



The different roles of charged and neutral atomic and molecular oxidising species in silicon oxidation from ab initio calculations

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Abstract

We examine the roles of charged and neutral oxidising species based on extensive ab initio DFT calculations. Six species are considered: interstitial atomic O, O⁻, O²⁻ and molecular species: O₂, O₂⁻, O₂²⁻. We calculate their incorporation energies into bulk silicon dioxide, vertical electron affinities and diffusion barriers. In our calculations, we assume that the electrons responsible for the change of charge state come from the silicon conduction band, however the generalisation to any other source of electrons is possible and hence our results are also relevant to electron-beam assisted and plasma oxidation. The calculations yield information about the relative stability of oxidising species, and the possible transformations between them and their charging patterns. We discuss the ability to exchange O atoms between the mobile species and the host lattice during diffusion, since this determines whether or not isotope exchange is expected. Our results show very clear trends: (1) *molecular species* are energetically preferable over *atomic* ones, (2) *charged species* are energetically more favourable than *neutral* ones, (3) diffusion of *atomic species* (O, O⁻, O²⁻) will result in oxygen exchange, whereas the diffusion of *molecular species* (O₂, O₂⁻, O₂²⁻) is not likely to lead to significant exchange with the lattice.

Our results show thermodynamic trends for oxidising species to capture electrons from Si during oxidation. We identify very different roles for atomic and molecular species and also for different charge states of those species. This points out to opportunities, usually not considered, for optimising thin oxide layers and interface properties for use in electronics devices. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

From the beginning of silicon technology there has been pressure to scale down the size of devices. This has led to requirement for growing high quality silicon dioxide with a very low concentration of intrinsic defects, which implies a need for better control and under-

standing of molecular processes during silicon oxidation. This work addresses question of character and roles of oxidising species and charging processes relevant to ultra-thin oxide layers.

Modern gate-dielectrics approach a thickness of a few nm, for which the deviations from classical linear-parabolic (Deal–Grove) theory [1] of oxidation are significant. Thermal oxidation at lower temperatures and lower pressures [2], electron-beam assisted oxidation [3], as well as plasma oxidation [4] cannot be described within linear-parabolic regime. One idea has been that charged oxidising species lead to different kinetics due to

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the electrostatic field within the oxide layer and image forces arising from difference in the dielectric constant of silicon and silicon dioxide. The effects of image forces were examined by Stoneham and Tasker [5] and the electric field within oxide and ionic conductivity in this field were the basis for power-parabolic ionic oxidation model [6].

The role of charged species in silicon oxidation has been stressed previously several times. Early stopping field experiments [7] have shown that oxidation can be enhanced, retarded or even stopped by applying bias voltage across the sample. More recent experiments [8,9] suggested ionic contribution to the transport processes in SiO_2 . The kinetics of the oxidation process has been shown to be strongly affected by the presence of a low energy electron-beam, and an anomalous temperature dependence has been observed for oxides less than 2 nm thick [3]. The initial oxidation at low temperatures has been shown to be enhanced by electron impact with the possible dissociation of adsorbed O_2 molecules to form O and O^- species [10]. Plasma oxidation kinetics was observed to follow trends expected for ionic species [4]. Cw-UV induced oxidation was shown to be consistent with model based on photoinjection of electrons from Si resulting in ionic species [11]. Oxygen absorption on SiO_2 surface has been reported to result in O_2^- species [12]. Also other phenomena like telegraph noise [13] and fixed oxide charge point to charge transfer processes as possible causes.

2. Atomic-scale processes in silicon oxidation and basic models

It is generally believed that diffusion of oxidising species and interfacial processes are the main factors controlling oxidation rate. Fig. 1 shows the main oxidation processes on the example of oxygen molecule being the oxidising species. The species sticks to the surface from the gas phase, incorporates into the silica lattice, diffuses toward Si/ SiO_2 interface and reacts with silicon. This is the underlying picture of the most classical model of silicon oxidation – the Deal–Grove model. This model, however, cannot account for proper kinetics of silicon oxidation for low temperature and pressures or for thin oxides [2]. Plasma or electron-beam assisted oxidation are totally beyond the scope of Deal–Grove model. This simple picture of oxidation can be complicated by adding other intermediate stages.

