First-principles molecular-dynamics simulations of a hydrous silica melt: Hydrogen diffusion mechanisms and electronic properties

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ABSTRACT

We study a sample of liquid silica containing 3.84 wt.% H_2O with *ab initio* molecular dynamics simulation in its liquid state at temperatures of 3000 K and 3500 K. At these temperatures the liquid can be brought into equilibrium after several picoseconds. Hence we are able to investigate possible diffusion mechanisms for hydrogen atoms. It turns out that intermediate states in the liquid play a decisive role for the diffusion of hydrogen. Quenches of selected configurations to ambient temperature allow us to study the electronic structure of the material. In particular we find electronic states in the band gap of amorphous silica. The correlation of these electronic states with the structural intermediate states that are present in our system and which we make responsible for the hydrogen diffusion has already been discussed for a long time.

Keywords: hydrous silica, *ab initio* molecular dynamics, hydrogen diffusion, electronic structure

1 Introduction

The design of appropriate dielectrics for semiconductor devices has been one of the challenging tasks in micro electronics over the past decades [1], [2]. This research was driven by the requirement of high storage capacity at low dielectric constant. With progressing miniaturization in forthcoming microchip generations the dielectric constant of the oldfashoined dielectric silicon dioxide (k=3.9 to 4.2) has to be decreased. The development of dielectrics with ultra low dielectric constants is inevitable. Silica (SiO_2) replacements are still under (partly discouraging) investigation [1]. In addition, since device manufacturing is a highly cost-driven business, replacement materials have to be easily and cheaply synthesizable. Appropriate candidates are not yet found and therefore silica is still the material of choice for oxide gates.
One of the reasons for the degradation of dielectric properties of silica are impurities that produce charges in the bulk material and/or at the silica silicon interface. Hydrogen and/or water once introduced as passivant for interface traps or at other stages of the fabrication process was made responsible for various instabilities of the dielectric SiO_2. Such instabilities or defects like Si-O dangling bonds are naturally electrically active and hence degrade the insulating properties. Generally, water is dissolved partly to SiOH groups when added to silica at elevated temperatures, a balance that follows the equation

$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}- \; + \; \mathrm{H_2O} \; \longleftrightarrow \; 2(\mathrm{SiOH})$$

Many other reactions that set off hydrogen atoms, hydrogen molecules or oxonium ions have been proposed [3]. However, the formation of the electrical active centers in combination with the hydrogen and water diffusion has, according to ref. [3], never been understood.
At this point, the analytic power of molecular dynamics computer simulations comes into play. Unfortunately, they so far struggled with the difficulty of finding appropriate potentials describing all possible water silica adducts (water molecules, SiO-H groups, Si-H groups, oxonium ions,..). This problem can be overcome with the use of recently developed *ab initio* techniques. Especially *ab initio* Car-Parrinello molecular dynamics techniques [4] have already been successfully applied to a considerable number of silica systems [5].

2 The Method

Here we present an *ab initio* molecular dynamics approach in order to understand the dissolution and diffusion of water in bulk amorphous silica. In a first stage we studied a melt of SiO_2 with 3.84 wt.% H_2O (30 SiO_2 units and 4 H_2O units). The calculations were stably driven over a time of 25 ps with the Car-Parrinello code CPMD [6] in the liquid state at temperatures of 3000 K and 3500 K. The electronic system was treated with a density functional approach in a general gradient approximation using the PBE functional [7], [8] and for the core electrons we used Troullier-Martins pseudopotentials [9]. The technical details of the simulation are given elsewhere [10]. At these high temperatures the liquid attains equilibrium after the mentioned time. The diffusion process of hydrogen is, for the first time, directly observable in the time window present days *ab initio* molecular dynamics simulations can offer. The high water concentration chosen in this model allows us

to obtain a statistically significant picture of the transition states that are involved in the hydrogen diffusion. The question whether an extrapolation of the diffusion processes to lower temperatures (especially below the glass transition temperature) is possible remains to be addressed. However, quenching the equilibrated liquid to ambient temperature allows us comparisons with experimental data on the structure. Due to the *ab initio* character of the simulation, the electronic structure of the material is accessible in particular.

