

## Photochemical generation of E' centres from Si-H in amorphous SiO<sub>2</sub> under pulsed ultraviolet laser radiation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 9967

(<http://iopscience.iop.org/0953-8984/18/43/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 14:27

Please note that [terms and conditions apply](#).

## Photochemical generation of E' centres from Si–H in amorphous SiO<sub>2</sub> under pulsed ultraviolet laser radiation

F Messina and M Cannas

Dipartimento di Scienze Fisiche ed Astronomiche dell'Università di Palermo, Via Archirafi 36, I-90123 Palermo, Italy

E-mail: [fmessina@fisica.unipa.it](mailto:fmessina@fisica.unipa.it)

Received 1 September 2006, in final form 21 September 2006

Published 13 October 2006

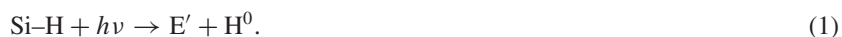
Online at [stacks.iop.org/JPhysCM/18/9967](http://stacks.iop.org/JPhysCM/18/9967)

### Abstract

*In situ* optical absorption spectroscopy was used to study the generation of E' centres ( $\equiv\text{Si}^\bullet$ ) in amorphous SiO<sub>2</sub> occurring by photo-induced breaking of Si–H groups under 4.7 eV pulsed laser radiation. The dependence on laser intensity of the defect generation rate is consistent with a two-photon mechanism for Si–H rupture, while the growth and saturation of the defects are conditioned by their concurrent annealing due to a reaction with mobile hydrogen arising from the same precursor. A rate equation is proposed to model the kinetics of the defects and is tested on experimental data.

The E' centre, consisting of an unpaired electron on a threefold coordinated silicon atom ( $\text{O}_3\equiv\text{Si}^\bullet$ ), is one of the fundamental point defects in amorphous silica (a-SiO<sub>2</sub>). The generation of this centre upon exposure of silica to laser radiation is often the main cause of transmission loss of the material in the ultraviolet (UV) range, due to its absorption band peaked at 5.8 eV [1, 2]. Many papers have been devoted to study of the generation of E' under laser radiation, pointing out a variety of possible mechanisms, such as conversion of oxygen-deficient centres, strained bonds or Si-bonded impurities or non-radiative decay of self-trapped excitons [2–11].

One of the most common precursors of the E' centre is the Si–H group, from which the defect can be generated by a photolysis process under UV laser photons [5–7, 10, 11]:



E' centres produced by process (1) are transient, at least at room temperature. In fact, hydrogen atoms H<sup>0</sup> produced in (1) dimerize in H<sub>2</sub> which diffuses and recombines with E' [8, 10–15]:



If E' centres have been generated from Si–H by a pulsed laser irradiation, after the laser is switched off reaction (2) causes the decay in a typical timescale of a few hours of almost

all the defects initially produced [14, 15]. Moreover, the reaction is also expected to occur during the irradiation session, mainly in the time interval between a pulse and the successive one (interpulse); hence, even the growth kinetics of the defects is conditioned by the interplay between pulse-induced generation (1) and interpulse annealing (2). Due to its characteristics, only a limited number of data are available for process (1), whose comprehensive study requires *in situ* measurements which have only been widely available for a few years [9–11, 15, 16]. *In situ* measurements are suitable for monitoring the transient kinetics of  $E'$  and are also the most appropriate way to find out whether UV-induced Si–H breaking is a single- or two-photon process.

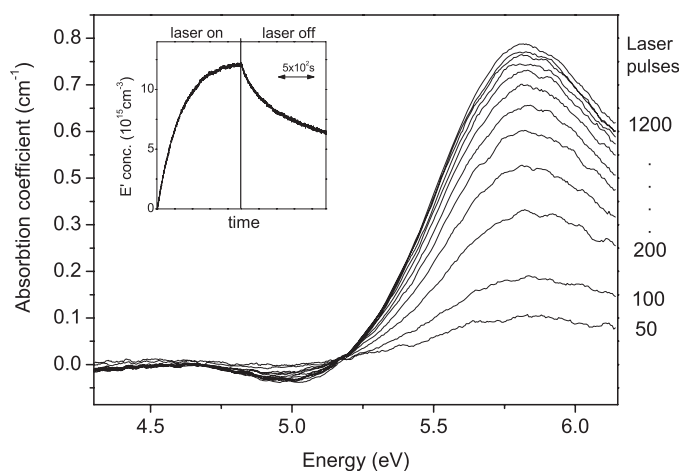
The main purpose of this work is to study the generation of  $E'$  centres by UV-induced breaking of Si–H in a system where this process can be isolated; the material of choice for this is wet fused quartz, where in a recent experiment founded on *in situ* optical absorption (OA) measurements it was demonstrated that formation of  $E'$  centres under 4.7 eV pulsed laser radiation is due to reaction (1) [15]. Moreover, it was found that there are no other OA signals significantly overlapping with the 5.8 eV band; hence, the generation of  $E'$  from Si–H can be isolated and studied selectively.