- The oxidising species could react with the silica network exchanging oxygen atoms. This however is in disagreement with isotope exchange experiments [14] which show that oxygen exchange takes place only close to the two interfaces.
- Defects could be generated to accommodate the lattice mismatch at the Si/ SiO_2 interface (the volume per Si atom in silica is twice that in c-Si).
- There can be many different kinds of charge transfer processes involved. For example, electrons can

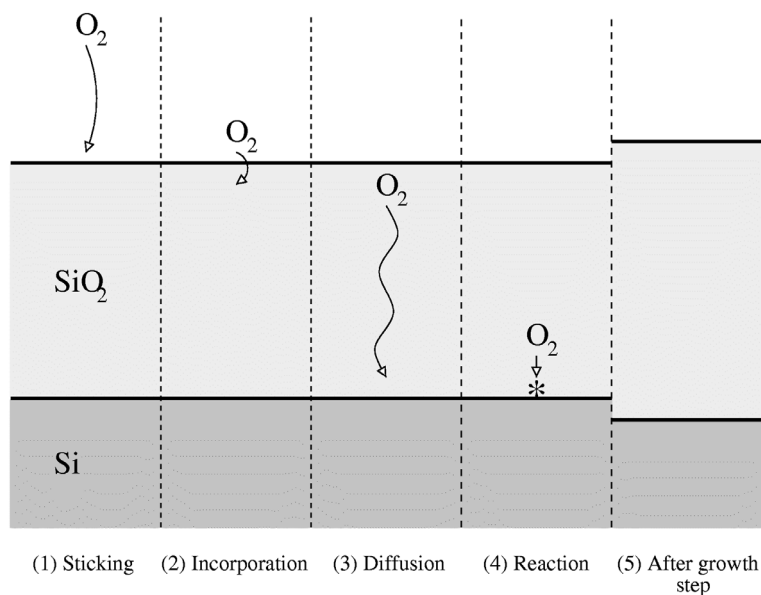


Fig. 1. The main oxidation steps on a example of neutral oxygen molecule being the oxidising species. Adsorption from the gas phase (1), followed by incorporation into bulk SiO_2 (2), diffusion towards Si (3), and the reaction at the Si/ SiO_2 interface (4), resulting in expansion of the volume of silica (5).

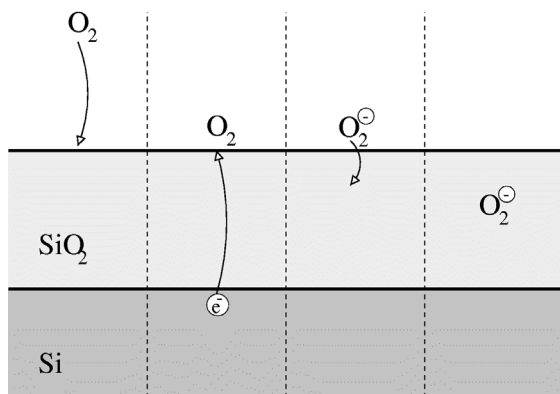


Fig. 2. Electron transfer to species adsorbed at the ambient/silica interface. This process is likely for initial stages of oxidation for which direct tunnelling can be efficient.

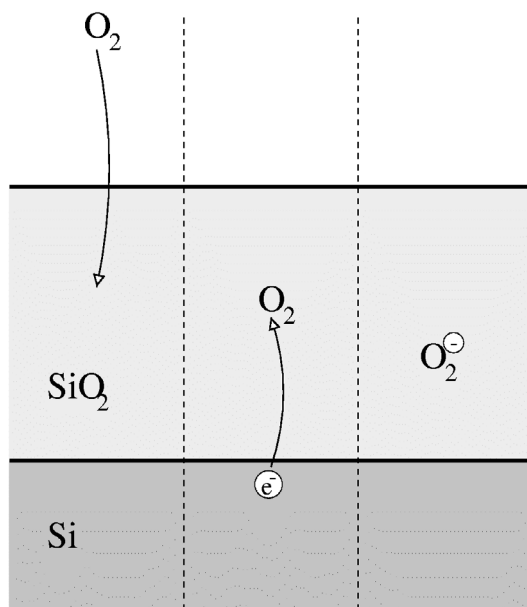


Fig. 3. Electron transfer from Si to oxidising species already incorporated into bulk SiO₂. This process can be important for species within electron tunnelling range from Si.

be transferred from Si to oxidising species which are either adsorbed at the ambient/silica interface or already incorporated in the bulk SiO₂. Those two processes are shown schematically at Figs. 2 and 3. The former is more likely to happen for thin oxide layers for which a direct tunnelling from Si is possible, the latter could happen within tunnelling range from the Si/SiO₂ interface.

