

CHARGE AND THE UNEXPECTED: SOLID STATE PROCESSES INVOLVING CHARGED SPECIES

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We explore links between performance under electrical stress and the way in which charge is localised in two contrasted systems. Both systems are amorphous. In one case inhomogeneity which plays a role; for the other, it is topology. For silicon dioxide, the gate dielectric of microelectronics, we show that the charge state of the oxidising species (mobile atomic or molecular oxygen) is critical for ultra-thin oxides. The surprises are firstly that the difference between crystalline and amorphous oxides are substantial, and secondly the way that the important charge states should vary systematically through the oxide thickness. We identify ways in which the oxide performance might be improved. For an amorphous polymer, we establish that the mesostructure (spaghetti structure) of the polymer can have significant effects on its performance, both for insulating and conducting polymers. In the case of conducting polymers, the surprise is that modelling shows that, even for "trap-free" cases, electrons can be trapped for times long compared to average transit times because the local configuration of other carriers obstructs the direct routes to the anode. In neither case is a simple continuum space charge description valid. We also present results from self-consistent molecular dynamics which show that electronic excitation can cause local rebonding in ways which appear to resemble the initiation of electrical breakdown.

Introduction

It is clear that electrical breakdown and space charge are closely linked. The nature of that link is far less clear. The maximum stored energy is only 0.5-5meV per atom at breakdown, much less than the 5eV or so needed to cause a typical irreversible change on the atomic scale. There is therefore a need for energy localisation. Associated with energy localisation is charge localisation. Can we give a simple description of the charge localisation? In some systems, such as large single crystals containing both localised charges and localised species with sharp electronic transitions. Measurements of the transition lineshape provide the distribution of local fields, and normally is consistent with randomly-distributed charges, perhaps with modest corrections for close charges [1]. But randomly-distributed charges can only be regarded as a continuous distribution of space charge on averaging over regions larger than typical charge spacings. In the cases we shall discuss, such a continuous charge distribution is unhelpful and misleading.

What are the atomic processes by which irreversible change is achieved? It is not enough to say that there is a large polarisation energy. Just how can that energy might be released so as to cause irreversible change? Energy localisation, essential for breakdown, implies electronically-excited states [2]. We shall give examples where we are able to identify the types of mechanism involved. The identification, whilst preliminary, can suggest ways that breakdown performance might be improved.

Charged species in silicon oxidation and degradation

The amorphous oxide on silicon is a major factor in silicon's dominance of microelectronics: it passivates the Si surface, it can be exploited in processing, and is the outstanding gate dielectric. Yet no means is known to meet the gate dielectric reliability targets in the Semiconductor Industry's Roadmap. Even ultrathin (<5nm) oxides will be required to sustain the few volts typical of modern microelectronics. The failure process has several elements. One is damage initiation by an atomic rearrangement, perhaps triggered by charge capture. It probably involves electron-hole recombination as a means to energy localisation. Existing reliability data suggest random oxide defect creation until a conducting channel of overlapping defects forms [3]. For the thinnest oxides, a single defect might be problematic. In thicker oxides, a series of such events may be needed to create a channel which allows electron transport and further degradation.

What might be done? Squeezing extra performance from silicon's oxide requires going beyond average oxide structures and incremental experiments. One possible way forward is to reduce or eliminate the features at which damage initiates. These vulnerable features are not identified with certainty. A critical defect for stress-induced leakage currents is credibly believed to be the H bridge[4], with H associated with an intrinsic defect. Other critical defects may be those formed from Si/SiO₂ interface defects (like P_b centres) after the oxide has grown past them. Elimination of such unusual sites during the oxide creation would require a deeper understanding of the oxidation process.

Some clues come from the "problem features"[5], including systematic deviations from reaction-diffusion kinetics (the Deal-Grove model). There is layer-by-layer growth on surface oxide terraces, roughness oscillating with oxide thickness, oxygen isotopes usually incorporate only near the Si/SiO₂ interface, and there are effects of electronic excitation and, perhaps more important, of electron injection [6]. In our state-of-the-art electronic structure theory [7] and Monte-Carlo calculations [8] go beyond standard models, we consider atomic and molecular oxidising species, both charged and neutral, in the *amorphous oxide*, and also processes associated with the Si/oxide interface. Our results suggest a new picture of silicon oxidation, arising from the atomic and charged species created by tunnelling near the Si/oxide interface. This picture rationalises the "problem features" and also suggests novel approaches to oxide control and optimisation.

