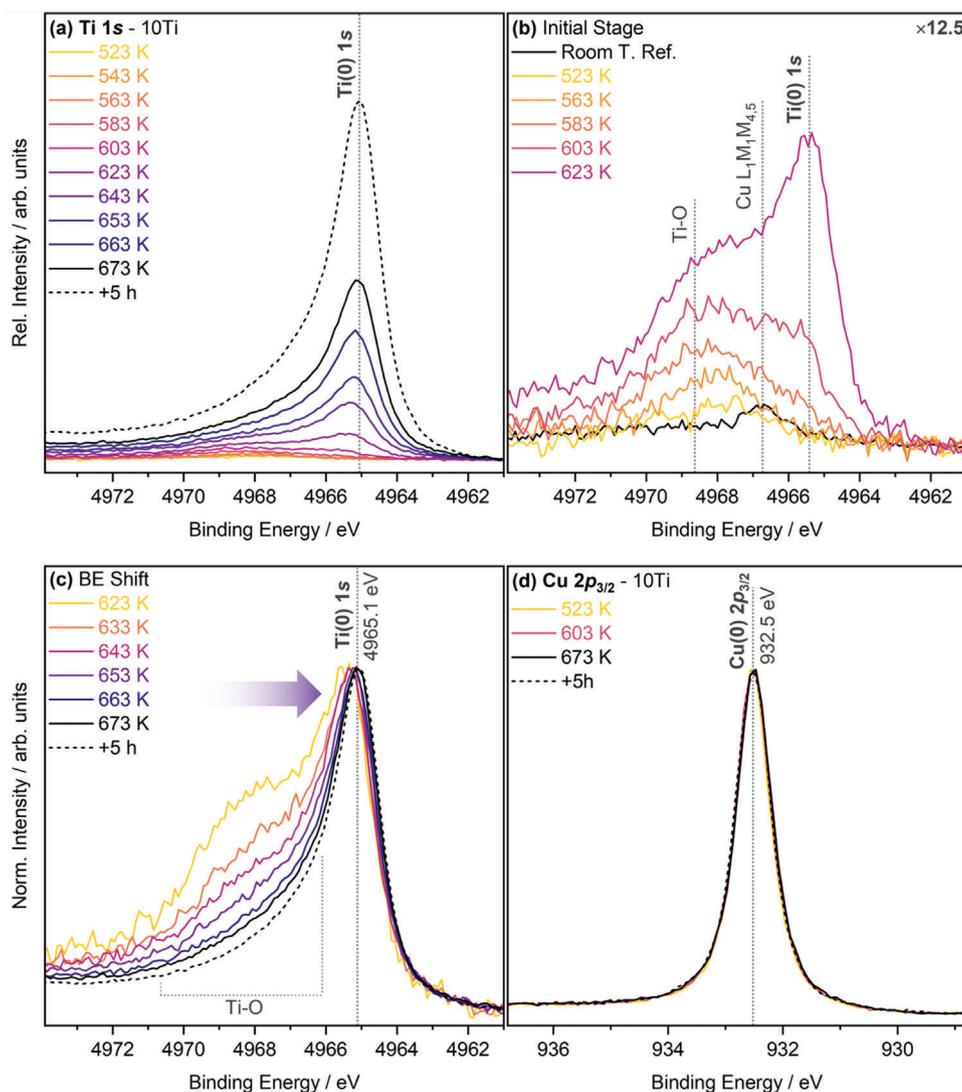


Figure 6. Initial stages of annealing (523–673 K) monitored using the Cu $2p_{3/2}$ and Ti 1s core level spectra. a) Raw Ti 1s core level spectra collected (i.e., with no intensity normalisation) at each temperature increment, with +5 h referring to the data collected at the end of the 5 h 673 K holding period. b) A magnified view of the raw Ti 1s core level spectra collected between 523 and 623 K and a room temperature reference measurement on the same sample (i.e., before annealing) to highlight the Cu Auger contribution. c) Normalised (0-1) Ti 1s core level spectra to emphasise the change in line shape as a function of temperature. d) Normalised (0-1) Cu $2p_{3/2}$ spectra taken at selected temperatures. (a) and (b), and (c) and (d) are plotted on the same y-axis scale, respectively (note the $\times 12.5$ magnification of the y-axis scale of (b)).