3. Techniques

Our calculations use spin-polarised version of density functional theory (DFT) with the Perdew–Wang functional and the generalised gradient approximation (GGA) [15,16] implemented within VASP code [17,18]. The Kohn–Sham orbitals were expanded in plane-wave basis set with a cutoff energy of 400 eV. Oxygen atoms were represented by ‘ultra-soft’ pseudopotentials, and silicon atoms by norm-conserving ones. Our reference structure is 72-atom fully relaxed hexagonal periodic unit cell of α -quartz. For other calculations, the lattice vectors were fixed and all atoms were allowed to relax. Defects are separated by more than 10 Å. The Brillouin zone integration includes the Γ -point only. We use a neutralising background for charged unit cells, with the Makov–Payne monopole–monopole energy correction [19]. This procedure and our large unit cell minimised the influence of the periodic images of the defects, and thus ensures that our results provide good models of isolated defects in a non-defective host lattice.

The geometry relaxation used conjugate gradient (CG) energy minimisation, with two search methods for the transition state. The ascending and descending valley points method combined with CG energy minimisation gave two estimates of the transition state position on both sides of the saddle point. The join of those two points was then assumed to be a good approximation to the direction of the transition state and the system geometry was driven towards the saddle point by reversing the force along this direction and using a semi-Newtonian relaxation algorithm. The transition states found are configurations of maximum energy along the lowest energy path joining two energy minima on the many dimensional energy surface. All relaxation procedures were terminated when forces on atoms were smaller than 0.05 eV/Å.

The analysis of charged species energies in a periodic model is complicated. A neutralising background is needed to converge Ewald summations. This introduces errors into the total energy expression which can be handled in first order by the Makov–Payne monopole–monopole energy correction, which improves the convergence of the total energy with respect to the size of the unit cell. In our calculation, when an electron was added or removed from the system, the electron came from or went to the zero energy level on the eigenvalue scale. This zero energy level is not normally the experimental vacuum level for bulk calculations, since there is no surface which would determine the position of band levels with respect to the vacuum level. Also, the Ewald sum is defined up to a constant which can affect the position of zero energy. However, in our VASP calculation zero energy is a good reference level since it stays in the same position with respect to the SiO₂ valence band regardless of the type of species and its charge

state. This in turn means that all results with energy converged with respect to the size of the unit cell correspond to an isolated point defect in an infinite non-defective crystal. The charging electrons are assumed to come from the bottom of silicon conduction band at the Si/SiO₂ interface. We can use the experimental information on the band offset at the interface [20,21] (4.6 eV for Si/SiO₂ valence band offset, 1.1 eV for band gap of Si) and the position of the top of valence band of SiO₂ in our calculations to estimate the energy of an electron E_{el} at the bottom of the conduction band of Si with respect to the theoretical zero energy level [22]; it is easy to adjust energies for another source of electrons.

The only meaningful comparisons are of energies between systems with the same number of electrons. The incorporation energies are calculated for lowest energy configuration of the system with respect to the non-defective quartz structure and an isolated oxygen molecule:

$$E_{inc} = E_{system} - (E_{quartz} + fE_{O_2} + nE_{el})$$

where $f = 1$ for molecular oxygen incorporation and $f = 0.5$ for incorporation of atomic species; n is the number of excess electrons. The vertical electron affinities are calculated by adding an electron to the lowest energy configuration of the system and looking at the energy change without allowing for any further relaxation:

$$E_{aff} = -E_{charged,unrelaxed} + (E_{system} + E_{el})$$

We should note that our model is approximate. In particular, we neglect the band bending, image interactions and electric field build-up due to redistribution of charge associated with charging of oxidising species. However, we use the experimental information about the band offset at the interface which should account partly for those effects. The supercell calculation does not include all of the long-range polarisation effects

which means that full treatment of polarisation would favour the charged species even more.

