Available online at www.sciencedirect.com
ScienceDirect
Journal of Non-Crystalline Solids 353 (2007) 605–609
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Computed paramagnetic properties for an E′ center produced from the twofold coordinated Si or Ge in silica

J. Garapon, L. Favaro, B. Poumellec *

Laboratoire de Physico-chimie de l'Etat Solide à L'ICMMO, UMR CNRS-UPS 8182 Université Paris Sud Batiment 414, 91405 ORSAY cedex, France

Available online 21 February 2007

Abstract

This paper introduces a model of the E'_γ center involving a twofold coordinated silicon or germanium atom as precursor. This one relaxes in its positively charged state through interaction with a neighboring oxygen atom forming a threefold coordinated silicon atom having characteristics of the well known E'_γ center. By neutralizing the hole, we have observed that this relaxation is reversible without activation energy. The contribution of the central atom to the isotropic hyperfine coupling constant is found to be 44 mT in agreement with the experimental value: 42 mT.

PACS: 76.30.Mi; 42.70.Ce

Keywords: Fibers and waveguides; Radiations effects; Modeling and simulation; Ab initio; Luminescence; Photoinduced effects; Silica; Poling; Defects

1. Introduction

Silica-based glasses are materials used extensively for optical communications, integrated optical devices and in silicon microelectronics. Point defects play an important role in determining the physical properties, and, in particular, paramagnetic defects, which are threefold coordinated Si or Ge atoms bearing an unpaired electron. The E′ type defects constitute a wide family first discovered by Weeks in 1956 [1]. They are called $E'_{1,2,3,4}$ in crystalline materials (for a review see [2]) and E'_α [3], E'_β [4], E'_γ [5], E'_δ [6,7] in amorphous materials. Table 1, taken from [3] shows the isotropic hyperfine coupling constants of E′ defects in amorphous materials. The E'_γ defect shows a strong hyperfine interaction ($A \sim 42$ mT) between the unpaired electron and the Si atom on which it is located [8]. On the other hand, it absorbs photons at 5.8 eV [9]. Indeed, it has been proved that an oxygen deficient center (ODC) absorbing at 5.0 eV is a precursor of E'_γ centers [10] which are thought to be involved in photosensitivity and poling. However, *ab-initio* calculations [11,12] show that oxygen vacancy (quoted V_O and corresponding to an oxygen missing between two Si atoms) absorbs at larger energy than 5.0 eV. On the contrary, these authors demonstrate that twofold coordinated Si atom indeed absorbs around 5.0 eV and thus may be a precursor of an E'_γ center. On the other hand, in a previous study [11], we have computed the interconversion from ODC(I) to ODC(II) (see Fig. 1). We have found that it is endothermic in pure silica (+1.1 eV), and exothermic in Ge-doped silica (−0.6 eV), suggesting that in Ge-doped silica, GeODC(II) should be the main precursor of E'_γ. Recently, Kuo et al. [13] found, by CRN-based MC and DFT that even for SiO2, the twofold coordinated Si atom is stable at surface.

We have investigated thus the possibility to produce a paramagnetic species from twofold-coordinated silicon or germanium.

* Corresponding author. Tel.: +33 1 69 15 51 59; fax: +33 1 69 15 63 51.
E-mail address: bertrand.poumellec@lpces.u-psud.fr (B. Poumellec).

0022-3093/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2006.10.045

Table 1
A_{iso} experimental coupling constants of the different types of E′ defects from Ref. [3]