Auger peak is also present in this region, however, given that the main Cu $2p_{3/2}$ core level peak decreases with annealing duration and temperature, the observed increase in spectral intensity in this region cannot be explained by any interference from the Auger peak.

The transition from predominantly Ti oxide to metal is evident in Figure 6c, showing the Ti 1s spectra normalised to the maximum peak height. This figure shows that the main intensity peak signal shifts toward lower BEs across the temperature range of 623–673 K (highlighted with an arrow), and this is accompanied by a decrease in the relative intensity of the Ti-O region. The observed shift is due to the emergence of the Ti(0) 1s metal peak and the overall reduction of the Ti-O contribution to the total spectral line shape. Lastly, Figure 6d displays the Cu $2p_{3/2}$ spectrum

recorded at different temperatures across the measurement window, and no discernible change is observed in the spectra. Additionally, Content XIII (Supporting Information) shows that the same observation is true when comparing the Cu $2p_{3/2}$ line shape across all three samples. This indicates that only the Ti, not the Cu, is undergoing changes to its chemical state at the developing interface.

Therefore, oxidation of the surface accumulated Ti is also observed in sample 10Ti but is more evident during the initial stages of annealing where the rate of metal Ti diffusion and quantity of accumulated Ti is small. The same holds true for sample 15Ti as seen in Content XII (Supporting Information). Beyond the qualitative analysis of the Ti 1s/2p spectra, an accumulation profile of Ti at the Cu surface across the measurement window

can be obtained. The Ti accumulation profiles for the samples were extracted from the Ti 1s core level spectral areas and are displayed in Figure 4b (the equivalent Ti 2p profile can be found in Content XIV, Supporting Information). Before discussing these profiles, it is important to reiterate that they represent changes in the quantity of surface-accumulated Ti with respect to time and not temperature, but with increasing time, the temperature also rises.

The temperature at which Ti is first observed at the Cu surface (i.e., the onset), is difficult to identify with full confidence as the signal is very small, especially for samples 5Ti and 10Ti. For these two samples, the temperature range between 553 and 563 K (i.e., within the first 2 h of Stage 2) is when a Ti signal is clearly detectable. The detection of these small Ti signals was only possible through analysing the Ti 1s core level as it was much more intense and sharper than the Ti 2p (Content XV, Supporting Information, provides a comparison of the Ti 2p and Ti 1s measured at the same point to highlight this issue). In contrast, for sample 15Ti, it is obvious from Figure S15b (Content XII, Supporting Information), which Ti is observed from the start of the measurement window (i.e., 523 K) and may have even begun to accumulate during Stage 1 of the annealing process.

The Ti profile displayed in Figure 4b shows that with increasing the concentration of Ti within the TiW film, a greater out-diffusion of Ti is observed and thus, a greater accumulation of Ti on the Cu surface occurs. From the profile, it is apparent that the rate of diffusion and the quantity of accumulated Ti differs significantly across the three samples. Focusing on the last data point in the Ti profile at the end of the 673 K holding period, the Ti 1s/Cu 2p_{3/2} area ratios of samples 5Ti and 10Ti are 3.7±0.5 and 18.2±0.5 %, respectively of that of sample 15Ti. This indicates that a linear relationship between the Ti concentration in the film and the quantity of accumulated Ti on the Cu surface does not exist (i.e., they do not scale proportionally).

Sinojiya et al. studied similar Ti_xW_{1-x} films across a composition range and observed that above a certain Ti concentration threshold, segregation of Ti toward the grain boundaries was favored, and this enrichment increased with increasing Ti concentration.^[66] Additionally, they observed that the change in Ti concentration not only enhances the segregation of Ti but is also accompanied by a change in stress, microstructure, and grain boundary density within the TiW films. A columnar grain boundary structure was also observed at higher concentrations as well as a relatively higher grain boundary density. Therefore, in our case, for sample 15Ti it is possible that a greater quantity of Ti was already segregated from the TiW grains within the as-deposited films or that annealing promoted a greater segregation compared to samples 5Ti and 10Ti, and consequently that this led to the differences observed in the Ti accumulation profile between the three samples. Furthermore, based on the work of Sinojiya et al., the expected differences in the microstructure across samples 5, 10, and 15Ti will also contribute to the changes observed in the Ti diffusion profile as properties such as grain boundary density will affect the rate of diffusion.

