Theoretical investigations on atomic-silicon cryptates in siloxanic networks

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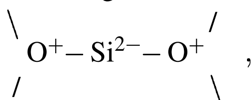
Since its relevance in integrated-circuit processing, the thin film (in the length scale in the interval $1-10$ nm) produced by high temperature oxidation in O_2 of single crystalline (100) silicon is certainly one of the most studied materials. Though the Si-SiO_2 *interface* and the '*bulk*' SiO_2 have been the matter of extended experimental and theoretical investigations, not much attention has been posed to the SiO_2 *surface*. This fact is somewhat surprising, especially because it plays a fundamental role on the performances of some devices (erasing of flash memories) and it also manifests anomalous reactivities (compared to that of the oxide underneath) toward O_2 and H_2. A theory of silicon oxidation by O_2 has recently been proposed by Kageshima, Shiraishi and Uematsu to account for these anomalies. In that theory the tensile stress accumulated at the silicon-SiO_2 interface is relieved by injection of silicon atoms not only into silicon but also into the growing SiO_2. In view of its expected high reactivity, atomic silicon was assumed to react with dissolved oxygen and to evaporate as SiO (for thin films) or transform into SiO_2 (for thick films). The isotope-exchange experiments of Gusev *et al.* and the hydrogen-desorption experiments of Baumvol *et al.*, suggest however the presence of $Si^{(n)}$ (silicon in an oxidation state n with $n<4$) at the SiO_2 surface. Actually, though the redox reaction, in which atomic silicon cleaves two siloxanic bridges,

$$\mathrm{Si}^{(0)} + 2(-\mathrm{O})_3\mathrm{Si}^{(4)}\mathrm{OSi}^{(4)}(\mathrm{O}-)_3 \downarrow [(-\mathrm{O})_3\mathrm{Si}^{(3)}]_2\mathrm{Si}^{(2)}[\mathrm{OSi}^{(3)}(\mathrm{O}-)_3]_2, \tag{1}$$

is certainly an exothermic process, the possibility that silicon remains in the silica in an atomic form is not manifestly absurd, especially in view of the high activation energy required to cleave the Si−O bridge forming the silica network. An octet configuration may be achieved by donation of lone pairs from two oxygen atoms of two oxo bridges between silicon, the resulting Lewis formula of the center being



$$\mathrm{O}^{+}-\mathrm{Si}^{2-}-\mathrm{O}^{+},$$

where an unterminated bond implies bonding to silicon (or to hydrogen, at the surface of hydroxylated silica). To verify this hypothesis we have thus performed density functional calculations, using model molecules to mimic the oxide. Our study supports the view that atomic silicon injected in bulk SiO_2 cannot be trapped therein in localized states; stationary localized states are possible only at the surface where the reticulation degree of the oxide is partially lost because of hydroxyl terminations.

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