Stability of Ge-related point defects and complexes in Ge-doped SiO$_2$

Carlo Maria Carbonaro, Vincenzo Fiorentini, and Fabio Bernardini

INFM and Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy

(Submitted to Phys. Rev. Lett. Jan 10, 2002)

We analyze Ge-related defects in Ge-doped SiO$_2$ using first-principles density functional techniques. Ge is incorporated in SiO$_2$ in concentrations of the 1–10 mol % range. As is generally true of defects in solids, the identification and characterization of Ge-related defect centers in SiO$_2$ is a difficult task, and far from completion despite intense recent investigation. This is the case, for instance, for the understanding of oxygen-deficient Ge-related centers and the so called Ge($n$) [$n$=0,1,2,3] centers, for which rather disparate models have been proposed. First-principles defects theory can play a key role in this context, predicting the stability regimes and concentrations of Ge and related defects in SiO$_2$, and their extrinsic electronic levels and potential magnetically active states. Recently, for example, these techniques were used to pinpoint the correlation of the E' center in SiO$_2$ with the singly-charged O vacancy and the role of hydrogen in determining the leakage current across thin silica layers.

Using a similar methodology, here we study the energetics, extrinsic levels, and solubility of Ge in SiO$_2$. We predict experimental signatures of a selection of Ge-related defects, including Ge-oxygen vacancy complexes in various stable and metastable configurations and charge states. We demonstrate that oxygen off-stoichiometry occurs naturally in Ge-doped SiO$_2$, and specifically that oxygen deficiency (i.e. O vacancy formation) occurs preferentially near substitutional Ge$_{Si}$ sites. The electronic structure of Ge$_{Si}$ may explain the observed effective reduction of the gap in Ge-doped silica. Single and paired substitutional Ge and their complexes with an O vacancy are all found to have accessible paramagnetic states: Ge$_{Si}$, and the Ge$_{Si}$-Ge$_{Si}$ or Ge$_{Si}$-V$_{O}$-Ge$_{Si}$ complexes, are candidates, respectively, for the Ge(1) and Ge(2) electron-capturing centers; two metastable E’-like Ge-related centers correlate with the Ge(3) hole center.

Our method can be summarized as follows. The equilibrium concentration of a defect $D$=

$$N_s \exp(-F_{form}/k_BT_s)$$

is determined by the growth temperature $T_s$, the number $N_s$ of available sites, and the formation free energy $F_{form}=E_{form}-T_{S}S_{form}$. The latter 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 electrons reservoir made up by the whole crystal. Given the formation energies of the relevant defects, the concentrations and the electron chemical potential $\mu_e$ are determined self-consistently to satisfy charge neutrality, as detailed in [1]. 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 $\mu_e$, or when a sufficiently high energy barrier prevents its disappearance. The formation energy for a defect in charge state $Q$ can be written as

$$E^Q_{form} = E^Q_{def} + Q\mu_e + M(Q) - n_{Si}\mu_{Si} - n_{Ge}\mu_{Ge} - n_{O}\mu_{O},$$

where $E^Q_{def}$ is the total energy of the defected system in charge state $Q$, $\mu_e$ the electron chemical potential (equaling the Fermi level $E_F$ in our $T=0$ calculations), and $M(Q)$ a defect- and charge state-dependent multipole correction. The $n_{Si}$, $n_{Ge}$, and $n_{O}$ atoms considered in the modeling of a specified defect, possess the chemical potentials $\mu_{Si}$, $\mu_{Ge}$, and $\mu_{O}$, discussed further below.

Energies and forces are calculated from first-principles within density-functional theory in the local approximation, using the ultrasoft pseudopotential plane-wave method as implemented in the VASP code [8]. An isolated defect is simulated in periodic boundary conditions via repeated tetragonal 71- and 72-atom supercells of crystalline $\alpha$-quartz SiO$_2$ having the (theoretical) linear dimensions 18.49, 16.02, and 20.44 atomic units. Atomic geometries are optimized for all $Q$s (which are modeled by removing or adding electrons as appropriate, the added charge being compensated by a uniform background) until all residual force components in the system are below 0.01 eV/A. No symmetry restriction is imposed. A (222) Monkhorst-Pack mesh is used for k-space summation (4 points in the supercell Brillouin zone). Total energy differences of different charge
The relevant extremal conditions are then:

1. O-rich, Si- and Ge-lean: \( \mu_O = \mu_{\text{bulk}}^{\text{O}}, \mu_{\text{Si}} = \mu_{\text{bulk}}^{\text{Si}} + \Delta H^{\text{SiO}_2} \) and \( \mu_{\text{Ge}} = \mu_{\text{bulk}}^{\text{Ge}} + \Delta H^{\text{GeO}_2} \).

