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Why model high- k dielectrics?

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Abstract

New dielectrics need more than a high dielectric constant. They need to satisfy various constraints concerning band offsets, limits on charge traps, processability, reproducibility, and stability against degradation and breakdown. It seems unlikely that purely empirical approaches will produce a dielectric which justifies major investment. I discuss some of the atomistic modelling which can aid selection, and which might indicate routes around some of the interface-related and defect-related problems. These include diffusion during processing or in operation, the use of interface engineering to adjust band offsets, and the issues of crystallinity and of stoichiometry. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Few in the semiconductor industry doubt that new materials will be needed. There are wide-ranging pressures towards the ultimate limits of miniaturisation and of device speed, and possibly increasing pressure towards low-power operation. In a primitive industry, most of the challenges could be met by trial and error. But the microelectronics industry is far from primitive or simple. Any new material has to fit in with other materials, both in use and during the many process steps, and with the constraints of the capital-intensive fabrication equipment [1,2]. Already, semiconductor engineering is exploiting the classical continuum theories (electromagnetism, thermody-

namics, elasticity) in equipment design and process optimisation. But even these powerful approaches are inadequate on the smallest scales anticipated in several of the many variants of Moore's law. Neither experienced empiricism nor extrapolation from the large scale will suffice for some of the challenges.

Turning to high-dielectric (high- k) constant materials, is there a role for theory? 'Theory' includes anything from simple analytical theories to the types of state-of-the-art computer-based modelling likely to be available over the next few years. Theory can have several different roles. The simplest is as a framework for understanding, those ideas which are so familiar that they are not regarded as theory. An example might be the parabolic rule for diffusion-controlled oxidation, or its natural generalisation as the Deal–Grove (reaction–diffusion) model, which continues to be used as a reference picture even when it fails [3]. A second role for theory is *scoping*, estimating which

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features will be important and which less so. Related to this are studies of sensitivities, especially as an aid to optimisation (e.g., what processes are possible, including diffusion). Thirdly, theory can help to unravel a mix of phenomena, especially those which are inconvenient to untangle experimentally. These can include highly non-equilibrium processes, or evolution over an extended lifetime, notably including the mechanisms of failure or of degraded performance.

The limits of empirical approaches are a strong reason for seeking other methods. Empirical approaches rely on *knowledge* of materials in similar states to those to be used. But experimental static dielectric constants are often extremely unreliable, for reasons which are easily identified. This is especially so when the material can be non-stoichiometric, or when the constituent ions have more than one possible charge state. Moreover, thin film materials will often be inhomogeneous because of the different epitaxial constraints at the two interfaces. The problems are more serious when one does not know some of the important structural and electronic aspects of a dielectric. It is one thing to understand a crystal of Si, and quite another to describe properly, let alone understand, a typical thin silica film with an amorphous, probably inhomogeneous, structure. Other thin film dielectrics may be nanocrystalline, perhaps admixed with a silicate glass. In some circumstances, especially where there are step or kink sites for polar materials, there can be quite large local electric and stress fields. These affect trapping and defect processes.

In this paper, I shall address the modelling of materials which have been proposed as high-*k* dielectrics, and especially the prediction of some of the key properties.

2. Choosing a material: critical criteria

Impressive lists of needs have been drawn up, some essential, others merely helpful. We may group them into three main classes. *Class I needs* refer to basic properties *as a dielectric*. *Class II needs* ensure the dielectric can be processed without deterioration or interference with other mate-

rials. *Class III needs* relate to performance in a microelectronic device. There is some interdependence and scope for compromise, which offers opportunities for modelling.

Class I needs, the basic properties, provide the initial selection criteria. The dielectric constant should probably lie in the range 15–25, although a wider range (say 10–30) might be acceptable. Ferroelectric materials are less desirable because of their non-linear electrical response. The dielectric must be an insulator, so it should have a band gap above about 5 eV, with adequate band offsets for use with silicon.