4. Results for oxidising species in quartz

We have calculated properties of six oxidising species in alpha-quartz which we regarded in first approximation as an acceptable mimic of amorphous silica. The typical relaxed geometries of the species are shown in Figs. 4 and 5. Our results are summarised in Table 1, in which a positive value of incorporation energy means that this energy has to be supplied to the system in order to incorporate the species into the lattice. The diffusion barrier gives the lowest possible energy barrier which a species encounters during diffusion from one energy minimum to another. We quote the diffusion barriers calculated along the c axis of alpha-quartz; diffusion barriers along other directions were calculated only for some species. A positive value of the vertical electron affinity means that the species can capture an electron from the bottom of Si conduction band by resonant tunnelling. This value is calculated for the lowest energy configuration of the species. Some important conclusions can be drawn on the basis of our results:

- *Molecular species* are energetically more favourable than *atomic species*, in line with earlier views on oxidation. For example, the incorporation energy of two interstitial atomic oxygens is 4.1 eV whereas incorporation energy of oxygen molecule is 2.1 eV, which means that dissociation of interstitial oxygen molecule into two atomic species requires 2.0 eV of energy and that atomic oxygens react exothermically to form molecules. However, interstitial atomic oxygen once incorporated into lattice may never encounter another oxygen to react with (given the low oxygen solubility in silica). As a consequence, for instance, it can be expected that plasma

Table 1

Key energies for different species in α -quartz. Extra electrons are assumed to be taken from the bottom of the Si conduction band^a

Species	Incorporation energy (eV)	Diffusion barrier along c (eV)	Diffusion barrier other axes (eV)	Electron affinity (eV)	Exchange with lattice
O ₂	2.07	0.09		0.7	No
O ₂ ⁻	-0.5	0.57		-0.2	No
O ₂ ²⁻	-1.9	2.1		No affinity	No
O	2.03	1.30	1.42	-0.5	Yes
O ⁻	-0.7	0.19	0.60	-0.3	Yes
O ²⁻	-2.8	0.19		No affinity	Yes

^a Positive incorporation energy means that energy must be supplied to incorporate the species from the gas phase. A positive vertical (constant atomic positions) electron affinity means exothermic capture of an electron from the bottom of the bulk Si conduction band. For all quoted species the charge and spin densities are localised on the species with the exception of neutral O and doubly bounded O⁻ for which the interstitial and lattice oxygens are in the same charge state (which implies some charge transfer from the lattice to the interstitial oxygen). Therefore, those two species should be thought as complexes. The third excess electron cannot be localised on the species and hence the double negative species do not exhibit any electron affinity.

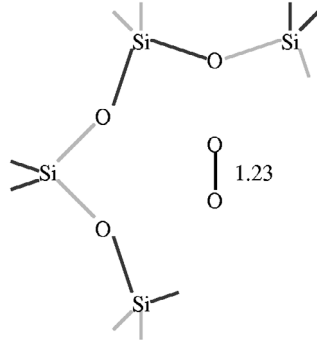
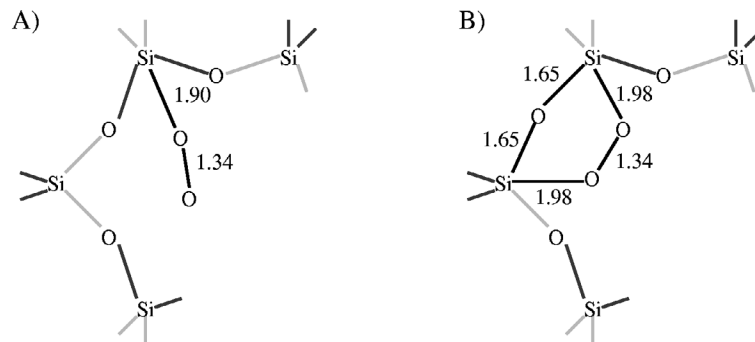
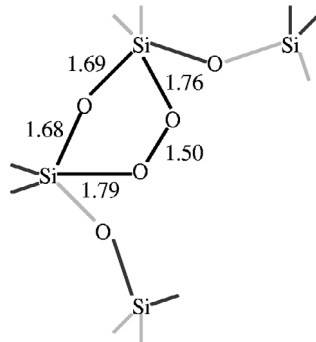
Interstitial oxygen moleculeNegative interstitial oxygen moleculeDouble negative interstitial oxygen molecule