We point out that the information derived here may also be relevant for the understanding of other systems, such as Si/SiO<sub>2</sub> interfaces, where Si–H breakage is a very common process resulting in the formation of  $P_b$ -type interface centres (whose structure is Si<sub>3</sub>≡Si<sup>•</sup> at the (111)Si/SiO<sub>2</sub> interface), this being an important mechanism of degradation of microelectronics devices [17, 18]. In particular, under laser radiation, breakage of Si–H at Si/SiO<sub>2</sub> interfaces has been observed to occur either by a photothermal mechanism or by direct photolysis [19].

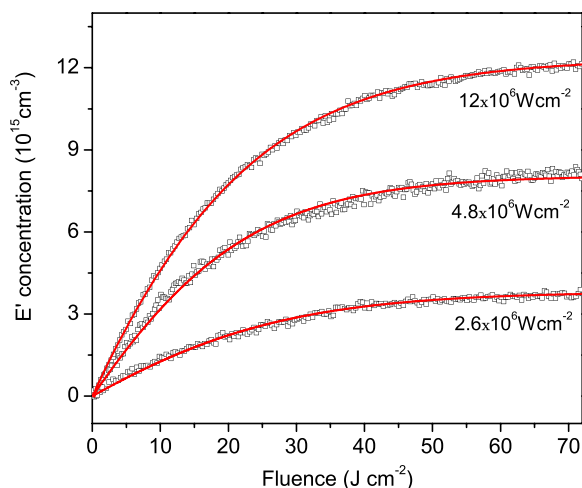
The experiments reported here were performed on Herasil 1 a-SiO<sub>2</sub> samples, of size 5 × 5 × 1 mm<sup>3</sup>, with an OH content of ~200 ppm and optically polished on all surfaces. The presence of Si–H groups was checked by preliminary Raman measurements showing their typical 2250 cm<sup>-1</sup> signal [20, 21]. The Si–H concentration was roughly estimated to be ~5 × 10<sup>17</sup> cm<sup>-3</sup>. In regards to the possible presence of H<sub>2</sub> already dissolved in the material prior to laser exposure, in previous experiments we found that the post-irradiation decay rate of the  $E'$  centres is controlled by radiolytic hydrogen generated together with  $E'$  by (1), at least for concentrations of  $E'$  starting from a few 10<sup>15</sup> cm<sup>-3</sup>. This fact allows us to fix an upper concentration limit for native H<sub>2</sub> of ~10<sup>15</sup> cm<sup>-3</sup> [15].

Samples were irradiated at room temperature perpendicularly to their minor surface by the fourth harmonic of the pulsed radiation emitted by a  $Q$ -switched Nd:YAG laser ( $\tau = 5$  ns duration,  $\Delta t = 1$  s interpulse, pulse energy  $h\nu \approx 4.7$  eV). The laser beam was checked to have a uniform intensity profile over a (6.0 ± 0.1) mm diameter circular spot; then, pulse energy was measured by a pyroelectric detector. Finally, the ratio of pulse energy to the beam section and duration gives the laser peak intensity  $\Gamma$ . We verified that during laser irradiation the temperature of the samples did not vary significantly from  $T_0 = 300$  K.

We performed eight irradiation sessions on different virgin samples at different laser peak intensities, from (2.6 ± 0.2) × 10<sup>6</sup> W cm<sup>-2</sup> to (19 ± 1) × 10<sup>6</sup> W cm<sup>-2</sup>, each session consisting of a few thousand pulses. We measured *in situ* the absorption profile of the sample in UV, once during each interpulse, by a single-beam AVANTES S2000 optical fibre spectrophotometer system, based on a CCD detector and working in the 200–400 nm spectral range. The difference OA profiles measured after different numbers of pulses  $N$  during an irradiation session (figure 1) show that laser radiation induces the growth of the 5.8 eV band of the  $E'$ -centre [1, 2]; the defect is absent in the as-grown material as checked by the absence of a paramagnetic signal in preliminary ESR measurements. The 5.8 eV band grows during irradiation without significant width variations. The small negative component at ~5.1 eV is due to the bleaching of the Ge-related B<sub>2β</sub> band [14, 15].