The Ti accumulation profile displayed in Figure 4b, collected across the measurement window of all three samples, exhibit two different diffusion regimes. The first regime occurs before the 673 K target is reached (i.e., during Stage 2), wherein a rapid exponential increase in intensity occurs when ramping the temper-

ature. Once the 673 K target is reached (i.e., during Stage 3), the second regime occurs wherein the diffusion rate begins to decelerate and starts to plateau. A plateau is observed for sample 5Ti, and signs of a plateau are present for sample 10Ti by the end of the measurement window. In contrast, the profile for sample 15Ti does not show signs of plateauing, indicating that Ti continues to accumulate at the Cu surface under the temperature and measurement window tested in this experiment. By fitting the linear portions of the Ti 1s profile collected during Stages 2 and 3 of annealing, the rate of increase (i.e., slope) in the Ti 1s signal intensity relative to sample 15Ti can be determined. The gradients of the linear fits of Stage 2 for samples 5Ti, 10Ti and 15Ti were found to be 0.7, 4.1 and 17.9, respectively, and for Stage 3 were found to be 0.2, 1.3, and 10.3, respectively, with an absolute error of ±0.5. These values highlight the dramatic decrease in the Ti accumulation rate during Stage 3 of annealing. Multiple processes could be responsible for these changes in the accumulation rate. For instance, only a finite quantity of Ti may be available to segregate from the TiW grains, therefore, after annealing for several hours, a plateau is reached as no more Ti is available to diffuse.^[19] Additionally, the accumulation appears to decelerate after the 673 K mark is reached. This deceleration may imply that when subjected to a constant temperature rather than a temperature ramp, the rate of diffusion levels off as a steady-state system is reached due to the thermal input remaining at a constant rate.

3.1.3. Tungsten

Figure 7 displays the collected W 4d core level spectra for all samples during the 5 h 673 K holding period (Stage 3). W is not observed within this period for the 10Ti and 15Ti samples, however, it is detected for sample 5Ti, whose TiW film contains the lowest Ti concentration. This confirms that W co-diffuses to the surface only for sample 5Ti, and given that it is already detected at $t = 0$ h of the 673 K holding period, the diffusion likely occurred prior to Stage 3. The BE position of the W 4d_{5/2} peak is at 243.2 eV, in good agreement with metallic W.^[67] Within the 5 h period, the concentration of surface accumulated W does not increase in intensity with increasing annealing duration, suggesting that the accumulation has plateaued and the diffusion has subsided. The presence of W at the Cu surface may also influence the oxidation behavior of the accumulated Ti as observed in the previous section.

Figure 4c displays the relative accumulation profile of W at the Cu surface across the measurement window for all three samples. Due to the poor signal-to-noise ratio (SNR) of the W 4d spectra, it is difficult to have complete confidence in determining the exact temperature at which W is first observed for sample 5Ti. However, the signal becomes apparent at 553–563 K, similar to when Ti was observed at the surface of the same sample. The poor SNR is also responsible for the large scatter in the accumulation profile, leading to an area change greater than 100 rel.%. Fitting the data points with an asymptotic curve shows that a plateau is reached when crossing from Stage 2 to 3 of the annealing process, with the 673 K holding period profile flattening, similar to what was observed for the Ti profile. The observed plateau indicates that a finite quantity of W is able to migrate from the barrier