The polarisation of the dielectric will have both electronic and ionic components. The electronic part by itself (related to the refractive index) can be high only if there is a low band gap. It is essential that the main polarisation be *ionic*. In principle, this could include the effects of reorientable fixed dipoles, including H₂O. The *consequence* of a large ionic polarisation is often that defect formation is easier (formation energies of charged defect are reduced by polarisation), including possible non-stoichiometry.

Many measurements of dielectric constants for oxides and related ceramics are of dubious value because there are conducting regions, non-stoichiometry, or impurities. For a number of crystalline systems, it may be more accurate to calculate the dielectric constant than to measure it. For amorphous systems, there is a problem to ensure that the structure for which the dielectric constant is measured (or calculated) actually corresponds to that which will be used. It is not always clear that the dielectric will be *homogeneous*. The problems can be ones of stoichiometry or of alloy fluctuations should not matter. These are issues even for crystalline systems, e.g., in controlling Ba/Sr titanate. One further area which may cause problems for polar dielectrics is that *ions* may provide the major means of atomic transport (unlike, say, O₂⁰ in silica), especially in an applied field.

Class II needs relate to processing and dielectric creation. The way the dielectric is made will, of course, depend on whether the microstructure is to be amorphous, polycrystalline, or epitaxial. It is not necessarily a problem that a dielectric oxide can exist in many closely related forms; indeed,

SiO₂ is precisely such an oxide, and minor variations in structure rarely seem to have been an issue. However, it is very important that the dielectric is what it is supposed to be. Generally, it should be *non-reactive*, reacting neither with Si [4] nor with the gate contact. Likewise, the interfaces should be largely *stress-free*. If not, the interfacial constraints will tend to force either defect creation (dislocations, possibly point defects like P_b centres) or conceivably new phases, such as amorphous forms of oxides usually crystalline (MgO, Al₂O₃,...). Such new phases may have non-optimal properties. If the dielectric is to be *amorphous*, then *it must remain amorphous at processing temperatures, and also during the operating life*. This appears to be satisfactory for alumina, for Si-doped Zr aluminate, and possibly other systems. However, another condition might be required. The Al₂O₃/Y₂O₃ alloys have two liquid phases of different density [5], and it is well known that many glasses will phase-separate. The homogeneity of composition and of properties must be retained. This includes *maintaining stoichiometry accurately*. The precise definition of stoichiometry for thin layers is not always clear, and one might prefer to think in terms of a co-ordination criterion for a system like SiO₂. We shall discuss the criterion of *diffusion* in a later section. For *processing conditions*, one might think of 15 s at 1050 °C; an *operating lifetime* might correspond to six years (2 × 10⁸ s) at room temperature.

Class III needs relate to performance. The dielectric should *behave as an insulator*. This means a *low leakage current* (Pr₂O₃ is said to be very good, Al₂O₃ relatively poor [2]) and a *low loss tangent*. The leakage current will include contributions ranging from tunnelling to defect-related channels involving dislocations, grain boundaries, or point defects. The loss tangent describes how well the polarisation follows an applied field. For DRAM, when fields change on nanosecond time scale, the loss tangent should be less than 0.005. There should be a *low effective fixed charge* to cause carrier scatter in the Si; alumina is said to be relatively poor. Further issues relate to degradation and failure. For Ba/Sr titanate, there is ‘resistive degradation’, apparently due to O vacancy motion. Other effects seem to be related to electrode

roughness, possibly analogous to those seen for silica and for other oxide films.

3. Defining the challenges

3.1. Amorphous versus crystalline dielectrics

Three of the many basic fallacies concerning amorphous systems are these: (1) there is only a single amorphous structure for a given composition; (2) for that amorphous structure, the *mean* energies of defect formation or of trap ionisation are sufficient to understand behaviour, and (3) crystals of the same composition have values for defect and trap energies which are essentially the same as those for the amorphous system. This third fallacy also applies to dielectric constants and band offsets, especially when the ionic polarisation contributions are substantial. How a dielectric layer is created, manipulated or shaped can be important.