3 Structure

The structure of the liquid has been analyzed regarding commonly discussed quantities like the radial pair distributions, angle distributions, coordination numbers and Q^n species [10]. These quantities indicate that the water is dissolved and forms SiOH groups with the SiO_2 matrix. Hence the silica tetrahedral network is partially broken. Free water molecules, free hydrogen atoms or molecules and SiH units are not present. The nature of the OH bonds is highly covalent. The Si-OH groups constitute "dead-end-pieces" in the structure having a high radial mobility. This radial mobility facilitates the approach of an SiOH oxygen to a second silicon atom and therefore the formation of oxygen tri-clusters of the form $\overset{\text{Si}}{\text{Si}}>\text{OH}$ (bridging hydroxyl group). Since the threefold coordinated oxygen atoms violate the stoichiometry, the system aims for a re-compensation of this stoichiometry violation. Such a charge re-compensation can only be performed by one fold coordinated oxygen atoms. In fact the detailed analysis of the structure revealed the presence of SiO dangling bonds. Water like structures are also found in the liquid but occur much less than the dangling bonds and the $\overset{\text{Si}}{\text{Si}}>\text{OH}$ bridging hydroxyl groups. Those water molecules are not free but mostly attached to a silicon atom in the form $\overset{\text{H}}{\text{H}}>\text{OSi}$ which constitutes another oxygen tri-cluster. A snapshot of the structure at 3500 K including oxygen tri-clusters and SiO dangling bonds is displayed in Fig. 1.

4 Hydrogen Diffusion

In this section we analyze the mechanisms of hydrogen transport in the liquid. In particular we investigate the contribution of the intermediate states displayed in Fig. 1. Since we know from Section 3 that the hydrogen atoms are accommodated in the form of OH groups, the question of hydrogen transport reduces to that of the formation, the rupture and the motion of OH groups. Since we find two oxygen coordinated hydrogen atoms and almost no zero oxygen coordinated hydrogen atoms, it becomes also evident that hydrogen atoms do not drift

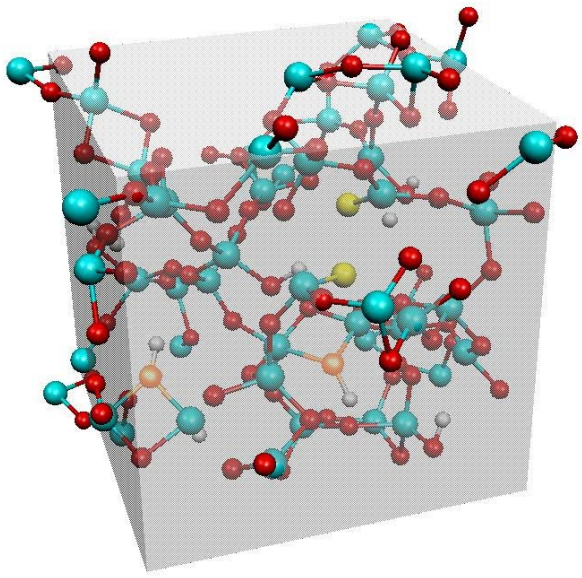

Figure 1: Snapshot of the structure at 3500 K (silicon green, oxygen red, hydrogen white). The structure contains intermediate states like SiO dangling bonds (yellow) and oxygen tri-clusters (orange).

freely through the silica network if an OH bond is broken. Furthermore, in almost all cases, a second OH bond (of the same hydrogen atom) is formed before the rupture of the initial OH bond. Analyzing the nearest neighbor environments of the oxygen atom of the initial OH bond and of the oxygen atom of the formed OH bond, we find the following balances:

$$\text{SiOH} + \text{O} < \overset{\text{Si}}{\text{Si}} \longleftrightarrow \text{SiO} + \text{HO} < \overset{\text{Si}}{\text{Si}} \qquad (1)$$

$$\overset{\text{Si}}{\text{Si}} > \text{OH} + \text{O} < \overset{\text{Si}}{\text{Si}} \longleftrightarrow \overset{\text{Si}}{\text{Si}} > \text{O} + \text{HO} < \overset{\text{Si}}{\text{Si}} \qquad (2)$$

$$\text{SiOH} + \text{HOSi} \longleftrightarrow \text{SiO} + \overset{\text{H}}{\text{H}} > \text{OSi} \qquad (3)$$

$$\text{SiO} < \overset{\text{H}}{\text{H}} + \text{O} < \overset{\text{Si}}{\text{Si}} \longleftrightarrow \text{SiOH} + \text{HO} < \overset{\text{Si}}{\text{Si}} \qquad (4)$$