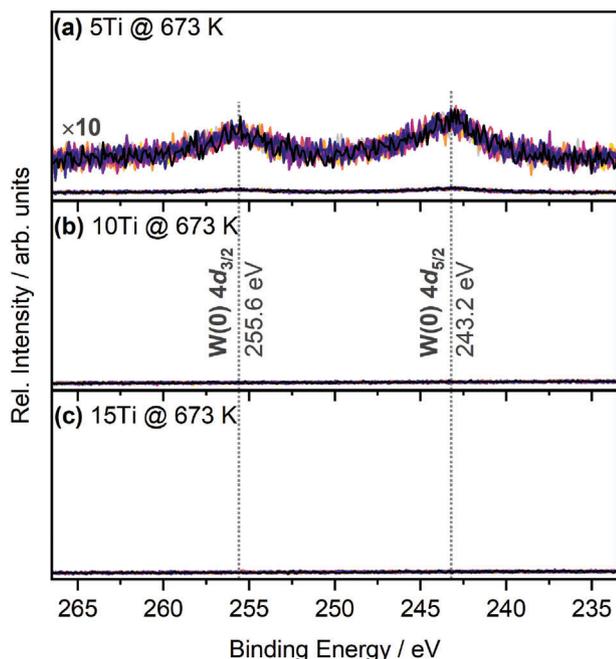


Figure 7. W 4d core level spectra collected during the 673 K holding period (Stage 3) for samples a) 5Ti, b) 10Ti, and c) 15Ti. Spectra for each core level are plotted over the same y-axis scale to show the differences in intensity across the three samples. Note the $\times 10$ magnification of the spectra for sample 5Ti in (a). The spectra have not been normalised, but a constant linear background has been removed. Additionally, spectra recorded every other spectral cycle are displayed to aid with the interpretation of the data. For sample 5Ti (a), the inset shows a $\times 10$ magnification of the spectra to aid with viewing. The legend is the same as that used in Figures 3b and 5b. Here, $t = 0$ h refers to the start of the 5 h holding period.

and that a steady state is reached within the measurement window explored.

The diffusion of W is surprising as the vast majority of studies on TiW only report the out-diffusion of Ti. For example, even studies on pure W diffusion barriers,^[68–71] or on a TiW barrier with a relatively low Ti concentration (4.9 at.%)^[72] do not report any mobility of W. However, some studies observe W diffusion from a W or TiW barrier within thin film stacks at temperatures below 600°C, although no details are given on a possible reason as to why this occurs.^[73–75]

Based on the present results, it is hypothesised that the Ti concentration of the TiW film dictates the overall stability of the diffusion barrier. If it is too low (i.e., in the 5Ti sample), a small amount of W becomes mobile and is free to migrate through the Cu overlayer alongside Ti and accumulate at the surface. This suggests that Ti plays an active role in stabilising the barrier and achieving the desired microstructure necessary for good barrier performance. Therefore, tuning the Ti concentration to an optimum value can significantly improve the barrier performance.

3.2. Elemental Distribution Across the In Situ Annealed TiW/Cu Bilayer

From the in situ annealing results, it is clear that under the conditions tested, the out-diffusion of Ti from TiW and through the Cu

metallisation is observed for the two samples with the higher Ti concentration - 10Ti and 15Ti. Whereas, for the lowest Ti concentration sample (5Ti), both Ti and W diffuse through the copper metallisation. To quantify the elemental ratio of Cu, Ti, and W across the metallisation, depth profiling using laboratory-based SXPS was conducted on the in situ annealed samples (i.e., post-mortem). Survey spectra collected at each etch cycle for all three samples can be found in Content XVI (Supporting Information), showing the change in composition and transition between the Cu overlayer and TiW sublayer.

The depth profiles for the three samples displayed in Figure 8 highlight the distribution of Ti across the Cu layer and confirm what was observed in the in situ measurements, in that at the Cu surface, the quantity of accumulated Ti increases in intensity as the Ti concentration of the film increases. The profiles further confirm that Ti is found throughout the Cu film after annealing. However, its distribution is not uniform, with more Ti observed at the Cu/air and TiW/Cu interfaces. Despite the strong out-diffusion, distinct Cu and TiW zones are still observable in the depth profiles, showing that the TiW/Cu bilayer has not failed when stressed under these conditions.