That these are fallacies is evident especially for SiO₂. Navrotsky’s work [6] and [7, p. 277] on the enthalpies and molar volumes for silicas shows significant ranges of values. At the molar volume of α-quartz, amorphous systems have an energy per molecular unit larger by about 0.25 eV; the lowest energy amorphous ‘phases’ have about 30% larger molar volume than the quartz. There is similar information for other glass systems. At the very least, the density must be defined for an amorphous system, not just the composition. More generally, amorphous materials depend on the way they are created, and especially on any thermal treatment.

Szymanski et al. [8] have used a combination of molecular dynamics and density functional methods to create realisations of amorphous SiO₂ with density similar to that of thermal oxide. They then analysed the energies of oxidising species (O and O₂ in their neutral, negative and doubly negative charge states). The results were striking in several respects. First, the molecular species had a very different character from the atomic forms. Whereas O₂⁰ was a relatively simple interstitial, O⁰ formed a peroxy linkage (essentially, two oxygens in a bent structure between two silicons). This structural difference has the interesting consequence that the

atomic form is very efficient at isotope exchange, whereas the molecular species only exchanges with network oxygens at special sites. Secondly, electrons with energies corresponding to the bottom of the Si conduction band could create ions, or induce reactions with ionic products. Thirdly, there was a substantial variation of insertion energies (and indeed also of diffusion barriers) from site to site in the amorphous system. This variation *had a significant component associated with medium range order, not just the closest shells of ions*. Fourthly, the values of key energies for the oxidation process (e.g., the insertion energy for moving an oxygen molecule from the gas phase into an interstitial site) were very different for the amorphous oxide and for quartz. The values for the amorphous oxide combined to give an activation energy for the oxidation process in good agreement with experiment.

This work illustrates two characteristic areas for modelling. The first is the prediction of a structure (possibly amorphous or nanocrystalline) under constraints. The second is the demonstration that earlier, simplistic ideas of key defects were misleading. The defects and their nature underpin processing, performance and degradation.

We may usefully compare the advantages and disadvantages of four classes of dielectric, namely: (i) amorphous SiO₂; (ii) some other amorphous oxide, where we might think of a glassy Si-rich (Si/Hf) oxide; (iii) a polycrystalline oxide, where we might think of an Hf-rich (Si/Hf) oxide; (iv) an epitaxial crystalline oxide on silicon. In making the comparison, we shall assume a dielectric constant for the alternative oxide of about four times that of silica. Silica has notable good points: its effectiveness in passivation, its consistency of stoichiometry, and its uses in processing, not to mention the wealth of current experience. Likewise, it has problems: the very thin oxide is vulnerable, perhaps even to a single critically placed defect, and tunnelling will be a problem. On the other hand, there are ways to minimise charged defects.

A number of factors favour an amorphous dielectric: there are no dislocations or grain boundaries; stress can be taken up by modest topological variations in a random network, rather than through misfit dislocations (for the oxide on Si, it

is possible that P_b centres play a role in accommodating the misfit, since they correlate in number with the interfacial stress [9]); a continuous random network tends to minimise electrically active defects. However, the randomness of structure will often give rise to shallow traps. The density may be hard to control, and composition fluctuations are likely (e.g., there may be regions relatively rich in Hf and regions relatively rich in Si in an Hf/Si oxide).

Polycrystalline materials will contain grain boundaries and dislocations. These defects offer fast diffusion pathways, and can trap charge. They may give rise to field concentration and breakdown initiation. In polar solids (which these dielectrics are, cf. Section 1) diffusion is likely to involve ions. This suggests problems with changes of stoichiometry and the development of static charge. The electric fields associated with such charges can be large, if only local, and may have secondary effects. Interfacial stress has to be taken up somehow. For very thin films, elastic deformation may suffice; in other cases, strain may lead to misfit dislocations or alternate phases. Epitaxial crystalline forms can be largely free of grain boundaries, and possibly even largely free from dislocations. However, growing such defect-free layers needs sophisticated (i.e., expensive) methods, probably an unwelcome change from simple oxidation.