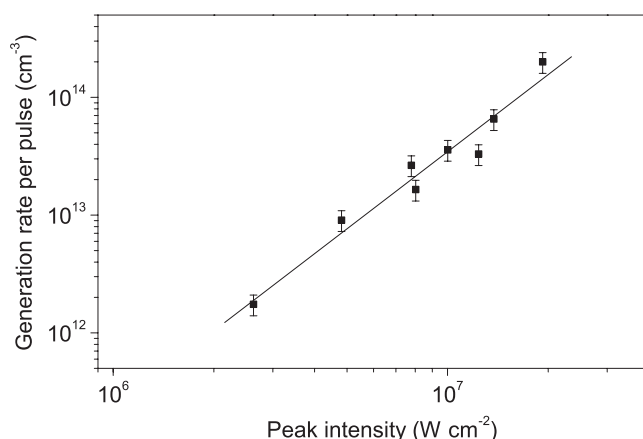
**Figure 1.** Induced OA measured *in situ* after different numbers of 4.7 eV laser pulses with  $\Gamma = 12 \times 10^6 \text{ W cm}^{-2}$  peak intensity. Inset: growth and decay of E' concentration, as calculated from the peak of the 5.8 eV OA.



**Figure 2.** Kinetics of [E'] (open symbols) during three irradiation sessions performed with different laser intensities. The continuous lines are least-square fits with analytical solutions of equation (4), with  $\alpha$  as a free fitting parameter.

(This figure is in colour only in the electronic version)

From the peak 5.8 eV absorption coefficient and the known absorption cross section [22], we calculated the concentration [E'] of the defects, which is plotted in figure 2 as a function of irradiation fluence ( $F = \Gamma \times \tau \times N$ ) for three representative irradiation sessions. We see that the kinetics show a saturation tendency above  $\sim 50 \text{ J cm}^{-2}$ , but the saturated concentration [E']<sub>S</sub> increases with laser intensity. We note also that the initial slope  $d[E']/dF$  ( $F = 0$ ) of the curves increases with  $\Gamma$ . The initial slope may be determined by a linear fit in the first  $\sim 3 \text{ J cm}^{-2}$ ; hence, the values so obtained are converted to generation rates per pulse, given by  $R = d[E']/dN = \Gamma \times \tau \times d[E']/dF$ ;  $R$  is plotted in figure 3 versus  $\Gamma$ . By a least-square fit of



**Figure 3.**  $E'$  initial generation rate per pulse against laser intensity. The line is a least-square fit of the data with the function  $y = ax^b$ , yielding  $b = 2.2 \pm 0.2$ .

these data with the function  $R = a\Gamma^b$  (the continuous line in the plot) we obtain  $b = 2.2 \pm 0.2$ ; this means that the behaviour of  $R$  is consistent with a quadratic dependence from  $\Gamma$ .

As discussed in the introduction, for this material exposed to 4.7 eV laser light  $E'$  centres are transient since they arise from the breaking of Si–H precursors [14, 15]. Indeed, as soon as the laser is switched off, we observe a progressive decay of the centres, bringing their concentration almost to zero in a few hours. As an example, in the inset of figure 1 we show the kinetics of  $[E']$  comprising also the first  $\sim 10^3$  s of the post-irradiation decay stage, for a sample irradiated with 1200 laser pulses of  $\Gamma = 12 \times 10^6 \text{ W cm}^{-2}$  peak intensity (the kinetics is plotted as a function of time). The post-irradiation decay was dealt with in previous papers [14, 15]; from now on, we will focus only on the generation stage of the process, which is the main interest of this paper.

Data in figure 3 permit us to address an important feature of the laser-induced breaking process of Si–H (reaction (1)). Indeed, the quadratic dependence of  $R$  on peak intensity demonstrates that two-photon processes are involved in  $E'$  generation. A two-photon mechanism is consistent with experimental and simulation data on the Si–H group: this centre does not show any measurable OA at energies below the silica bandgap, and its lowest transition is predicted at  $\sim 9$  eV, leading to an anti-bonding state [6, 23]. Hence, the simplest  $E'$  generation mechanism consistent with present results is two photon absorption (TPA) by Si–H leading to the excited state with consequent breaking of the bond. Yet, other nonlinear processes are conceivable, such as production of excitons by TPA followed by non-radiative decay on Si–H. Finally, we should consider the possibility of extrinsic impurities in the material playing some role in  $E'$  generation, since we showed that in synthetic  $\text{SiO}_2$  irradiated in the same conditions  $E'$  are not generated; impurities may for example serve as intermediate states in two step absorption assisting the generation of hole–electron pairs [24].

