Proof of the thermodynamical stability of the E' center in SiO₂

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The E' center is a paradigmatic radiation-induced defect in SiO₂ whose peculiar EPR and hyperfine activity has been known since over 40 years. This center has been traditionally identified with a distorted, positively-charged oxygen vacancy V‴O. However, no direct proof of the stability of this defect has ever been provided, so that its identification is still strongly incomplete. Here we prove directly that distorted V‴O is metastable and that it satisfies the key requirements for its identification as E', such as thermal and optical response, and activation-deactivation mechanisms.

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Understanding defects in solids is a key factor in improving device performance and materials quality. Defect identification combines experimental observation and theoretical predictions, and a major ingredient in this process is the theoretical justification of the thermodynamical stability of the defect. If this information is missing, the identification is arguably incomplete or uncertain. Surprisingly, this is the case for the E' center [1,2], a radiation-induced defect first observed experimentally as early as 45 years ago [1] in SiO₂, a material of prime current importance in microelectronics and fiber optics [3]. E' is traditionally identified with a positively-charged distorted oxygen vacancy V‴O, with important support from calculations of hyperfine couplings [4] and optical activity [5]; its thermodynamical stability, however, was never theoretically proven, and the mechanisms involved in its activation and deactivation are still debated. Here, using the ab initio theory of defect formation in solids [6], we show that the conditions for E' stability are naturally realized in stoichiometric or neutron-irradiated SiO₂, and conclusively put on firm ground the identification of the E' center.

Our model of the stability of E' is based on two native defects: the oxygen vacancy V‴O and the oxygen interstitial O‴. The motivation is that E' is observed chiefly (though not only) in neutron-irradiated material [1,3], where V‴O and O‴ are both abundant. Indeed, we find that it is their concurrent presence that produces the conditions for the existence of E', in neutron-irradiated as well as non-neutron-irradiated material. In the former, vacancies V‴O and interstitials O‴ are essentially produced in pairs by knock-on, kick-out events; in the latter, they form in thermal equilibrium and, as it turns out, in similar concentrations. As will become apparent below, our argument on E' applies to both cases without modifications, except for the fact that neutron-produced defects appear in concentrations determined by the irradiation dose, whereas the concentration of thermally formed defects depends on formation energies, which can be directly predicted.

At a growth temperature Tg and with Ns available sites, the equilibrium concentration of a defect is D= Ns exp(−Fform/kBTg). The formation free energy Fform = Eform − T Sform depends on the chemical potentials of atoms added or removed, on the defect charge state, i.e. the charge released to or captured from the thermodynamic reservoir constituted by the surrounding crystal, and on the electronic chemical potential μe of the latter. Once the formation energies of the all relevant defects (vacancy and interstitial in our case) are known, the defect concentrations and the chemical potential μe are determined self-consistently, subject to charge neutrality, as detailed in [6]. A specific defect configuration or charge state is predicted to exist if its formation energy is lower than that of all other defect states for some value of μe. Also, the defect is metastable if a non-zero energetic barrier prevents its deactivation or disappearance into other lower-energy configurations of the same defect, or recombination with other defects. The formation energy for our defects in charge state Q reads

\[
E_{\text{form}}(Q) = E_{\text{tot}}^{\text{def}}(Q) - E_{\text{tot}}^{\text{undef}} + Q\mu_e + M(Q) + P
\]

where E_{\text{tot}}^{\text{def}} and E_{\text{tot}}^{\text{undef}} are the total energies of the defected and undefected system, respectively, μe is the electron chemical potential (equaling the Fermi level E_F in our T=0 calculations), M(Q) is the defect-dependent multipole correction for charge state Q of Ref. [6], P = μO for V‴O and P = −μO for O‴, and μO is the oxygen chemical potential. The latter is fixed to stoichiometric conditions, i.e. at the center of its variation range μmol/2 + ΔH/2 < μO < μmol/2 determined by the total energy μmol of the O₂ molecule, and the calculated formation enthalpy ΔH of SiO₂. Ionization energies, i.e. the energy needed to promote (say) an electron from the valence band to an empty acceptor level, are defined via total energy differences of different charge states. Formation entropies are beyond the scope of the method used here; plausible estimates are used when needed.

Energies and forces are accurately calculated from first-principles within density-functional theory in the local approximation, using the ultrasoft pseudopotential plane-wave method as implemented in VASP [7]. An iso-
lated defect is simulated in periodic boundary conditions via the repeated supercell approach. We use crystalline α-quartz SiO$_2$ supercells of tetragonal symmetry, comprising 71 to 73 atoms and of linear dimensions 18.49, 16.02, and 20.44 atomic units (theoretical lattice parameters [12], matching experiment to about 0.5%). Atomic geometries of the defects are optimized for each $Q$ (obtained by removing or adding electrons as appropriate) until all residual force components in the system are below 0.02 eV/Å. No symmetry restriction is imposed on geometry optimization. Improving slightly on the setting of Ref. [13] a (222) mesh is used for k-space summation (4 special points in the supercell Brillouin zone). Our use of a crystalline SiO$_2$-based model of the E$'$ defect, which is observed both in amorphous and crystalline phases, is justified by the closely similar behavior of several E$'$ variants in crystalline and amorphous SiO$_2$ in experiment [14] as well as theory [15]. In addition, the simulated structure of amorphous silica [12] deviates moderately from that of crystalline a-quartz SiO$_2$.