The same problems of sophistication and process complexity also apply to the more complicated oxides, such as oxide superlattices grown by laser ablation or other means. Such ‘stacks’ have been produced for various systems, including SiO₂/Ta₂O₅, SiO_x/ZrO₂, SiO₂/Al₂O₃, BaTiO₃/SrTiO₃, BaTiO₃/PbTiO₃, MgO/TiO₂, ZnO/Mg_xZn_{1-x}O and Si/SiO₂. The layers are crystalline in some cases, amorphous in other cases. In principle, such stacks could be used to solve a number of the competing materials challenges.

3.2. Processing and non-stoichiometry

Oxides can be non-stoichiometric in many ways [10]. Whereas SiO₂ usually has a composition with two oxygens per silicon (alternatively, O is bonded

to two Si and each Si bonded to four O), other systems can deviate a lot from their nominal composition. Examples are systems for which cations can easily exist in more than one charge state (such as TiO_{2-x}) or where interstitial oxygen is readily formed (like ZrO_2). Why might non-stoichiometry matter? First, the defects which enable non-stoichiometry often have charge carriers associated with them. These can give rise to charge transport (in some cases by activated small polaron transport) or to dielectric loss. Conduction along grain boundaries or dislocations may be especially worrying [11]. Secondly, these defects are involved in degradation processes, such as resistance degradation. This degradation may become more important for very thin films, since the dielectric will have statistical variations in composition, and some regions will be more vulnerable than others. In certain cases, doping can help: for SrTiO_3 , for instance, doping with Er apparently suppresses O vacancies and reduces the rate of resistance degradation [12]. Thirdly, there are likely to be sample-to-sample variations. These will arise both from the nature of the material as created and from changes during subsequent process steps.

How significant will diffusion be during processing? One should think of 15 s at 1050 °C. If the relevant diffusion distance is 2 nm, then this means that one would prefer the diffusion constant at 1050 °C to be less than $0.3 \times 10^{-14} \text{ cm}^2/\text{s}$. Data for many oxides are available (e.g., p. 258 of [13]). Many of the oxides shown fail, sometimes by cation motion (even Mg in MgO and Ca in CaO; Y in Y_2O_3 probably fails), sometimes by anion (O) motion (in calcium-stabilised zirconia (CSZ), TiO_2 and Y_2O_3). Most non-stoichiometric oxides fail the criterion. Alumina seems safe so long as there are no grain boundaries, although Ag or Cu may diffuse fast enough to break the criterion [14]. It is possible that the criterion given is marginally too stringent, in that O in fused SiO_2 is close to failing.

One should also ask about that ubiquitous impurity, hydrogen. For all oxides studied, the H diffusion rate is substantially in excess of the critical value [15] (LiNbO_3 , LiTiO_3 , TiO_2 (parallel and perpendicular to the *c*-axis), $\alpha\text{-SiO}_2$, MgO, MgO:Li, Al_2O_3 , $\text{Al}_2\text{O}_3\text{:Mg}$, BeO, and also in certain ceramics (spinel MgO- Al_2O_3 , amorphous

cordierite $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$). Thus, H can readily diffuse across a 2 nm film in 15 s at 1050 °C.

3.3. Interfaces and interface engineering

As Robertson has observed [16], an effective gate dielectric needs adequate band offsets from those of Si. The band offset is, however, a subtle quantity [17,18]. The energy required to take a charge from one medium into another will depend on any dipole layer associated with the interface. Indeed, for MgO and perhaps Al_2O_3 it is not entirely clear what sign the electron affinity has. The results will depend on what the oxide is actually in contact with, as noted later. There are various ways to calculate relative levels for infinite solids, and there are various experimental measurements [19, p. 371]. A comparison of electron affinities is illuminating. Some electrochemical values are Ta_2O_5 3.7 eV (Robertson 3.3 eV), TiO_2 4.3 eV (3.9), ZrO_2 3.3 eV (2.5), HfO_2 2.9 eV (2.5). This shows that Robertson's calculations are rather successful, and that agreement would be even better with a dipole correction of perhaps 0.4 eV. A very incomplete survey of offsets from various sources (including SiO_2 , Al_2O_3 and ZrO_2 [20]) suggests that some of this variation may be associated with the method of preparation or subsequent processing, so that there may be some relatively simple means of control. However, more may be needed.

