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13. ABSTRACT (Maximum 200 words) This report results from a contract tasking Universita di Milano as follows: The contractor will investigate point defects in crystalline and amorphous silica. Three main topics will be studied: 1. the electronic structure of the E' centers, and various models for them; 2. electron trapping in silica, for which new, larger models which increase electron affinity of the system by allowing a delocalization of excess negative charge over many atomic centers will be investigated; 3. hydrogen diffusion in silica, specifically, mechanisms to explain the observed temperature dependence of hydrogen emission under electron injection in silica.				
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Project:

Theory of point defects in SiO₂-based electronic devices: optical transitions, EPR properties, formation energies

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Description of the work performed

The activity was planned in three specific directions closely related to actual problems in the metal/oxide semiconductor (MOS) field effect transistor (FET) technology.

In each of these directions significant results have been achieved. These results have been reported in a few publications (appeared, accepted, or in press) where the financial support of the European Office of Aerospace Research is explicitly acknowledged. A copy of the papers where the work performed is described in detail is enclosed.

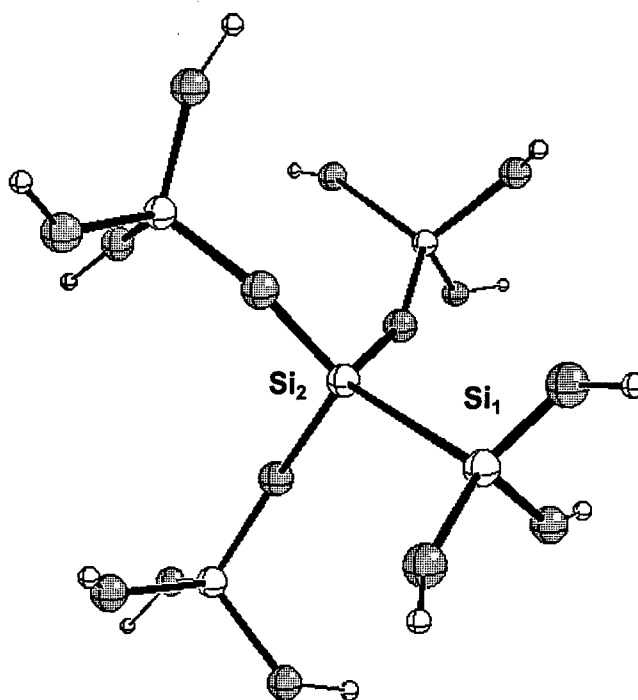
The E' center ground state structure

Results related to this problem have been reported in the following publication: **"EPR and IR spectral properties of hydrogen-associated bulk and surface defects in SiO₂: *ab initio* calculations"**, by G. Pacchioni and M. Vitiello, Phys. Rev. B 58, 7745 (1998) (Publication n. 1)

In this work the EPR and IR spectral properties of hydrogen-associated centers in silica have been studied by means of first principles Hartree-Fock and Density Functional Theory calculations. The geometric and electronic structure of the paramagnetic centers ($\equiv\text{Si-O}$)₃Si[•], ($\equiv\text{Si-O}$)₂Si[•](OH) and ($\equiv\text{Si-O}$)₂Si[•](H), and of the corresponding diamagnetic centers formally derived from the addition of one H atom, ($\equiv\text{Si-O}$)₃Si(H), ($\equiv\text{Si-O}$)₂Si(OH)(H), and ($\equiv\text{Si-O}$)₂Si(H)(H) have been determined using cluster models. A substantial agreement is found between the computed hyperfine splittings and those measured for bulk paramagnetic centers in high-purity amorphous silica. The different experimental hyperfine splittings obtained for ($\equiv\text{Si-O}$)₃Si[•] centers at the surface of mechanically or thermally activated silica are explained in terms of small structural differences from the bulk counterparts. An almost quantitative agreement with the experiment is found also for the vibrational properties of the Si-H groups of the silylhydride centers. The calculations have made possible a firm assignment of the spectral features to specific point defects in silica.

Electron trapping at diamagnetic point defects in silica

One unsolved problem in silica electronic structure is that the formation of the positively charged E' center must be accompanied by an electron trapping process at some lattice site. So far, the trapped electron in silica has not been seen and its existence is still matter of debate. One possibility is that electrons are trapped at an oxygen vacancy, giving rise to a V_O^- center. Calculations suggest that this center could explain a negative g -shift in the EPR spectrum of ODC in silica and that it could give rise to hyperfine coupling constants in close agreement with the experimentally observed hcc of about 410 G. The problem is that electron trapping seems to be an energetically unfavorable process, at least within the models considered so far.



A model of the oxygen vacancy in the bulk of silica

The problem of the electronic structure of a neutral oxygen vacancy in Ge-doped silica has been addressed in a separate paper: **"First principle calculations of the optical properties of a neutral oxygen vacancy in Ge-doped silica"**, by G. Pacchioni and A. Basile, J. Non-Cryst. Solids, submitted (**Publication n. 2**)

In this paper we have reported *ab initio* configuration interaction calculations of the optical properties of a neutral oxygen vacancy in Ge-doped silica. This defect center, $V(\text{SiGe})$, is supposed to involve a missing O atom between a Si and a Ge atom with formation of a direct Si-Ge bond, $\equiv\text{Si-Ge}\equiv$. Several calculations have been performed using cluster models in order to obtain a reliable estimate of the excitation energy. The lowest fully allowed singlet-singlet transition in $V(\text{SiGe})$ occurs in a spectral region around 7.3 eV according to the calculations, i.e.

not too far from the absorption band at 7.6 eV attributed to a V(SiSi) center in pure silica. The emission properties of V(SiGe) and the reasons for the similar transition energy in V(SiSi) and V(SiGe) centers have also been studied.

Hydrogen diffusion in silica

Hydrogen diffusion in silica is of considerable importance since it may result in degradation of the MOSFET devices and in the formation of positive charges in the dielectric. Recently, non-volatile field effect transistor memories involving proton motion in SiO₂ have been developed. Proton motion in Si/SiO₂ interfaces is therefore of great fundamental and technological interest. One open problem in this respect is the response of the hydrogen-containing material to electron injection. Electron injection occurs via irradiation of the material with UV photons. It may be assumed that photons of this energy can excite the silanol groups, $[=Si-OH-Si=]^+$, a proton attached to a lattice oxygen, to a dissociative excited state with formation of a neutral H^{*} atom and a hole trapped in the lattice $[=Si-O^+-Si=]$; this latter center is known as self-trapped hole, STH. A study of self-trapped holes in silica is presently carried out in our laboratory.

The study of the mechanism of H release is protonated silica under the effect of electron injection has led to a common publication: "**Microscopic mechanisms of radiation induced proton density decay in SiO₂ films**", by S.P. Karna, R.D. Pugh, J.R. Chavez, W. Shedd, C.P. Brothers, B.K. Singararaju, M. Vitiello, G. Pacchioni and R.A.B. Devine, IEEE Journal, in press (**Publication n. 3**)

In this paper we have considered the potential energy curve for the interaction of a proton with a bridging oxygen in silica. The calculations have been performed for both ground and excited singlet and triplet states at the Hartree-Fock level of theory. It is found that the excited state curves are purely repulsive. This would implies that the optical excitation of one electron from the ground state to the excited state results in hydrogen dissociation. Two mechanisms for proton decay have been proposed on the basis of the theoretical results.