2. Ge- and Si-rich, O-lean: \( \mu_{\text{Ge}} = \mu_{\text{bulk}}^{\text{Ge}}, \mu_{\text{Si}} = \mu_{\text{bulk}}^{\text{Si}}, \) and \( \mu_{O} = \mu_{\text{bulk}}^{O} + 0.5 \Delta H^{\text{SiO}_2} \).

3. Ge-rich, O-lean with respect to GeO\(_2\), and Si intermediate: \( \mu_{\text{Ge}} = \mu_{\text{bulk}}^{\text{Ge}}, \mu_{\text{Si}} = \mu_{\text{bulk}}^{\text{Si}} + (\Delta H^{\text{SiO}_2} - \Delta H^{\text{GeO}_2}), \) and \( \mu_{O} = \mu_{\text{bulk}}^{O} + 0.5 \Delta H^{\text{GeO}_2} \).

These three cases are indicated in Fig. 1, which depicts the solubility region of Ge in SiO\(_2\) in the \( \{\mu_O, \mu_{\text{Ge}}\} \) plane.

To substitute as much Si as possible with Ge, one should work in comparatively Ge-rich and Si-lean conditions. Case 3 above, the most favorable in this respect, demands at the same time that O be lean with respect to GeO\(_2\) formation. As a consequence, the material will contain both a high Ge concentration, and a large amount of oxygen deficient centers (as shown below, these tend to localize near Ge atoms). The minimum formation energy of Ge\(_{\text{Si}}\), 0.88 eV, is obtained indeed in case 3 above.

The ensuing solubility of Ge at a typical growth temperature \( T_g = 1700 \text{ K} \) (which we assume throughout) is 0.2 mol \%. This encouragingly high value falls well within the experimental range assuming a plausible formation entropy of 3–4 k\( \text{B} \).

![FIG. 1. Solubility region of Si-substituting Ge in SiO\(_2\) as a function of the impurity and oxygen chemical potentials. Relevant limiting values of the latter are indicated, numbered as in the text. The oblique line is the solubility limit due to GeO\(_2\) formation. The limit given by GeO formation is irrelevant and is not displayed.](image1)

![FIG. 2. Formation energy of Ge-related defects: Ge\(_{\text{Si}}\), Ge-adjacent oxygen vacancy, substitutional Ge pair with and without O vacancy. The slope of the formation energies is equal to the charge state (possible values are 0, –1, and –2 in the present case). The vertical dotted line indicates the calculated Fermi level. All the centers possess accessible paramagnetic (\( Q = -1 \)) states.](image2)
Ge$_{Si}$ is neutral over most of the Fermi level range, and captures electrons in strong $n$–type conditions. Structurally, neutral Ge$_{Si}$ is relatively trivial, with Ge–O bonds (unsurprisingly slightly longer, 1.67 and 1.68 Å, than the bulk Si–O bonds of 1.58 and 1.59 Å) and the other structural parameters (Ge–Si distance : 3.09 Å, O–Ge–O angle : 109°, and Ge–O–Si angle : 142°) being characteristic of an isotropically expanded but otherwise regular tetrahedron. The charge state $Q=−1$, one of the models proposed for the paramagnetic Ge(1) center, is not stable in the as-grown material, but it may be observed in $n$-type or electron-irradiated material. Upon electron capture, the Ge substitutional moves off-center causing an orthorhombic distortion with two short and two long Ge–O bonds (differing by ~ 0.2 Å), in good agreement with the report of Ref. 1.

The properties of Ge$_{Si}$ also match the main Ge-related optical signature in highly doped samples, namely the apparent reduction of the absorption gap to about 7 eV. Indeed, our calculated concentration and electronic structure predict an absorption into the Ge$_{Si}$ extrinsic level starting around 6.5-6.8 eV with an effective final density of states (DOS) of about $\sim 10^{20}$ cm$^{-3}$. Assuming an impurity bandwidth of 1 eV, likely to occur at such high Ge concentrations, it appears that the valence-to-Ge$_{Si}$ extrinsic state is as relevant as the fundamental interband transition, even accounting for reduced oscillator strength, since the effective conduction band DOS of SiO$_2$ is in fact about $1 \times 10^{19}$ cm$^{-3}$ at room temperature. In summary, the large absorption red shift in Ge:SiO$_2$ is impurity-related, as opposed to a standard alloying effect: a simple Si$_{1-x}$Ge$_x$O$_2$ alloying picture would predict (the gap of GeO$_2$ being 5.6 eV) a shift of less than 0.1 eV instead of the observed $\sim 2$ eV at the typical Ge concentration $x \sim 0.02$. The behavior just discussed is similar to the impurity-level (or -band) effects observed e.g. in InGaAsN at low N concentration.