Whenever one deals with highly *polar* materials, there is an ionic dipole layer which will affect offsets. For example, atoms placed on a surface which transfer some electronic charge to the substrate (like Cs, or like H on diamond) will decrease the electron affinity, even occasionally leading to negative electron affinities. However, space charge, or modified probabilities of different charge states of defects or impurities can also contribute. There can also be an image charge effect, when the dielectric has a dielectric constant significantly different from that of Si. The dipoles can be quite large. Again, there are a very few predictions. For BaO/NiO [21], predicts a 2 eV potential barrier (corresponding to 4 eV for a 2+ ion) stabilising positive charges in the NiO. This suggests that *interface engineering* (such as having at least one

layer of ions of chosen electric charge) might resolve the offset problem, even if this is easier said than done.

One factor in the interfacial dipole is certainly interfacial stress. Most oxides have a relatively poor mismatch with silicon. Basically, there are five main ways to take up the strain. For very thin films, elastic strain may suffice, as in strain-layer systems. For thicker, crystalline films, misfit dislocations are expected. A third possibility is that there is a thin layer of a different phase. Point defects are another possibility. It is known that the P_b centre concentration correlates with interfacial stress [22], and it is plausible that P_b centre creation does relieve the stress to some degree. Topology changes in an amorphous oxide are another way to reduce mismatch stress. One should bear in mind that the dielectric may be in a metastable form. The interface stress will certainly affect the dipole, especially for piezoelectric oxides.

3.4. Characterisation

Given a dielectric, what should one characterise? Average quantities are barely adequate, whether composition, structural features (average crystal structure or pair distribution function for an amorphous system), or even dielectric constant. Key features of performance depend on local properties, e.g., whether there are dislocations or grain boundaries, whether there are significant concentration fluctuations, or whether there are large local electric fields associated with some interface structure. There is potential, at least, to devise good scanning probe microscopy experiments to identify variations in ϵ_0 or potential weak spots. One approach is to use an atomic force microscope to apply a perturbation, taking good care to work in high vacuum to avoid effects from water condensation. This has been done [23]. There are several possible interpretations of the results, but my personal view is that the effect comes from the lowering of defect formation processes because of the mechanical stress. Mechanical stress is not the only option, and localised electric fields are an obvious possibility. Here theory (e.g., [24]) is especially important, both because the results of such a local probe can be counter-intuitive, and

also because theory enables one to *quantify* the experimental analysis.

3.5. Reliability in operation

Reliability in operation primarily involves defect processes. Are new defects created by electron–hole recombination? Is charge redistributed so as to give dielectric loss? Does damage build up in a systematic way, like the development of conducting channels? Is there diffusion which affects composition, or which allows electron traps to be exposed or eliminated? Will the breakdown be soft or hard?

One should not forget that we are seeking a material with both a large band gap (so a large energy is released on electron–hole recombination) and with a high dielectric constant (so formation energies of charged defects will be low), precisely the conditions to make damage in operation likely [7].

Just as most of the high- k materials are ionic, so most of their defects and impurities are charged species. There are rare exceptions, e.g., O_2 interstitials in a-SiO₂, but ions are the norm. In most other cases, ionic diffusion is equivalent to electrolysis. Diffusion, either thermal or driven by applied fields, may lead to charged defects in inconvenient places. Sometimes the ions are associated with mobile carriers, e.g., O^{2-} interstitial ions may bind two holes to compensate, and these holes may be removable in an operating device. A critical question concerns just which charge states are stable. This is a more complicated question that might be evident at first, since the use of simple one-electron (band) diagrams is grossly misleading. The polarisation energies are not handled adequately in many treatments. This is true even for the so-called ‘first-principles’ or ‘a priori’ methods, since there are often crucial working approximations.