Several studies on Cu/Ti bilayer films have identified that a reaction between the two films can occur as low as 325°C, leading to the formation of intermetallic CuTi and Cu₃Ti compounds at the interface.^[76–78] As shown in Figure 6c, the shifts observed for the Ti 1s core line are representative of a changing oxide-to-metal ratio rather than the formation of an intermetallic compound, whereas the Cu 2p_{3/2} spectra displayed in Figure 6d show no change in the line shape. If an intermetallic compound were to form, one would expect some systematic change to the spectra with increasing annealing duration and temperature or for samples with a higher Ti concentration in the TiW film, as these will cause the greatest surface enrichment of Ti on the Cu. The possibility of such a reaction is difficult to answer from the core level spectra alone. The depth profiles can aid with this discussion. At etch cycle 0 (i.e., as-received surface), the Ti:Cu ratio for sample 15Ti is 7.5:92.5. Of course, this may be slightly skewed as the surface is oxidised, and so there may be additional diffusion of Ti across the metal/oxide interface, and a carbon surface layer is present which may affect the quantification. Nevertheless, this ratio is insufficient to form stoichiometric CuTi or Cu₃Ti intermetallic phases that were reported in previous studies on the Ti/Cu interface.^[76] Therefore, based on this literature, the presented spectra and the quantified Ti:Cu ratio, a reaction between Cu and Ti at the developing Cu/Ti interface does not occur due to the relatively small amount of diffused Ti, which again may explain why no systematic shifts in the core level spectra commensurate with a Cu-Ti reaction were observed. However, it should be noted that it may not be possible to observe intermetallic compounds as (a) the quantity of diffused Ti is very small, and (b) the Cu 2p_{3/2} core line is known to have small chemical shifts.^[79]

In terms of W, the depth profiles shown in Figure 8 confirm that W is only observed at the Cu surface for sample 5Ti and is not present at the surface or within the Cu bulk for samples 10Ti and 15Ti. Figure 8a shows that for sample 5Ti, the W profile is fairly constant across etch cycles 0–3, suggesting that W is homogeneously distributed throughout the Cu metallisation and is not accumulated at the Cu/air interface like Ti. Quantification of the Cu, Ti and W signals reveals that at the surface of sample

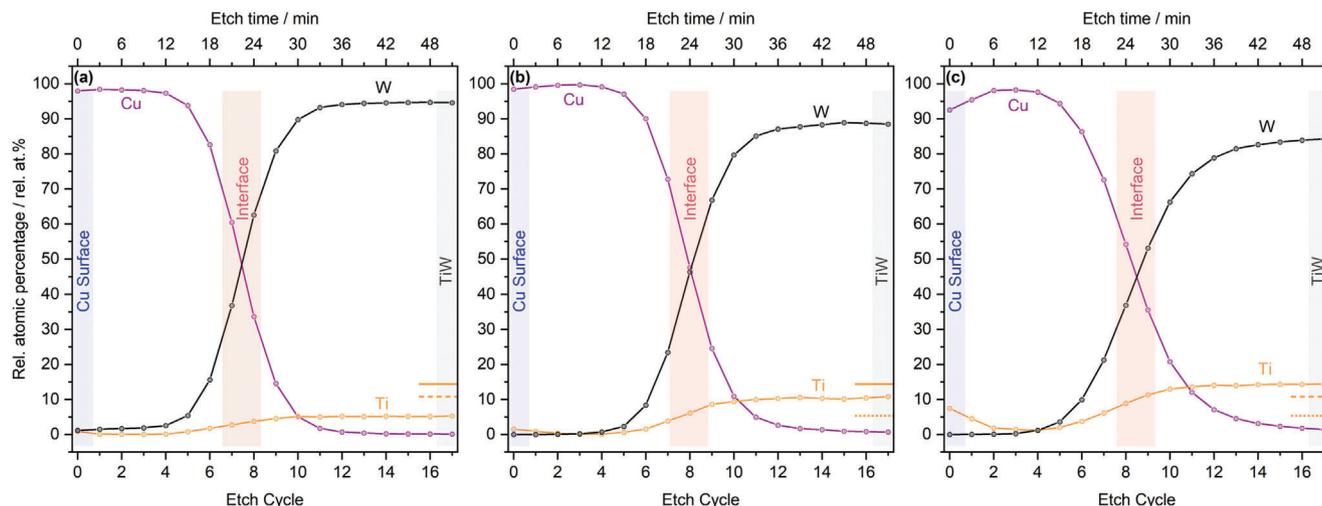


Figure 8. Post-mortem laboratory-based SXPS sputter depth profiles collected across samples a) 5Ti, b) 10Ti, and c) 15Ti after in situ annealing at beamline I09. Etch Cycle 0 refers to the spectra collected on the as-received sample (i.e., before any sputtering). Horizontal guidelines are added to show the final Ti at.% for each sample, with the dotted, dashed and solid orange lines referring to samples 5, 10, and 15Ti, respectively.