![FIG. 1. Minimum formation energies (eV) of the oxygen vacancy (dash-dotted line) and split-interstitial oxygen (dashed) as a function of the Fermi level, and calculated Fermi level position (vertical solid). Fermi level zero is the valence band top.](image)

The helical tetrahedra chain, with $\sim 1$ eV of energy gain with respect to the starting site. Details will be discussed elsewhere: here we note the main consequences of this result: a) the stabilization in the s-O$_i$ configuration (which is found to be quite close to that suggested in Ref. [13]) prevents O$_i$ from easily recombining with vacancies, because the detachment from the split-interstitial configuration costs about 1.2 eV; b) as seen in Fig. 1, s-O$_i$ is a (negative-U) deep double acceptor with second ionization energy at $3.3$ eV above the valence band top Ev. The Fermi level, calculated as in [16], is pinned at $E_F = E_v + 3.3$ eV (vertical solid line in Fig. 1). Thus a consequence of vacancy-interstitial pair formation, is that moderately $p$-type conditions are achieved; this is indeed often observed in irradiated samples [8,11]. In the absence of s-O$_i$, the Fermi level would be at midgap, $E_v + 4.4$ eV. From the formation energies one can estimate the chemical concentrations of s-O$_i$ and V$_O$: for a typical $T_s$ of $1500$ K, and assuming a reasonable formation entropy $S_{\text{form}} = 5$ kBT, the concentration of both defects is $\sim 10^{14}$ cm$^{-3}$. This figure matches well E$'$ concentrations measured [11] in non-neutron irradiated samples after UV, $\gamma$, or X illumination fall, and therefore supports the hypothesis that the vacancy is the parent defect of E$'$. Neutron irradiation of course produces dose-dependent [8], typically much higher concentrations ($> 10^{19}$ cm$^{-3}$). The key point is that, since the concentrations of vacancies and interstitials are essentially the same in both cases, and because only the interstitial has electrical activity (via its double acceptor level), the Fermi level is pinned at the same value in both cases, so that the theory of E$'$ stability and activation discussed below applies identically to both cases.

It appears from Fig. 1 that the +1 charge state of the vacancy, V$^+_{O_i}$, is not among the thermodynamically stable ground states of the defect. Therefore, if this state of V$_O$ is to be identified with E$'$, it must at least be proven metastable; if it is metastable, a mechanism for its creation starting from the ground state (the neutral vacancy) must be identified. As to the first point, since the +1 vacancy has a formation energy that increases linearly with the Fermi level while the neutral one remains constant, V$^+_{O_i}$ or a distorted variant thereof, may only be metastable in a limited range of that variable: we show below that the Fermi level pinning due to split-O$_i$ produces naturally the conditions for the metastable existence of E$'$. As to the second point, experiments indicate that E$'$ is activated by ionizing radiation [8,11,17] such as $\gamma$, X, or UV photons shone onto vacancy-containing samples, or concurrently with neutron irradiation (causing knock-on vacancy creation). Indeed, since the vacancy ground state is the neutral undistorted configuration, the distorted +1 state (alias E$'$) can only be accessed by ionization of V$^+_{O_i}$; our picture provides consistently such activation mechanism.

We proceed to study the behavior of the vacancy when
subjected to the undistorted-to-puckered transition as proposed in earlier studies [4–6]. In accord with the results discussed above, we fix the Fermi level at $E_F + 3.3 \text{ eV}$. The creation of a vacancy starting from the perfect lattice results in moderate local distortions in both the neutral and +1 charge states. The puckered configuration is obtained by moving one of the two vacancy-adjacent Si$_1$ and Si$_2$ atoms (specifically the “long-bond” Si$_1$Si$_2$) away from the vacant site, and pushing it across the basal plane of the incomplete tetrahedron centered on Si2 itself. When Si2 pokes through this triangular constriction, it gets strongly and suddenly bound to a backbonding oxygen, O$_b$. Upon completion of the distortion, Si$_2$ regains 4-fold coordination, and backbonding O$_b$ becomes 3-fold coordinated (see also A,B), while it was originally 2-fold coordinated as all tetrahedron-bridging oxygens in SiO$_2$. Si$_1$ remains instead 3-fold coordinated: in the +1 charge state, its dangling bond is half-filled, and causes the observed EPR signature which identifies E'$_0$. It may appear at first sight that the puckering distortion should be symmetric in Si$_1$ and Si$_2$. This is not the case, however, because of the intrinsic asymmetry of the quartz structure. As already noted earlier on A, only Si$_2$ finds the backbonding oxygen O$_b$ in the correct position. This applies largely also to amorphous silica, whose structure is moderately different at the local level from that of quartz B. The backbonding oxygen is therefore the main stabilizing agent of the E' defect.