Several works in the literature have discussed the generation mechanisms of  $E'$  in silica under laser radiation, distinguishing between single- and multi-photon processes [3–7, 9–11, 25, 26], but most of them dealt with permanent defects, and only a few have directly observed *in situ* the transient  $E'$  centres originating from the Si–H precursor [10, 11, 25]. Only in [10] and [25] was the dependence on laser energy density of the initial generation rate of transient  $E'$  centres studied in synthetic  $\text{SiO}_2$  exposed to KrF (5.0 eV) or ArF (6.4 eV) laser radiation; it was reported to be respectively linear and sublinear.

These results are in disagreement with the quadratic dependence found here. At the moment the reason for this discrepancy is unclear, but it may be related to differences in the materials employed, leading to the activation of different mechanisms leading to Si–H breaking, or to the coexistence of (transient) E' centres not arising from Si–H.

Finally, it may be interesting to compare the present results with what is known about laser-induced Si–H breaking on Si/SiO<sub>2</sub> interfaces. In these systems, theoretical work has fixed the bonding–nonbonding electronic transition of Si–H to be at 8.5 eV [27], not far from the value of 9 eV found in a-SiO<sub>2</sub>; consistently, Si–H photolysis was observed to occur by single-photon absorption of F<sub>2</sub> laser (7.9 eV) radiation [19]. On the other hand, breaking of Si–H under less energetic photons occurs efficiently by a photothermal mechanism peculiar to the Si/SiO<sub>2</sub> system, in which the Si–H bond is broken by providing the ~2.6 eV dissociation energy by heating due to strong absorption of the laser light by the silicon substrate [19, 28, 29].

We now proceed to address the issue of quantitatively modelling the growth kinetics of the defects. The kinetics of E' (figure 2) show a saturation at high fluences: this fact cannot be due to exhaustion of the Si–H precursor, whose native concentration estimated from Raman measurements is more than one order of magnitude higher than [E']<sub>S</sub>. Moreover, [E']<sub>S</sub> is found to depend on Γ, whereas saturation by precursor exhaustion would fix [E']<sub>S</sub> to a value independent of irradiation conditions. Then, the saturation must be due to an equilibrium between generation and a concurrent depletion mechanism of the induced E' population. Due to the behaviour of E' in the post-irradiation stage, we argue that reaction (2) is also effective in the interpulse time span, and is a possible candidate for the depletion mechanism.

In this scheme, the kinetics of [E'] on the scale of many laser pulses (figure 2) should be described by the following rate equation, provided that *N* is approximately treated as a continuous variable:

$$\frac{d[E']}{dN} \approx \frac{\Delta[E']}{\Delta N} \approx R - 2k_0[E'][H_2]\Delta t = R - k_0\Delta t[E']^2 \quad (3)$$

where *R* is the generation rate, which equals the initial growth slope of the kinetics (figure 3), while the negative term accounts for the decrease of [E'] during the Δ*t* = 1 s interpulse due to reaction (2), calculated within the stationary-state approximation<sup>1</sup> for H<sup>0</sup> (the factor 2 derives from each H<sub>2</sub> passivating two E') [14, 30]. For the last equality we have used the relation [H<sub>2</sub>] = [E']/2, which derives from H<sup>0</sup> and E' being generated together and from the absence of dissolved H<sub>2</sub> prior to laser exposure [15]. The reaction constant *k*<sub>0</sub> between E' and H<sub>2</sub> at room temperature had already been measured to be *k*<sub>0</sub> = (8.3 ± 0.8) × 10<sup>-20</sup> cm<sup>3</sup> s<sup>-1</sup> [15].