We now turn to V$_O$–Ge$_{Si}$ centers. The isolated oxygen vacancy at the chemical potentials giving maximum Ge incorporation, has a formation energy of 3.31 eV, i.e. 0.4 vacancy at the chemical potentials giving maximum Ge density of states (DOS) of about $\sim 10^{20}$ cm$^{-3}$. InGaAsN at low N concentration [10].

In summary, the large absorption red shift in Ge:SiO$_2$ is impurity-related, as opposed to a standard alloying effect: a simple Si$_{1-x}$Ge$_x$O$_2$ alloying picture would predict (the gap of GeO$_2$ being 5.6 eV) a shift of less than 0.1 eV instead of the observed $\sim 2$ eV at the typical Ge concentration $x \sim 0.02$. The behavior just discussed is similar to the impurity-level (or -band) effects observed e.g. in InGaAsN at low N concentration.

We now turn to V$_O$–Ge$_{Si}$ centers. The isolated oxygen vacancy at the chemical potentials giving maximum Ge incorporation, has a formation energy of 3.31 eV, i.e. 0.4 vacancy at the chemical potentials giving maximum Ge density of states (DOS) of about $\sim 10^{20}$ cm$^{-3}$. InGaAsN at low N concentration [10].

Given the larger amount of vacancies and their preference for the vicinities of Ge, and accounting for the $^{73}$Ge and $^{29}$Si isotopic abundances of $\sim 8\%$ and $4\%$, the concentration of Si-Ge E$^+$ measured by EPR should be a factor of $10^4$ that of E$^+$ in SiO$_2$. Observed values [17] are in a range upwards of $10^2$. In agreement with the observed axial symmetry of Ge(3), the bond lengths between the EPR-active Ge and the three first-neighbor oxygens are about the same. Also, the fact that the puckered configuration is lower in energy than the unpuckered one agrees with the observation of Ge(3) defects even in non irradiated samples [1].

As mentioned, the thermodynamical stability of Si-Ge E$^+$ is possible only at rather extreme $p$ conditions ($\mu_e \sim 1.6$ eV), not realized in as-grown material. This center should therefore be observed only upon (radiation-induced or electrical) hole injection. In as-grown material, it may still be possible that, after its excitation to the positive state by e.g. an optical excitation, the return of Ge-Si E$^+$ to the neutral (and thence to the unpuckered) state is slowed down due to selection rules and/or disorder, neither of which have been considered here.

So far we identified possible candidates for the Ge(1) electron-capturing and Ge(3) E$^+$like centers. We now move on to Ge-pair defects, consisting of two corner-sharing Ge-centered tetrahedra. In the neutral state, the tetrahedra exhibit Ge-O bonds and angles close to those of the isolated Ge$_{Si}$ in their neutral state.

As seen in Fig. 4 the formation energy of two Ge
impurities at neighboring substitutional sites is almost exactly twice that of isolated Ge$_5$$^-$; therefore, there is neither a driving force for, nor an energetic hindrance against, the clustering of Ge$_{Si}$. Kinetics, and hence thermal and growth history will play the deciding role. Once more, the $Q$=−1 charge state is not a ground state of the defect in as-grown material, but it may be observed in $n$-doped irradiated material, and thereby become a candidate for the Ge(2) paramagnetic center, as suggested in Ref. 18.

Finally we consider the formation of $V_{O}$ between the two Ge atoms: it costs 0.15 eV less than between a Ge and a Si (Fig. 3), because of the previously discussed natural tendency of the two Ge to host off-stoichiometry of oxygen nearby them; this gives a concentration of a further factor of 3 higher than for the Ge-neighboring vacancy. In this case, the negative charging level is just slightly (∼0.1 eV) above the Fermi level so that, given the uncertainties on the energy levels, it may well turn out to be already occupied in weakly, unintentionally $n$-type as-grown material, or will readily be become occupied in moderately $n$-doped or irradiated material. Thus Ge-$V_{O}$Ge stands out as well as a candidate for the Ge(2) paramagnetic center.

Once more, the unpuckered +1 vacancy is not a stable ground state; its E$'$-like puckered-Ge configuration becomes metastable below $\mu_{e}=1.5$ eV \cite{13}. As the metastable energy minimum is found to be 0.45 eV higher than the undistorted one, the EPR-active Ge-pair E$'$-like configuration is far less frequent than the Si-Ge one (∼10$^{-7}$ at room temperature, although it is possible that, as for the standard E$'$, a confinement barrier exists prolonging its existence). This suggests that the proposed \cite{11} attribution of the Ge(3) center to this complex is unlikely to be correct.