The total energy of the system in charge state Q is calculated as a function of the separation between Si$_1$ and Si$_2$. Only the modulus $d_{Si-Si}$ of the Si$_1$-Si$_2$ connecting vector is constrained, and all other degrees of freedom are fully relaxed: the minimum energy path is thus mapped out for the undistorted-puckered transformation in the constrained-$d_{Si-Si}$ configurational subspace. In Fig. we display the full level diagram for the neutral, +1, and +2 charge states of the vacancy as a function of the puckering distortion, quantified by $d_{Si-Si}$. All energy curves depend on the Fermi level through Eq.1; they can be directly compared on the same energy scale because $E_F$ is fixed at the natural value of $E_v + 3.3 \text{ eV}$ determined above.

The outstanding feature of Fig. is that for the natural Fermi level of stoichiometric or neutron-irradiated silica, the candidate E', i.e. distorted V$_O^+$, is indeed the stable defect state for the distorted geometry. We stress that the Fermi level position is essential here: if $E_F$ were at midgap, the +1 curve would be 1.1 eV above its position in Fig.. Then E' would be unstable towards magnetically-inactive V$_O^0$. Globally, E' is metastable with a confining barrier of 0.8 eV. The barrier to enter the metastable state is 1.1 eV, and the undistorted state is lower than the distorted by 0.3 eV [this difference to Ref. 8, where the distorted state was lower by the same amount, is possibly due to our improved k-sampling]. Clearly, in the absence of excitation, V$_O^+$ will remain trapped in the metastable E' state and will show EPR activity. When thermally activated to overcome the barrier, the puckered center will transform into undistorted, and by electron capture it will become neutral. Therewith, E' disappears permanently, and so does its magnetic activity, because Si1 and Si2 combine their dangling bonds to bind into a dimer A,B. (The same deactivation route is not readily available for the level ordering of Ref. 5, which implies that i) E' remains activated at equilibrium, and that ii) concurrent barrier jump and electron capture are required to quench it.)
in Fig. with two successive one-photon ionizations of $V^0_O$ into $V^{+2}_O$, followed by non-radiative decay into $E'$. This path is efficient since the +1 undistorted state is kept populated by sustained illumination (a much less efficient double-photon excitation of $V^0_O$ into $V^{+2}_O$ may also occur). The excitation energies for path A are both near 4–4.5 eV if the ionized electron is transferred to the Fermi level, i.e. to the $E_F$-pinning impurity; if it is promoted to the conduction band, the energies are instead about 7 eV. Both processes are possible with $X$ or $\gamma$ radiation, whose energy vastly exceeds that needed in the transition. In UV irradiation, the center is often activated by pumping at 5 eV, and clearly only Fermi-level capture matches this figure. (There are, however, qualitative indications that the 5 eV excitation may activate $E'$ via alternate routes involving other pre-existing defects.)

The second excitation route, path B, involves an optical excitation of $V^0_O$ into undistorted $V^{+}_O$, and a thermal excitation of the latter into the puckered state. The energy difference (0.3 eV) between the two $V^{+}_O$ states implies that only a fraction of $10^{-5}$ of the vacancies gets promoted into the distorted state in equilibrium at room temperature, on sustained illumination. Therefore, though admissible, this path is preempted by path A. With the level ordering of Ref. [8], also path B competes with path A. (Our ordering, however, matches better the thermal behavior, as discussed above.)

Other calculated observables of our $E'$ model are consistent with previous studies [9,11,12]. For instance, the optical absorption of the neutral undistorted state at 6.9 eV correlates well with the 7.6 eV absorption band usually attributed to the neutral vacancy [13,14]. For $E'$ (metastable puckered $V^0_O$) we find an absorption at 4.7 eV (defect-to-conduction promotion) followed by slow non-radiative decay back into $E'$. Since it is not followed by any emission or $E'$ deactivation, this absorption correlates with the broad 5.8-eV band typical of $E'$ [10,11], which exhibits the same behavior in experiment.

In summary, we conclusively put on firm ground the identification of the singly positive O vacancy in SiO$_2$ with the $E'$ center proving its thermodynamical stability via first principles calculations. Our picture provides naturally activation and deactivation mechanisms, and other optical signatures, in agreement with known experimental observations. In addition, our picture naturally explains the moderate $p$ conditions produced by irradiation in SiO$_2$.

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