Even in simple oxides like MgO, transition metal ions can exist in three or perhaps four different charge states. Since ionisation potentials for the free ions are typically several times bigger than the band gap, and since there is negligible covalency, this is surprising. In fact, the polarisation energies and the Madelung potential are the

large contributions [25]. A further complication is that defects are created in operation only by having localised energy: one can understand the process only by considering the excited states. Typically, energy of the order of the band gap might be available for defect creation [7]. This is often less than defect formation energies in perfect crystalline oxides. Vulnerable regions will be those, perhaps at grain boundaries or dislocations, where energy localisation and modification are easy.

What are the atomic processes? A significant number have been identified in detail, especially for halides. A relevant example is α -quartz, where the self-trapped exciton has been studied in some detail [7, p. 178], with extensive experimental validation of detailed calculations [26]. Following band gap excitation, energy is localised in the form of a self-trapped exciton, in which the oxygen moves very significantly away from its perfect-lattice site. There is a small but finite probability of defect production (oxygen vacancies and interstitials) and of the nucleation of amorphisation [7, p. 232] and [27]. It is probable that similar processes are stimulated in the amorphous gate oxide a-SiO₂, and that these are among the processes which initiate breakdown. What is important about this intrinsic process is that it can be efficient in the use of energy, even if its overall probability is low. For very thin oxides, a breakdown *field* is inappropriate: even 5×10^7 V/cm will give an electron only 10 eV on traversing a 2 nm film. Such an energy can create defects in silica, albeit with low probability. An elastic collision process would have essentially zero probability at such low energies.

Processes efficient at low energies are also possible with interstitial oxygen present, or with hydrogen impurity. One interesting class of processes involves interstitial oxygen, its various charge states, and the molecular and atomic (peroxy-linkage) forms. Some of the processes need electrons only with energy corresponding to the bottom of the silicon conduction band. Whether or not the interstitial oxygen species have a direct role in breakdown is unclear; none has been demonstrated. However, there is the possibility that *tailoring* the interstitial oxygen species during the growth process might eliminate some of the more

vulnerable features in the oxide. For example, discussions of the optical writing of Bragg gratings in silica optical fibres often suggest processes starting from Si–Si bonds (*not* O vacancies, but wrongly coordinated silicons). Or there may be defects in the oxide which evolve from P_b centres at the Si/oxide interface on further oxidation (such defects cannot be eliminated except through reaction with single unpaired spins and a change of coordination). Could the right combination of atomic species be able to eliminate these defect? The answer may be yes [28], in that one has some control over both charge state and atomic/molecular form, especially if one chooses to apply electric fields during growth. The field can bias either electron tunnelling from the silicon, or the motion of negatively charged oxygen species. The time scales for these two processes differ, as do the signs of field, so the phasing and timings of the applied fields must be controlled, as well as their magnitudes.

The basic ideas might prove helpful for other proposed dielectrics, although the processes may differ. For crystalline oxides, dislocations are especially important. Dislocation densities rise rapidly in MgO under electrical stress, for example. Dislocation motion or even growth is assisted by the presence of electron–hole pairs. Such recombination-enhanced phenomena [7, Chapter 7] are seen in very many systems, from III–Vs to UO₂, and are presumably a part of dielectric degradation processes following damage initiation.

Are diffusion-controlled processes sufficiently fast to lead to significant degradation, even if diffusion is entirely thermal? In operation, one might think of a six year lifetime at 300 K. If diffusion is to occur over no more than 2 nm, the diffusion constant must be less than 2×10^{-22} cm²/s. For O diffusion, most oxides *except* clearly non-stoichiometric oxides are satisfactory. CSZ and Y₂O₃ fail; a-SiO₂ may fail marginally (corresponding to diffusion over about 50 nm in 10 years), but the extrapolation to low temperatures is unreliable. The situation is less clear for H diffusion. For some oxides (LiNbO₃, LiTiO₃, TiO₂ [both parallel and normal to the *c*-axis]) D is in excess of the critical value. For other oxides (MgO, MgO:Li, Al₂O₃, Al₂O₃:Mg, BeO) the diffusion rate is less than the critical value.