We found that equation (3) is in disagreement with the experimental kinetics. In particular, the saturation concentration of E', found from (3) when d[E']/d*N* = 0, is given by [E']<sub>SP</sub> = (R/*k*<sub>0</sub>Δ*t*)<sup>1/2</sup>; for instance we obtain [E']<sub>SP</sub> = 2.0 × 10<sup>16</sup> cm<sup>-3</sup> for the kinetics at Γ = 12 × 10<sup>6</sup> W cm<sup>-2</sup>, which is higher than the actual [E']<sub>S</sub> = 1.2 × 10<sup>16</sup> cm<sup>-3</sup> (figure 2). A similar situation is found for all the kinetics. Moreover, we verified that the agreement with experimental data is not improved by taking into account the statistical distribution of the diffusion parameters of H<sub>2</sub> related to the amorphous structure of the silica matrix [14, 16]. This implies that annealing driven by H<sub>2</sub>-diffusion (reaction (2)) significantly slows down the growth of the defects, but alone is insufficient to explain the observed saturation concentrations, which are still lower than predicted; for this reason, an additional negative term has to be added to the rate equation.

<sup>1</sup> The stationary-state approximation for H<sup>0</sup> automatically takes into account both reaction (2) and the reaction between E' and H<sup>0</sup> made available on the right-hand side of (2).

On this basis, we found empirically that all the kinetics can be well fitted by adding a linear term to (3) as follows:

$$\frac{d[E']}{dN} = R(1 - \alpha[E']) - k_0 \Delta t [E']^2 \quad (4)$$

this being equivalent to supposing a (linear) concentration dependence of the generation rate. In detail, best-fit curves of figure 2 were obtained by fitting to experimental data solutions of equation (4), depending on the free parameter  $\alpha$ . The values of  $\alpha$  all fall in the interval  $(5.7 \pm 1.4) \times 10^{-17} \text{ cm}^3$ .

A possible explanation of the linear term  $-R\alpha[E']$  may be the reaction of  $E'$  with molecular hydrogen already dissolved in the sample before laser exposure, in concentration  $[H_2]_0$ . In this case, the coefficient  $-R\alpha$  should be independent of laser intensity and, on the basis of the above reported upper limit  $[H_2]_0 < 10^{15} \text{ cm}^{-3}$ , it should equal  $-2k_0 \Delta t [H_2]_0 \sim 10^{-4}$ . However, this is almost two orders of magnitude smaller than the values of  $R\alpha$  coming from the fits, at least at the highest laser intensities. So, some other mechanism has to be invoked to explain the origin of the linear term. In this respect, we propose a simple qualitative interpretation, based on a more accurate discussion of the generation process (1): in general, a  $H^0$  produced by (1) diffuses in the matrix and may experience two different fates: it can either meet another  $H^0$  and dimerize in  $H_2$  or it can come across an  $E'$  and passivate it; for this reason, apart from slow annealing due to reaction (2), the  $E'$  centres undergo a much faster decay (FD) due to recombination with a portion of the  $H^0$  population made available by each pulse. Moreover, the portion of  $H^0$  involved in the FD is expected to increase with  $E'$  concentration, which enhances the probability of encountering an  $E'$  before meeting another  $H^0$ . A FD stage with similar features was directly observed *in situ* for non bridging oxygen hole centres (NBOHC) produced by  $F_2$  laser irradiation at  $T = 300 \text{ K}$ , and occurs on a typical timescale which is shorter than the 1 s interpulse [16]. Since the FD cannot be directly observed with the time resolution available here, it is incorporated *de facto* in the generation term, which must actually be interpreted as the net concentration of  $E'$  generated by (1) and surviving fast recombination with  $H^0$ .<sup>2</sup> Now, given that the portion of  $H^0$  quickly recombining with  $E'$  must increase with  $E'$  concentration as the irradiation session progresses, we expect a consequent reduction of the generation rate from its initial value  $R$ , which to a first approximation can be represented by a linear term in  $[E']$ , i.e.  $-\alpha[E']$  in (4). We acknowledge that measures resolved on a timescale shorter than the interpulse are required to confirm this interpretation by a thorough investigation of the dynamics involving fast atomic hydrogen diffusion. However, we point out that the main advantages of the simple model proposed here are that it permits us to understand the kinetics and the saturation of  $E'$  as a consequence of hydrogen-related reactions, and it is able to reproduce independent datasets coming from several irradiation sessions with only one free parameter, whose origin can be understood on a qualitative basis.

In conclusion, we studied the generation of  $E'$  centres from Si-H groups in a-SiO<sub>2</sub> under pulsed 4.7 eV laser radiation. The dependence of the initial generation rate on laser intensity is quadratic, demonstrating a two-photon mechanism for  $E'$  generation. The kinetics and the saturation of the process are the result of competition between the action of radiation and the annealing of  $E'$  due to reaction with hydrogen arising from the same precursor. On this basis, a rate equation model was proposed and tested against experimental data.