Obviously, as already anticipated above, the SiO dangling bonds and the two oxygen tri-clusters $\overset{\text{Si}}{\text{Si}}>\text{OH}$ (the bridging hydroxyl group) and $\overset{\text{H}}{\text{H}}>\text{OSi}$ (the water containing tri-cluster) constitute the acceptor and donator states for hydrogen transfer reactions. Hydrogen atoms can be transfered to the under saturated SiO dangling oxygen (reaction (1) and (3)) as well as saturated oxygens as the bridging oxygen $\overset{\text{Si}}{\text{Si}}>\text{O}$ as indicated in reactions (1), (2) and (4) and an hydroxyl group oxygen

(reaction (3) and (4)). Note that, by a hydrogen transfer to the latter one, the formation of a water-like unit of the form SiO $<^{H}_{H}$ occurs.
In Fig. 2 we present the probabilities of the decay products for the OH ruptures in reactions (1) to (4). Note that equations (1)-(4) are balances and hence forward and back reactions are counted. According to Fig. 2, the bridging hydrogen group $\equiv Si-O-Si>OH$ is the donator with the highest probability, followed by the SiOH unit and the water containing tri-cluster SiO $<^{H}_{H}$.

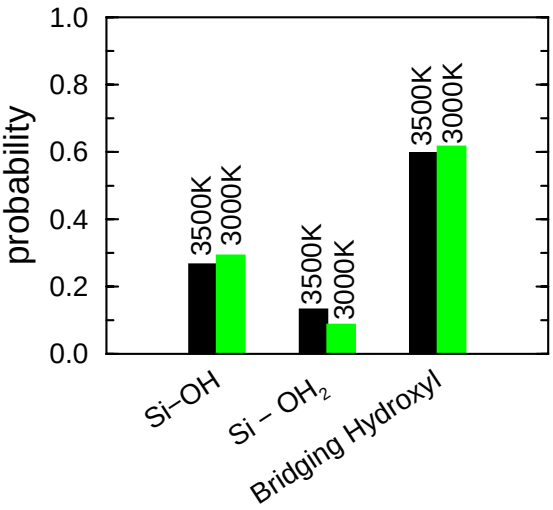

Figure 2: The hydrogen donators SiOH groups, water tri-cluster SiO$<^{H}_{H}$ and bridging hydroxyl groups $\equiv Si-O-Si>OH$ and their relative contribution to hydrogen release.

Apart from the hydrogen diffusion reactions associated to OH ruptures, we have also evidence for the transport of OH units. These hydroxyl units can be transfered from one silicon atom to another involving again a bridging hydroxyl group as intermediate state. The corresponding equation reads as follows:

$$\text{SiOH} + \text{Si} \longleftrightarrow \equiv Si-O-Si> \text{OH} \longleftrightarrow \text{Si} + \text{HOSi} \qquad (5)$$

5 Electronic Structure

As already discussed above, the major concern associated to hydrogen in silicon technology is the creation of electrical active deficiencies like SiO dangling bonds (according to reactions (1) and (3)). The insulating properties of bulk silica are due to its band gap of ≈ 9 eV . It is well known that hydrogen (atomic or molecular), molecular water, and also SiOH groups do not possess electronic states in the SiO_2 band gap [11]. If electronic properties are degraded, the degradation has to be due to the intermediate states like the dangling bonds. Hence it is mandatory to investigate the influence of these states on the electronic structure of the material with particular attention to the band gap. It has already been proposed that the SiO dangling bond created by reactions (1) and (3) produces a gap state at around 2 eV [11].