4. Conclusions: driving forces and the roadmap

The semiconductor roadmap [29] gives the industry view of future trends, possible and desirable. There are obvious challenges, if there is to be continuing, unrestrained, development along these lines. Some of these challenges are noted above. Those relating to silicon dioxide have been assessed by others [1,30,31]. There is a basic question: Are there ways to create a ‘super’ dielectric, compatibility with other materials and with processing? Broadly, there are at least three types of solution. In the first, one starts from a-SiO₂ and adds an ingredient X (possibly nitrogen, possibly La) to give a higher dielectric constant, or one controls the oxide growth so as to eliminate vulnerable features. In the second, one gives a new oxide an acceptable band offset by shifting its band edges by dipole layers to suppress tunnelling. In the third approach, one devises intermediate layers between dielectric and silicon, such that the layers have chosen properties. The fact remains that simply oxidising silicon has many indirect advantages, such as passivation, and that many alternative processes have worrying features.

One could also ask an irreverent question: Is the roadmap right? It presents an evolutionary view. This view has been exceptionally successful. One might say it has made the 20th century the century of the electron, just as the chemical and electrochemical industries made the 19th century the century of the atom. But there are alternative futures. One simple change would be for the single broad trend to give way to modest specialisation. If so, there a choice could be made between speed, smallness and low energy use, and the technical challenges would be more easily met through compromise. Another future might be to rebalance the wireless, fibre and silicon-based technologies in some way, so as to relieve the worst problem areas. But there are other technologies on the horizon, such as quantum computing. It is by no means clear that quantum computers will ever be effective, nor that their materials challenges can be met. Yet we should recognise that there are ways forward, whether this gate dielectric problem is solved or not.

Acknowledgements

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References

- [1] A.I. Kingdon, J.-P. Maria, S.K. Streiffer, *Nature* 406 (2000) 1032.
- [2] J.C. Demmin, *Solid State Technol.* 46, reviewing the 46th IEEE International Electron Devices Meeting (February 2001 issue).
- [3] C.J. Sofield, A.M. Stoneham, *Semicond. Sci. Eng.* 10 (1995) 215.
- [4] K.J. Hubbard, D.C. Schlom, *J. Mater. Res.* 11 (1996) 2757.
- [5] S. Aasland, P.F. McMillan, *Nature* 369 (1994) 633.
- [6] A. Navrotsky, *Diffus. Data* 53&54 (1987) 61.
- [7] N. Itoh, A.M. Stoneham, *Materials Modification by Electronic Excitation*, Cambridge University, 2000.
- [8] M. Szymanski, A.M. Stoneham, A.L. Shluger, *Microelectron. Reliab.* 40 (2000) 567;
A.M. Stoneham, M.A. Szymanski, A.L. Shluger, in: A. Edwards, T. Hattori, H. von Bardeleben, D.A. Buchanan (Eds.), *Dynamics of Silicon Oxidation MRS Symposia Proc* 592, 2000, p. 3;
M. Szymanski, A.M. Stoneham, A.L. Shluger, *Solid State Electrons* 45 (2000) 1233;
M.A. Szymanski, A.L. Shluger, A.M. Stoneham, *Phys. Rev. B* 63 (2001) 224207.
- [9] A.M. Stoneham, A.H. Harker, S.C. Jain, unpublished work, 1993.
- [10] C.R.A. Catlow, A.M. Stoneham, *J. Amer. Ceram. Soc.* 64 (1981) 234.
- [11] D.M. Duffy, A.M. Stoneham, *J. Phys. C* 16 (1983) 4087.
- [12] R. Kita, Y. Matsu, Y. Masuda, S. Yano, *Modern Phys. Lett. B* 13 (1999) 983.
- [13] A.M. Stoneham, L.W. Smith, *J. Phys. Condens. Matter* 3 (1991) 225 (Fig. 2);
W.D. Kingery, H.K. Bowen, D.R. Uhlman, *Introduction to Ceramics*, Wiley, New York, 1976.
- [14] A. Atkinson, 1993 UKAEA Report AEAT-Intec 1429; *Rev. Mod. Phys.* 57 (1985) 437.
- [15] R. Gonzales, private communication;
including data for TiO₂: O.W. Johnson, S.H. Pack, J.W. deFord, *J. Appl. Phys.* 46 (1975) 1026;
J.B. Bates, J.C. Wang, R.A. Perkins, *Phys. Rev. B* 19 (1979) 4130;
a-SiO₂: A.J. Moulson, J.P. Roberts, *Trans. Faraday Soc.* 57 (1961) 1208;
MgO: R. Gonzales, Y. Chen, K.L. Tsang, *Phys. Rev. B* 26 (1982) 4637;
LiNbO₃: R. Gonzales, Y. Chen, K.L. Tsang, G.P. Summers, *Appl. Phys. Lett.* 41 (1982) 739;