Assume, consistent with our results for a-SiO₂, that charged and atomic interstitial oxygen species can be created in the oxide within an electron tunnelling distance (say 1nm) of the Si/oxide interface. Our Monte-Carlo calculations [8] show *charged* oxidising species explain many of the "problem features" (layer-by-layer growth on terraces, deviations from Deal-Grove for ultra-thin oxides, etc). This is because Si is more polarisable than a-SiO₂, and the polarisation energy biases key steps. These *charged* species will be far less important for thick oxide, where the standard picture holds: diffusion of neutral oxygen molecules is indeed the rate-determining process. Our predictions for O_{2i}⁰ in *amorphous* oxide agree with the observed energy of oxidation. Our results also suggest that isotope incorporation identifies where atomic species are formed. Exchange occurs primarily near the Si/oxide interface (a reactive layer may not be needed), as expected if they are formed by capture of electrons tunnelling from the Si. The observed effects of low-energy electrons, both on kinetics and on causing isotope incorporation throughout the oxide, are in line with our calculations.

Our results [7] show that the molecular species are more stable than the atomic interstitial species, in line with earlier views. Oxygen atoms will form molecules if there are other O with which to react. For a-SiO₂, it costs 3.8eV to incorporate two interstitial atomic oxygens, and 0.4 eV for O₂, so 3.4 eV is needed to dissociate the interstitial molecule. Incorporation of neutral and singly-charged molecular species into a-SiO₂ needs on average 1.7 eV and 0.7 eV less energy respectively to α-quartz. Calculations based on crystalline oxide models (e.g., α-quartz or coesite) give misleading predictions, although differences are smaller for atomic species. Qualitatively, larger interstices give lower energies, providing special sites for solubility. The atomic species (O_i⁰, O_i⁻, O_i²⁻) involve incorporation into the oxide network, implying easy isotope exchange with network oxygens. The structures of molecular species (O_{2i}⁰, O_{2i}⁻, O_{2i}²⁻) make significant isotope exchange unlikely, except at special network sites or substoichiometric regions, such as those proposed near the Si/oxide interface in the reactive-layer model. We predict *exothermic or approximately energy-neutral reactions in which interstitial molecules (relaxed initially) dissociate on electron capture*: O_{2i}⁻ can simply relax to O_{2i}²⁻, but could split into 2O_i⁻; the latter process is less likely, partly because the relaxation energy is less, and partly because the two O_i⁻ ions might recombine.

Charged species tend to be more stable than neutral when electrons are available from the bottom of the bulk Si conduction band. Even for doubly-charged species, spin and charge appear well-localised on the species itself. Incorporation energies fall as negative charge increases: charging could be relatively common, although in cases like O₂⁻ proceed by inelastic tunneling capture. In a-SiO₂, the electron affinity (and hence electron capture probability) varies from site to site. Oxide polarisation is only partially included in supercell calculations, and the terms omitted will favour charged species. Si substrate polarisation further favours localised charges. We expect a significant role for charged interstitial oxygens. Experimental shows effects of bias voltages and of ultralow-energy electrons[6] on oxidation. The effects of such ultra-low energy electrons on breakdown has not been explored, to our knowledge.

Current views on breakdown raise many questions. Are failures defined by the voltage or by the strength and duration of the electric *field*? Why does breakdown depends on the *maximum* (not *average*) electron energy at the anode? These questions could be answered if the creation of key defects (those which initiate breakdown) requires a specific energy. Why does the performance of thin oxide (<5nm) depend on the sign of field? The growth model we describe gives a natural asymmetry between oxide adjacent to Si and the oxide formed adjacent to the oxidising medium. Is there a "time to breakdown", or is the "charge to breakdown" still appropriate?