<sup>2</sup> It is worth noting that the FD due to partial recombination with the transient  $H^0$  population available just after each pulse is not taken into account in the  $-2k[E'][H_2]$  term, which is founded on the stationary state approximation for  $H^0$ , and so takes into account only  $H_0$  produced by (2).

## Acknowledgments

The authors thank Professor Boscaino and the group in Palermo for support and enlightening discussions, Y Ouerdane and K Médjahdi from Université J Monnet in Saint Etienne (France) for Raman measurements and G Napoli, G Lapis for technical support.

## References

- [1] Weeks R A and Nelson C M 1960 *J. Appl. Phys.* **31** 1555
- [2] Pacchioni G, Skuja L and Griscom D L (ed) 2000 *Defects in SiO<sub>2</sub> and Related Dielectrics: Science and Technology* (Netherlands: Kluwer–Academic) pp 73–196
- [3] Tsai T E, Griscom D L and Friebele E J 1988 *Phys. Rev. Lett.* **61** 444
- [4] Arai K, Imai J, Hosono H, Abe Y and Imagawa H 1988 *Appl. Phys. Lett.* **53** 1891
- [5] Nishikawa H, Nakamura R, Tohmon R, Ohki Y, Sakurai Y, Nagasawa K and Hama Y 1990 *Phys. Rev. B* **41** 7828
- [6] Imai H, Arai K, Hosono H, Abe Y, Arai T and Imagawa H 1991 *Phys. Rev. B* **44** 4812
- [7] Imai H and Hirashima H 1994 *J. Non-Cryst. Solids* **179** 202
- [8] Afanas'ef V V and Stesmans A 2000 *J. Phys.: Condens. Matter* **12** 2285
- [9] Kajihara K, Ikuta Y, Hirano M and Hosono H 2003 *J. Non-Cryst. Solids* **322** 73
- [10] Leclerc N, Pfeleiderer C, Hitzler H, Wolfrum J, Greulich K-O, Thomas S and Englisch W 1992 *J. Non-Cryst. Solids* **149** 115
- [11] Smith C M, Borrelli N F and Araujo R J 2000 *Appl. Opt.* **39** 5778
- [12] Edwards A H, Pickard J A and Stahlbush R E 1994 *J. Non-Cryst. Solids* **179** 148
- [13] Radzig V A, Bagratashvili V N, Tsygina S I, Chernov P V and Rybaltovskii O 1995 *J. Phys. Chem.* **99** 6640
- [14] Messina F and Cannas M 2005 *Phys. Rev. B* **72** 195212
- [15] Messina F and Cannas M 2005 *J. Phys.: Condens. Matter* **17** 3837
- [16] Kajihara K, Skuja L, Hirano M and Hosono H 2002 *Phys. Rev. Lett.* **89** 135507  
Kajihara K, Skuja L, Hirano M and Hosono H 2001 *Appl. Phys. Lett.* **79** 1757
- [17] Poindexter E H 1989 *Semicond. Sci. Technol.* **4** 961
- [18] Brower K L 1989 *Semicond. Sci. Technol.* **4** 970
- [19] Pusel A, Wetterauer U and Hess P 1998 *Phys. Rev. Lett.* **81** 645
- [20] Shelby J E 1994 *J. Non-Cryst. Solids* **179** 138
- [21] Schmidt B C, Holtz F M and Bény J-M 1998 *J. Non-Cryst. Solids* **240** 91
- [22] Cannas M, Costa S, Boscaino R and Gelardi F M 2004 *J. Non-Cryst. Solids* **337** 9
- [23] Robertson J 1998 *The Physics and Technology of Amorphous SiO<sub>2</sub>* ed R A B Devine (New York: Plenum) p 91
- [24] Cannas M and Messina F 2005 *J. Non-Cryst. Solids* **351** 1780
- [25] Shimbo M, Nakajima T, Tsuji N, Kakuno T and Obara T 2001 *Japan. J. Appl. Phys.* **40** 5962
- [26] Zoubir A, Rivero C, Grodsky R, Richardson K, Richardson M, Cardinal T and Couzi M 2006 *Phys. Rev. B* **73** 224117
- [27] Becker R S, Higashi G S, Chabal Y J and Becker A J 1990 *Phys. Rev. Lett.* **65** 1917
- [28] Brower K L 1990 *Phys. Rev. B* **42** 3444
- [29] Tuttle B and Van de Walle C G 1999 *Phys. Rev. B* **59** 12884
- [30] Griscom D L 1985 *J. Appl. Phys.* **58** 2524