E′ centers	a_{iso} (^{29}Si) (G)
E'_α	140
E'_β	420
E'_γ	420
E'_δ	100

2. Computational details

The cluster approximation is used to model divalent silicon in silica glass. We have saturated dangling bonds of the oxygen atoms with hydrogen atoms. This technique has been successfully used to describe some defect properties in glasses (see, for example [14] and references cited therein). Two different clusters were used for this study. The first one, $Si_9O_8H_{18}$ (see Fig. 2), describes the first neighbors covalently bonded to the divalent species. The divalent silicon is linked to two others silicon atoms by two oxygen atoms. These atoms are then linked to SiH_3 groups through oxygen atoms. For this calculation, we have fixed the position of the H atoms, and have performed optimizations with and without the positive charge at the level of Hartree–Fock (RHF and UHF) theory. This cluster is similar to the cluster used in a former study of Gritsenko et al. [15] except for the fact that H atoms in their study represent our SiH_3 groups. The second cluster, $Si_6O_{15}H_8$ (see Fig. 3), describes the lateral environment of the divalent species. The divalent silicon is linked through oxygen atoms to two other silicon atoms that are linked together through cycles. Two cycles are formed, of 5 and 4 silicon atoms, respectively. These cycles are thought to describe the lateral environment of the defect from a realistic manner because after ionization, the silicon atom will be sp^3 hybridized. This state is different from the sp^2 state of the uncharged divalent silicon, which has an sp^2 orbital pointing toward the top of the model. Thus, upon ionization, the main interaction between sp^3 orbitals and neighboring oxygen atoms will occur with the sides of the divalent silicon and not with the topside of the cluster, which is lacking in our model. Then, this lack is thought to have no impact in our calculations whereas the use of larger cluster, making up a roof, leads to a needlessly heavy computation. On the other hand, we think that a cluster model allows one to perform full *ab-initio* calculation that a periodic model cannot.

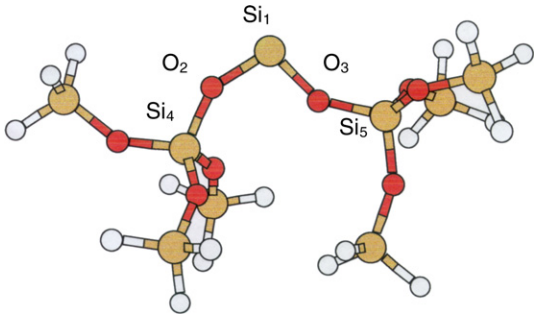

Fig. 2. Optimized structures of twofold coordinated Si, HF/6-311G* level of theory (first model).

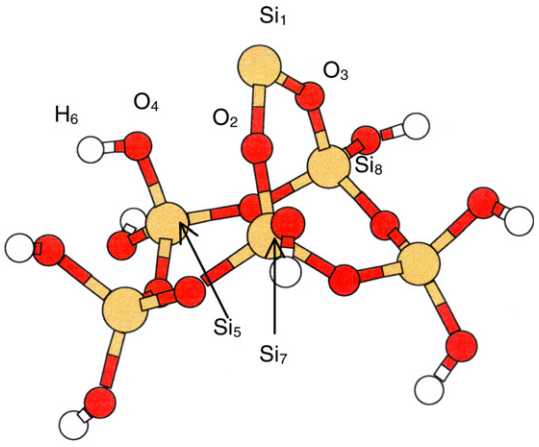

Fig. 3. Optimized structures of twofold coordinated Si, HF/6-311G* level of theory (second model).

We have carried out two geometry optimizations for the positively charged state at the Hartree–Fock (RHF and UHF) level of theory. The former is a full optimization without any symmetry or position constraint. The second is performed after having fixed the positions of the hydrogen atoms at their original position from the uncharged

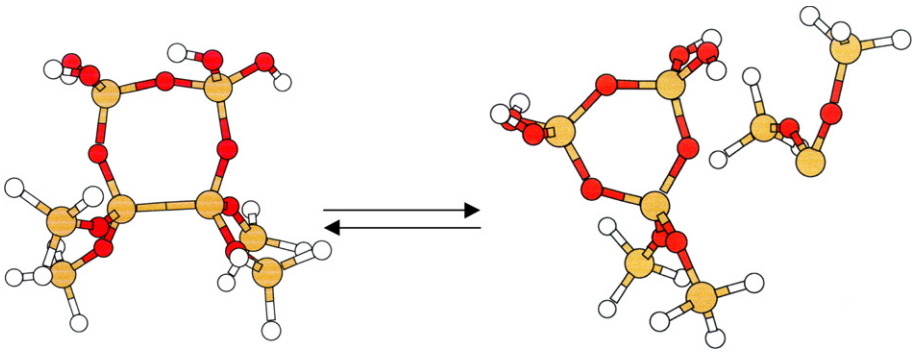

Fig. 1. Models of oxygen vacancy (ODC(I)) and divalent silicon (ODC(II)) in equilibrium from [11].