Reliability requires oxide fine-tuning to eliminate damaging or vulnerable features. Defects like O vacancies will react readily with atomic or molecular oxygen. Other defects (like a Si-Si neighbours) may react directly with O_{2i} only with difficulty, since two oxygens must find suitable sites. Yet a single O_i in an appropriate charge state could render the vulnerable feature harmless. Control of the proportions of atomic and molecular species (whether added ozone or atomic oxygen) offers one route to improvements in reliability. For very thin oxides, control of charge state might be even more important. We suggest using two distinct effects. Making Si the cathode encourages *electron emission*, affecting the proportions of different charge states. Making Si the anode influences *ionic diffusion* and the spatial distribution. These processes have

different timescales. *It is likely that oxide quality can be improved by a sequence of applied electric fields with well-chosen magnitudes, directions and durations.*

At this stage, we do not have a recipe. There is a complex interplay between the several processes. But our identification of features involving both space charge and oxidation processes suggests routes to address the "doomsday scenario" which have not been previously considered. It suggests that it may be possible to suppress some of the species (special sites) responsible for breakdown initiation. Essential ingredients of such an approach are It is especially clear first that the *amorphous* nature must be understood, not just postulated, and secondly that *all the charge states must be calculated properly*. It is not sufficient to calculate a neutral species and guess its trapping properties. Thirdly, we should consider the *excited states* and the route by which damage develops.

Other high dielectric constant ("high-k") materials

The difficulties with ultrathin SiO₂ have instigated a widespread search for alternative oxides. There are formidable demands, several associated with space charge: (i) It must be an insulator, with a wide gap of say 5-6eV; (ii) The band offsets with Si must be sufficient [] unless one can achieve a suitable dipole layer; (iii) The dielectric constant must be large, ideally 12-30 to fit to other constraints (both microelectronic design and the issue of non-linearities for ferroelectrics). For non-polar solids, this would mean a *low* gap. The main polarisation will be *ionic* (which could include the effects of reorientable fixed dipoles, including H₂O etc). In such cases (usually oxides), easy defect formation or non-stoichiometry are often encountered. (iv) No interface layer should form at contacts (e.g., SiO₂ adjacent to Si) since this would reduce the effective dielectric constant. (v) If the oxide is amorphous, it must remain amorphous at processing temperatures. More generally, the dielectric must be stable for typically 15s at 1050°C; (vi) The oxide must be *homogeneous* and hence stoichiometric and free from alloy fluctuations should not matter; (vii) The interfaces should be sufficiently stress-free to avoid defect creation, especially of dislocations; interface roughness should be unimportant. As regards these structural and electronic aspects, are amorphous or crystalline forms to be preferred? In favour of amorphous dielectrics are the absence of dislocations or grain boundaries, the fact that stress can be taken up topologically, and the way that a continuous random network tends to minimise electrically-active defects. However, there are likely to be shallow traps, and fluctuations in thickness and density.

The other electrical properties must be adequate: (i) There must be a low leakage current; (ii) There should be low effective fixed charge, to avoid interfering with carrier mobility in the adjacent Si (this will be hard to achieve with non-stoichiometric systems or when there are dislocations); (iii) There should be minimal "resistive degradation", such as from O vacancy motion; (iv) Dielectric loss should be such as to correspond to a loss tangents of order 0.005 on times of order nanoseconds.

It is far from clear that a satisfactory replacement for a-SiO₂ has been identified.

Polymer Mesostructure and the Meaning of Trapping

There are parallels between breakdown in silicon dioxide and that in polymer insulators. In both cases, the insulator is amorphous, and the non-crystallinity is

significant. The simplest continuum pictures of behaviour mislead. In both cases, charge localisation and energy localisation appear important, involving specific excited or charged states. For the polymers, however, effective trapping can occur for reasons which are arguably non-intuitive [9]: we find relatively common situations of transient charge trapping, when the nearest "mobile" charges block the natural progress of a charge from one electrode to the other. This has a significant effect on radiative and non-radiative recombination and on current inefficiency in organic light-emitting diodes. We believe there should be a similar effect for insulating polymers. Thirdly, the defect species in dielectric breakdown of SiO_2 are closely related to those formed in radiation damage. The same seems true of organic insulators: excited polymer molecules depend on their molecular structure in ways which are strikingly similar for both radiation damage and electrical stress (e.g., gas emissions and associated spectra, cross-linking versus degradation) [2, page 295; 10, 11]