- Al₂O₃: H. Engstrom, J.B. Bates, J.C. Wang, M.M. Abraham, *Phys. Rev. B* 21 (1980) 1520;
BeO: J.D. Fowler, D. Chandra, T.S. Elleman, A.W. Payne, K. Verghesse, *J. Am. Ceram. Soc.* 60 (1977) 155.
- [16] J. Robertson, *J. Vac. Sci. Tech. B* 18 (2000) 1785.
- [17] C. Herring, M.H. Nichols, *Rev. Mod. Phys.* 21 (1949) 185.
- [18] J.H. van Vechten, *J. Vac. Sci. Tech. B* 3 (1985) 1240.
- [19] W. Schmickler, J.W. Schultze, *Modern Aspects Electrochem.* 17 (1986) 357 (see especially p. 371).
- [20] V.V. Afanas'ev, M. Houssa, A. Stesmans, M.M. Heyns, *Appl. Phys. Lett.* 78 (2001) 3073;
A. Olbrich, B. Ebersberger, C. Boit, J. Vancea, H. Hoffmann, H. Altmann, G. Gieres, J. Wecker, *Appl. Phys. Lett.* 78 (2001) 2934;
H. Jungblut, H.J. Lewerenz, *Appl. Surf. Sci.* 168 (2000) 194.
- [21] A.M. Stoneham, P.W. Tasker, *Mater. Res. Soc. Symp.* 40 (1984) 291.
- [22] A. Stesmans, *Phys. Rev. Lett.* 70 (1993) 1723;
A. Stesmans, *Phys. Rev. B* 48 (1993) 2410.
- [23] S. Jeffrey, C.J. Sofield, J.B. Pethica, *Appl. Phys. Lett.* 73 (1998) 172.
- [24] L.N. Kantorovich, A.L. Shluger, A.M. Stoneham, *Phys. Rev. Lett.* 85 (2000) 3846.
- [25] A.M. Stoneham, M.J.L. Sangster, *Philos. Mag. B* 43 (1980) 609;
A.M. Stoneham, M.M.D. Ramos, *J. Solid State Chem.* 106 (1993) 2.
- [26] A.J. Fisher, A.M. Stoneham, W. Hayes, *Phys. Rev. Lett.* 64 (1990) 2667;
A.J. Fisher, W. Hayes, A.M. Stoneham, *J. Phys. Condens. Matter* 2 (1990) 6707.
- [27] N. Itoh, A.M. Stoneham, K. Tanimura, in: R. Devine, J.P. Duraud, E. Dooryhée (Eds.), *Structure and Imperfections in Amorphous and Crystalline Silica*, Wiley, 2000, p. 289.
- [28] A.M. Stoneham, M.A. Szymanski, A.L. Shluger, *Silicon Oxidation Phys. Rev. (Rapid Communications) B* 63 (2001) 241304.
- [29] Semiconductor Industry Association, *International Technology Roadmap for Semiconductors, 1999*. Available from <<http://www.itrs.net/nirs/publntns.nsf>>.
- [30] E.Y. Wu, J.H. Stathis, L.-K. Han, *Semicond. Sci. Technol.* 15 (2000) 425.
- [31] M. Hirose et al., *Semicond. Sci. Technol.* 15 (2000) 485.