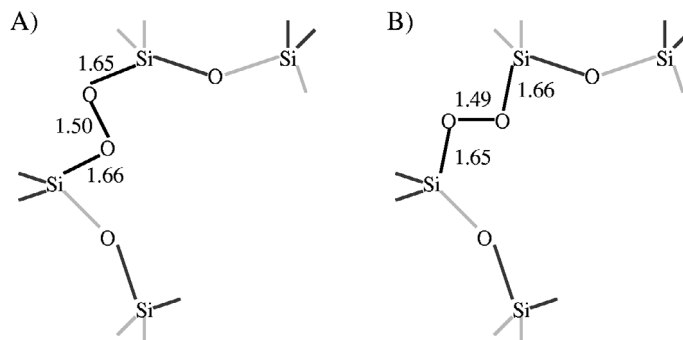
Fig. 4. Structures of molecular oxygen species in quartz.

oxidation happens mainly due to diffusion of atomic species (possibly in negative charge state). As long as the comparison of atomic and molecular species is done for systems with the same amount of excess charge and number of oxygens the conclusions are general and do not depend on the position of the electron source in our system.

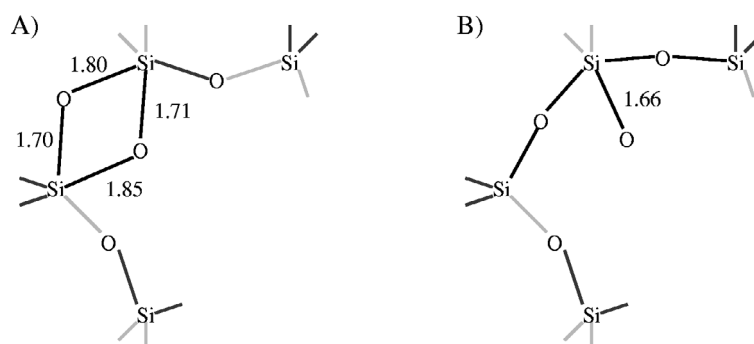
- *Charged species* are energetically more favourable than the *neutral species* (with assumption that electrons

are available at the bottom of the conduction band or above). The incorporation energy decreases with the increasing negative charge state (compare the incorporation energies in Table 1). Polarisation of silica is only partially included in supercell calculations and the part missing will favour charged species even more. Charging should happen if there is an efficient way of transferring an electron from Si to the species incorporated in silica, for instance if the species stays within an electron

Interstitial atomic oxygen



Negative interstitial ionic oxygen



Double negative interstitial atomic oxygen

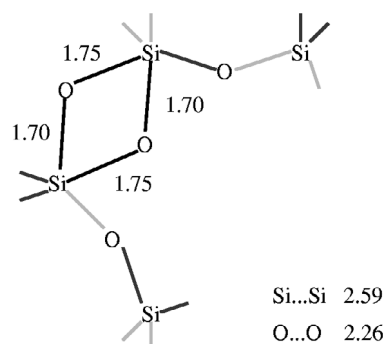


Fig. 5. Structures of atomic oxygen species in quartz.

tunnelling distance from Si for sufficient time. The electron affinities give the energy gain after species in its lowest energy configuration captures an electron from the bottom of Si conduction band without relaxation. During diffusion the species will sample a number of other higher energy configurations for which the electron capture may be more or less likely and therefore electron affinities quoted in Table 1 should be regarded only as rough estimates. Although it is energetically

preferable to have negative charge localised on oxidising species rather than in form of conduction electrons in Si, in some cases it may require inelastic tunnelling [23] to transfer the electron, as indicated by negative vertical electron affinities.

- The mechanism of diffusion of atomic species will lead inevitably to oxygen exchange with the lattice whereas diffusion of molecular species cannot easily lead to oxygen exchange with non-defective SiO₂ lattice (as

discussed in Ref. [24]). It is likely that the high barrier for motion of O_2^- will prevent the diffusion of its molecular form and the dissociation into two O^- seems to be a strong possibility (although we did not calculate the energy barrier for this process).