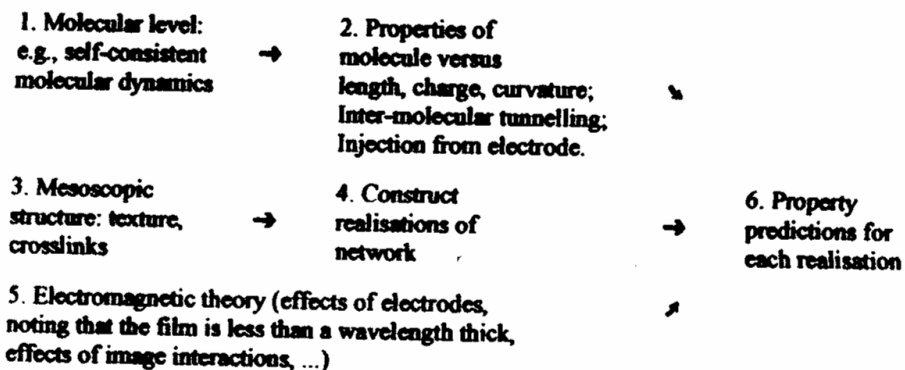
For crystalline semiconductors, optical properties are controlled by band-gap engineering. Many devices can be described successfully in terms of continuum properties such as carrier density and mobility. For amorphous semiconductors, like a-Si:H, properties depend both on composition and preparation. Transport can involve variable range hopping. Space charge, described by the Poisson equation, is important for both crystalline and amorphous cases, but a continuum charge density suffices. Topology on the atomic scale does not enter explicitly.

The situation for organic semiconductors is quite different. Typical polymers comprise of molecular strands of varied lengths, cross-linking, texture and overall density. The individual molecular strands determine some features, e.g., intra-molecular mobility; band edge positions; relative importance of radiative and non-radiative recombination. Connectivity and texture (the "spaghetti structure" as well as inclusions or voids) influence macroscopic mobility, and propensity to charge trapping; this is confirmed by experiment. Factors depending on both molecular structure and texture include carrier injection and molecule-molecule electron transfer.

For polymeric insulators, we expect analogous dependences on the molecular species and on the polymer texture. Once again, trapping can be subtle. Even in a polymer consisting of one molecular species and molecules with a single molecular weight, there will be traps associated with the texture. Many insulating polymers have negative electron affinity, i.e., added electrons have lower energy when between molecules, rather than on them, so that *the spaces between molecular strands* are significant. There is the potential to improve the performance of polymers by modifying the texture, whether for insulation or for semiconducting behaviour.

There are therefore several challenges factors which are interdependent. The first challenge is at the molecular level: how can one identify and model a molecule with the right electronic properties? One way is to use self-consistent molecular dynamics [12] and corresponding treatments of metal-organic interfaces. The second challenge concerns the identification of an acceptable production process. The third challenge concerns texture: how best can the ensemble of polymer molecules be organised to optimise performance for some application? This challenge [9] is the focus of our attention. For conducting polymers, there are compromises between trapping, transport across the film, radiative recombination, and non-radiative recombination, and are not always intuitive. Fourthly, there is an engineering design challenge: how to optimise the use of

macroscopic units (films, blobs, wires) in some application, including recognising the effects of electrodes on electro-magnetic behaviour of a film only a fraction of an optical wavelength thick.



For semiconducting polymers, the *total* applied field on each carrier is a critical factor in charge evolution after injection. This is the sum of the externally-applied external field, the field of other charges in transit or trapped within the polymer network, and the field due to electrode polarization. All charges must be treated *explicitly*, avoiding a continuum space-charge description which would be a spatially-averaged version of our more general approach.

We adopt a simple description of the charge distribution on an individual chain. Our results work entirely in *timesteps*, rather than real time. A timestep of order 10 ps ensures that all the physically-relevant times are reasonable. We assume rapid intrachain motion and sluggish interchain motion, typical of many conducting polymer systems. Soliton velocities along a chain might be of the order of the sound velocity (say 10^3 m/s), so that motion along a chain of 10 nm would take of order 10^{-11} s. Interchain hopping might be expected to have a rate of the form (some overlap factor) \times (jump rate of order 10^{13} s $^{-1}$) $\exp(-\epsilon/kT)$; for ϵ of 0.25 eV, the second factor would correspond to an interchain hopping time of order 10^{-9} s, or even longer if the overlap factor is small. Carrier arrival times, in line with other predictions, show a rapid rise as the first carriers cross the film, a maximum at the most probably arrival time, and tail in the distribution from those carriers which took long routes or were trapped transiently.