In summary, we have shown that thermodynamical growth conditions of Ge-doped SiO$_2$ naturally produce off-stoichiometry of oxygen, and that oxygen deficient centers form preferentially near Ge impurities; we find that energetics is neutral as to clustering of substitutional Ge, so that kinetics will be important. The calculated concentration (in agreement with experiment) and electronic structure of Ge$_{Si}$ show a large density of states starting at 6.5-6.8 eV which may explain the apparent gap reduction to about 7 eV in absorption. Our results contribute to the identification of the Ge(1), Ge(2), and Ge(3) centers. Ge(1) and Ge(2) are electron-capturing paramagnetic centers; the former is probably related to the singly negative states of Ge$_{Si}$; the latter may be associated with the singly-negative Ge$_{Si}$-Ge$_5$$^-$ or Ge$_{Si}$-V$_{O}$-Ge$_{Si}$ complexes. Ge(3) may instead be attributed to the Ge-Si E$'$-like center. Hyperfine-parameter calcula-

tions are underway to pinpoint these attributions. In any case, these centers should be preferentially observed in $n$-doped or irradiated material.

Work supported in part by the Parallel Supercomputing Initiative of INFM, and the European Union within the INVEST project.

\begin{thebibliography}{10}
\bibitem{1} E. J. Friebele, D. L. Griscom, and G.H. Sigel, J. Appl. Phys. \textbf{45}, 3424 (1974); E. J. Friebele and D. L. Griscom, in \textit{Defects in Glasses}, edited by E. L. Galeneer, D. L. Griscom, and M. J. Weber (MRS, Pittsburgh, 1985), p.319.
\bibitem{2} C.M. Carbonaro, V. Fiorentini, and F. Bernardini, Phys. Rev. Lett. \textbf{86}, 3064 (2001).
\bibitem{3} P. E. Blöchl and J. H. Stathis, Phys. Rev. Lett. \textbf{83}, 372 (1999); P. E. Blöchl, Phys. Rev B \textbf{62}, 6158 (2000).
\bibitem{4} G. Pacchioni and C. Mazzeo, Phys. Rev. B \textbf{62}, 5452 (2000).
\bibitem{5} J. Nishii, N. Kitamura, H. Tamanaka, H. Osono, and H. Kawazoe, Optics Lett. \textbf{20}, 1184 (1995); H. Hosono, H. Kawazoe, and J. Nishii Phys. Rev. B \textbf{53}, R11921 (1996).
\bibitem{6} C. G. van de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, Phys. Rev. B \textbf{47}, 9425 (1993).
\bibitem{7} M. Leslie and M. G. Gillan, J. Phys. C \textbf{18}, 973 (1985); G. Makov and M. C. Payne, Phys. Rev. B \textbf{51}, 4014 (1995).
\bibitem{8} G. Kresse and J. Furthmüller, Comput. Mater. Sci. \textbf{6}, 15 (1996); G. Kresse and J. Furthmüller, Phys. Rev. B \textbf{54}, 11169 (1996); and the web site \url{http://cms.mpi.univie.ac.at/vasp/}
\bibitem{9} J. R. Chelikowsky and M. Schlüter, Phys. Rev B \textbf{15}, 4020 (1977).
\bibitem{10} T. Mattila, S.-H. Wei, and A. Zunger, Phys. Rev. B. \textbf{60}, R11425 (1999).
\bibitem{11} H. Hosono, Y. Abe, D.L. Kinser, R.A. Weeks, K. Muta, and H. Kawazoe, Phys. Rev. B. \textbf{46}, 11445 (1992).
\bibitem{12} N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, and R. Scotti, Phys. Rev. B \textbf{60}, 2429 (1999).
\bibitem{13} At this energy, the puckered +1 state drops below the puckered neutral; the unpuckered neutral is always lower than unpuckered +1 (see e.g. \cite{11} for more details, in particular Fig.2).
\bibitem{14} T. Uchino, M. Takahashi, and T. Yoko, Phys. Rev. Lett. \textbf{84}, 1475 (2000).
\bibitem{15} M. Fujimaki, T. Watanabe, T. Katoh, T. Kasahara, N. Miyazaki, and Y. Ohki, Phys. Rev. B \textbf{57}, 3920 (1998).
\bibitem{16} T. E. Tsai, D. L. Griscom, and J. L. Friebele, J. Appl. Phys. \textbf{62}, 2264 (1987).
\bibitem{17} R. Crivelli, M. Martini, F. Meinardi, A. Paleari, and G. Spinolo, Phys. Rev. B \textbf{54}, 16637 (1996).
\bibitem{18} H. Kawazoe, J. Non-Cryst. Solids \textbf{71}, 231 (1985).
\end{thebibliography}