- Capturing an electron the molecular species can either relax in molecular form or dissociate into two atomic species in appropriate charge states. The former process is always more likely from thermal equilibrium point of view. It does not eliminate, however, the possibility of dissociation. Isotope exchange experiments during dry oxidation [14] show significant exchange only close to both interfaces. This exchange can be due to creation and motion of atomic species; in particular, near the Si/SiO₂ interface due to electron transfer from Si to oxidising species with some of them dissociating into atomic ones. If so, there may be no need for so called “reactive layer” near the Si/oxide boundary. The different properties of this layer could be explained by charging which changes the character of the oxidising species and dissociation of some of them after electron capture.

5. Oxidising species in amorphous SiO₂

Mott [25] pointed out that oxygen solubility data for silica can be only understood if there is small number favoured energy sites. This is obviously not so in quartz. The experimentally observed activation energy for oxidation (oxygen incorporation energy plus diffusion energy) is 1.2 eV. The calculated activation energy for oxidation by neutral O₂ in quartz is 2.2 eV. This suggests that crystalline SiO₂ could be a poor mimic of silica for some of the species. Our preliminary results for amorphous structures [26] show that we can expect significantly different results only in case of O₂ and O₂⁻; incorporation energies and electron affinities for other species are generally similar. For O₂ the average incorporation energy at three different interstitial sites in an amorphous sample is 0.4 eV (2.1 eV for quartz), for O₂⁻ 1.2 eV (-0.5 eV for quartz). There is also a relatively small number of low energy sites for the neutral interstitial oxygen molecule, in agreement with Mott’s prediction. As it can be seen from Fig. 4 the interstitial site for O₂ is in the middle of a void. Our calculations in amorphous sample show that the bigger the void in which oxygen molecule is placed, the lower the incorporation energy. The amorphous structure offers a number of much bigger voids than quartz and hence the incorporation energy is much lower. The diffusion barrier on the other hand will depend on the size of ring through which the molecule travels. The smaller the ring the bigger the barrier. From this perspective, diffusion of O₂ along the *c* channel of quartz is like a travel through

a tunnel of fixed diameter and hence the very low diffusion barrier. The diffusion in amorphous silica will involve hops between relatively big voids through narrower rings. Therefore we can expect diffusion barriers to be higher than in the case of quartz. If diffusion barriers are of order 0.8 eV, we get an excellent agreement with experimental activation energy for oxidation. Clearly, appropriate description of molecular species in amorphous silica requires some level of static disorder. However, despite the differences for the molecular species in quartz and amorphous structures all conclusions from previous section hold also for oxygen species of amorphous silica.

6. Roles of atomic and molecular species in oxidation and the consequences of charging

The two types of species: atomic and molecular may have very different roles in the oxidation processes (their incorporation energies and diffusion patterns are different). They may react with different sites at the interface and lattice defects. This may affect both the final oxide structure as well as the number of interfacial and bulk defects and, as a result, the breakdown reliability. Experiments show different properties (density and distribution of Si atoms) of the near-interfacial region for oxidation in dry O₂ and ozone [27]. It can be expected that ozone provides atomic oxygens during oxidation and hence changes ratio of atomic to molecular species arriving to the interface, which supports our predictions.

Charging of the oxidising species may have important consequences for the structure of the oxide and the Si/SiO₂ interface. The fact that incorporation energies and diffusion mechanisms differ for different charge states is likely to affect the reactivity of the species and change the potential reaction sites. Electron transfer will build up an electric field in silica and this field, in turn, will influence the spatial distribution and diffusion of charged species. A localised charge will also induce polarisation of Si which will result in an attractive force on the oxidising species towards Si. Applying a bias voltage across the sample can promote or prevent drift of the charged species and their redistribution resulting in different ratio of different charge species arriving to the Si/SiO₂ interface. The role of charged species identified here is different from suggested by other authors.

What we have shown is that different oxidising species have a variety of behaviours which can be exploited during silicon oxidation for optimisation of oxide quality and its properties. We point out to opportunities usually not considered. There are, however, strong interplays between different processes and we cannot offer any ready recipe. More understanding is needed concerning the role of disorder and we are currently

finishing a full study of oxidising species in amorphous oxides.

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