The transfer of carriers between chains is crucial, since the organic film thickness is typically tens or hundreds of molecular lengths. The main point is to select the most probable jump for a carrier. Close proximity and maximal field assistance are crucial. No two carriers of the same sign are allowed on a chain, in line with our electronic structure calculations. It is straightforward to generalise our approach to include the more complex effects of the electric field on jump- and recombination probabilities.

We find that *the carrier can be effectively trapped on a chain, even when the chain has the same electron affinity as the other chains*. Such a trapped charge still contributes to the space charge. We define a carrier as effectively trapped if (a) the total electrical field on the charge is zero, (b) the carrier meets a cross-link and also the electric field is less than a certain critical value, or (c) the jump probability per timestep to a neighbouring chain (w) is less than 10^{-3} . The timesteps are of order 10^{-11} s, so this value of

w corresponds to a rate of less than one thousandth of the typical interchain hopping rate at room temperature, i.e., a "trapped" carrier would remain localised for more than 1000 timesteps. Since almost all carriers traverse the polymer from one electrode to the other in a few tens of timesteps, the charge is indeed properly trapped as regards its influence on conduction. Whether it is trapped well enough to permit standard measurements of space charge is less clear. Clearly, a particular carrier may be trapped at one time and not trapped after some other charges have moved and the electric field has changed, or carriers have moved away from those strands adjacent to the trapped carrier.

Our model *shows trapping even when there are no impurities or structural defects (as normally defined)*. Trapping occurs because of interplay between the topology (linkage) of the polymer structure and the effect of the total *local* field. Similar results probably hold for insulating polymers. This type of transient space charge does not exist in a homogeneous, defect-free, crystalline semiconductor. For polymeric semiconductors, one should not use some of the analogies with standard semiconductors such as Si. Another difference is expected in the effects of pressure. In some pictures of damage initiation, electrons are accelerated within a microscopic cavity. The effect of pressure is likely to close up any such cavities, and inhibit breakdown initiation to some extent. This is seen (e.g., [13]). However, for the gate dielectric SiO₂, localised stress has the opposite effect [14]. For the gate oxide, the role of stress is probably to alter defect formation energies; rough calculations (A.M.Stoneham 1998, unpublished) suggest this has the right order of magnitude.

Atomic Processes of Breakdown Initiation

Which are the processes that initiate electrical breakdown? Surely enough is known about the electronic structure of polymers and about their physics and chemistry on the atomic scale to be precise? Understanding such processes opens the possibility of molecular design to reduce breakdown initiation. One approach to identify these processes might be this. We know that there must be *energy localisation* on a small number of polymer strands (probably one or two only), since energy is needed very locally to achieve irreversible atomic processes like scission or cross-linking. We know, from parallels with a very large number of systems, that there are often electronic excited states which decay by non-radiative processes that cause atomic displacements or rebonding. So let us use self-consistent molecular dynamics, in which the atoms of some simple polymer strands move under the forces which we calculate from their electronic structure at each timestep. The system we study should start in an electronic *excited* state. The excited electrons will be in non-equilibrium states. However, the equilibrium rate-theory and thermodynamic arguments used by many workers can still be applied to the atomic motions, with appropriate generalisations (see [2] Chapter 7). In the excited state, in our calculations, the atoms are driven by the self-consistent chemical forces. The polymer strands evolve with time, and may simply vibrate, or twist and turn. They may even rebond or break up in ways which we did not anticipate. If the strands do indeed rebond, or break up, this may be the initiation step in breakdown.

Our initial results do indeed show unexpected molecular degradation behaviour. This appears to be a mechanism for breakdown initiation in polymers. The implications are these. First, excited states of insulating organics can transform by scission or

rebonding, analogous to many inorganic systems. Such processes compete with those which merely emit heat and light. There is no need to assume electrons with energies large enough to cause knock-on. Nor need one continue to talk about unidentified processes, since the approach could be generalised to other, more significant, systems. Our results suggest checks of the mechanism through the observed light emission. This emission may be by *product* species, created in an excited state. Most important of all, the identification of a *specific* route by which relatively low-energy excited electrons could produce damage opens the possibility of *improving insulation by molecular design*.

We remark that a damage process initiated by electronic excitation should resemble that in radiation damage, especially electron damage below the threshold for knock-on. There are observed similarities in the nature of product species [15], in the topography of the polymer [11,12] and in the efficient use of energy [2]. One can understand these similarities if low energy electrons in radiation damage cause *electronic* excitation to the same states as in breakdown.

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