5Ti (etch cycle 0), the composition is 97.9 (Cu), 0.9 (Ti), and 1.2 (W) rel. at.%, showing that significant W diffusion has occurred.

Figure 8 shows that the Cu signal tends toward 0 rel. at.% for all samples when the interface is reached. However, Cu is still detected at the deepest point of the depth profile, with a composition at etch cycle 17 calculated to be 0.1 (Cu):99.9 (Ti + W), 0.7 (Cu):99.3 (Ti + W), and 1.4 (Cu):98.6 (Ti + W) rel. at.%, for samples 5Ti, 10Ti and 15Ti, respectively. Moreover, with increasing Ti concentration, the element profiles broaden, and their gradients toward the “interface” labeled zone reduce. This provides evidence that there is a degree of intermixing at the TiW/Cu interface, and for films with higher Ti concentrations, a greater intermixing is observed due to the larger rate of atomic flux of Ti across the interface during annealing. Therefore, the out-diffusion of Ti from the TiW also promotes the down diffusion of Cu into the TiW layer, and consequently, the TiW and Cu layers bleed into each other.

To summarise, the depth profiles show that clear TiW and Cu zones remain across all samples despite the diffusion and intermixing that occurs during annealing. Although the concentration of Cu observed at the deepest point of the depth profiles increases when the concentration of Ti in the TiW increases, it is difficult to determine how deep the Cu diffuses, as the measurement point of the last depth profile etch cycle is still within the surface region of the 300 nm thick TiW film. However, given the low concentration of Cu detected at this point (≤ 1.4 at.%), and the fact that distinct Cu and TiW zones still remain, one can be confident that under the conditions tested, the TiW barrier has not failed, and the majority of Cu is held above the barrier.

4. Conclusion

The thermal stability of the TiW barrier in conjunction with a Cu metallisation overlayer was evaluated in real-time using a combination of SXPS and HAXPES, and annealing the sample in situ to a target temperature of 673 K. The primary mode of degradation was the segregation of Ti from the TiW barrier and its

diffusion to the copper surface to form a surface overlayer. The concentration of Ti in TiW was shown to have a significant influence on the thermal stability of the TiW barrier. Two thresholds are observed when moving across the TiW composition window tested here: (i) below a certain concentration of Ti, W gains mobility, suggesting that the incorporation of Ti stabilises W, and (ii) above a certain concentration of Ti the diffusion drastically increases, suggesting that at higher concentrations grain boundary segregation of Ti from the TiW grains is favored, resulting in significantly more out-diffusion of Ti. Moreover, the surface-accumulated Ti is shown to undergo oxidation, and the extent of oxidation is linked to the quantity of Ti that has diffused. The Ti 1s spectra collected for sample 5Ti showed a nearly complete conversion from metal-to-metal oxide, whereas the spectra of sample 15Ti are Ti metal-dominated. The source of oxidation is assumed to be residual oxygen within the Cu metallisation and given its low concentration it is insufficient to oxidise significant quantities of accumulated Ti. The post-mortem depth profiles validate the effectiveness of TiW diffusion barriers as despite the degradation observed during annealing, the Ti depletion is not significant enough to lead to the failure of the barrier, as distinct Cu and TiW zones are still present. Overall, it is clear that the composition heavily dictates the stability of TiW, but under the conditions tested, all three barrier compositions remain effective at suppressing the permeation of copper. Based on this, the TiW alloy can cement itself as an excellent diffusion barrier to incorporate into future device technologies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

diffusion barriers, HAXPES, metallisation, power electronic devices, SXPS, XPS

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