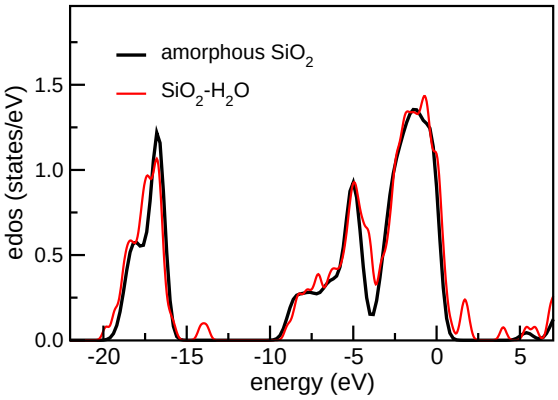

Figure 3: Electronic density of states (edos) of a quenched hydrous configuration comprising two SiO dangling bonds compared to the edos of amorphous silica.

Performing ultra rapid quenches from the liquid structure to 300 K, we can freeze configurations with SiO dangling bonds and other intermediate states and study their electronic properties. We note that a significant underestimation of the band gap is usual in DFT [12]. Nevertheless it is recognized in literature that the electronic states are well represented in pure silica, even if the DFT band gap is not greater than 5 eV [13]. In Fig. 3 we present the electronic density of states (edos) of a typical frozen configuration (including SiO dangling bonds that are stabilized by weak hydrogen bonds) compared to the one of bulk amorphous silica. We note that the water addition does not alter the electronic properties of silica dramatically. Nevertheless band gap states emerge. The determination of the maximally-localized Wannier functions (Wannier centers) [14] allows a description of the charge distribution in terms of well-defined and localized functions. For instance by a projection of the Wannier functions onto the Kohn-Sham density of states, we could indeed assign the peak at 2 eV in Fig. 3 to the electronic states associated to the SiO dangling bonds.
The most important question for the dielectric properties of the material is of course whether the transition states are electrically charged and if this charge is mobile. A well known tool to investigate this in quantum chemistry are the Hirshfeld charge density deformations [15]. These charges represent, in principle, the difference of the charge density of the bonded atom with respect to the one of the free atom. Integration of the Hirshfeld charge density over the (atomic) volume gives the total electronic charge of an atom $\mathcal{Q}_i$. The addition of the nuclear charge Z_i yields the net atomic charge q_i.

These net atomic charges are given in Table 1. Table

species	$q_i(SiO_2\text{-}H_2O)$	$q_i(SiO_2)$
Si	$+0.220 \pm 0.031$	$+0.218 \pm 0.010$
bridging oxygen	-0.101 ± 0.026	-0.109 ± 0.007
SiOH oxygen	-0.116 ± 0.021	-
SiO dangling O	-0.277 ± 0.046	-
bridging hydroxyl O	$+0.023 \pm 0.000$	-
H	$+0.038 \pm 0.030$	-

Table 1: Average Hirshfeld net atomic charges (average $\pm$ sigma) for the hydrous silica system and pure silica [13] . For hydrous silica the average was taken over the atoms of the same kind of one configuarion quenched to 300 K.

1 shows that the net atomic charges for the silicon and bridging oxygen atoms in the hydrous sample are very similar to those of pure silica from Ref. [13]. On the other hand, the charges of the different oxygen species in the hydrous sample differ considerably. In particular the SiO dangling bonds exhibit a net charge that is more than twice as high as the bridging oxygens' one. It becomes evident that these bonds constitute indeed electrical active centers in the network. In contrast, the tri-cluster is undersaturated with electrons and exhibits a positive charge.

6 Summary and Perspectives

In this work, we have studied the principle hydrogen diffusion mechanisms in hydrous silica and the important intermediate states for this diffusion were revealed. Especially the existence of the long-time predicted SiO dangling bond that is generated due to a hydrogen release could be confirmed. Quenches of configurations from the liquid to ambient temperature allowed conclusions on the electronic structure. It becomes evident that water addition and the resulting defects in the network are indeed responsible for states in the band gap and hence degrade the insulating properties of the material.
Several dopants to silica that should suppress hydrogen diffusion have been proposed [2]. The most prominent among them are fluorine and nitrogen. We point out that the presented method of investigation will be applicable also to these systems and that the suppression of hydrogen diffusion under parallel surveillance of the electronic properties could be studied.

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