High-temperature ac conductivity of amorphous SiO$_2$: Fused silica and thin thermal films

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High-temperature ionic conductivity of both fused silica and thin films thermally grown on a silicon substrate has been investigated in the temperature ranges 700–1400 and 570–830 K, respectively, by means of impedance spectroscopy. The results for both types of materials may be interpreted as being due to the existence of an extrinsic conduction mechanism related to the presence of dissociated sodium ions. The numerical analysis of the experimental results led to values of 1.3 and 0.6 eV for the dissociation and migration energies, respectively. The dissociation energy turns out to be in good agreement with the value obtained in crystalline quartz and related to the aluminum-alkali ($[AlO_4 - M]^0$) center; moreover, good agreement is also found between the mobility value obtained here and literature data evaluated on thin films by different electrical techniques. No influence of hydrogen content on alkali transport was found by considering wet and dry samples, at variance with results previously obtained on crystalline quartz. [S0163-1829(99)14515-6]

I. INTRODUCTION

The understanding of microscopic processes governing ionic transport in SiO$_2$ is an important aspect both for the basic understanding of the material properties and for the improvement of its performances in microelectronics device technology. While extensive investigation was devoted to ionic transport mechanisms in heavily doped glasses (see Refs. 1–3), fewer studies dealt with bulk amorphous silica of good purity (with impurity concentrations of the order of 10^2 ppm or lower): some discrepancies can be found in the activation energies for the conductivity, spreading from 0.9 to 1.6 eV for sodium ions, which could be related to the different temperature intervals considered (though rarely exceeding 900 K) and to different measurement techniques including both dc and ac methods.[4–12] On the other hand, attention was given also to ionic transport phenomena in thin SiO$_2$ films grown on silicon, due to the recognized electrical instabilities of electronic devices in the presence of alkali contaminations even in low concentrations (Ref. 13, and references therein).

In previous work dealing with ac conductivity of crystalline quartz with an impurity content of the order of 1–10 ppm,[14–16] it was found that ionic conductivity is due to the presence of extrinsic point defects: among the possible impurities that may be present, major attention was given to trivalent substitutional ions, most notably Al substituting for Si. The most common compensator of the charge deficiency due to Al in ''as-grown'' synthetic crystals are alkalis (M), giving rise to $[AlO_4 - M]^0$ centers. Although hydrogen impurities do not contribute directly to ionic conductivity as charge carriers, an indirect role on alkali transport was put in evidence in hydrogen-rich (as ''H-swept'') SiO$_2$ crystals: it appeared that the presence of hydrogen could lower the conductivity of alkali ions, giving rise to a sort of ''immobilization'' effect. The experimental results were recently interpreted on the basis of a model featuring two interacting dissociation reactions of the aluminum-alkali ($[AlO_4 - M]^0$) and aluminum-hydrogen ($[AlO_4 - H]^0$) centers, and the occurrence of a gradual decrease of hydrogen concentration due to high temperature treatments in vacuum:[16] in fact,

the decrease of hydrogen concentration during the annealings was later confirmed by thermal-desorption measurements, which put in evidence that desorption of H$_2$ molecules occurs at temperatures higher than 200 °C.[17] In this way, it was possible to account for the observed marked increase of the conductivity during prolonged annealings in the 700–1300-K range. Numerical analysis of the data led to values of 1.19 and 0.25 eV for the dissociation and migration energies, respectively.[16] The value of the migration energy is in fact relative to the electric-field orientation along the c optical axis, where the migration of alkali ions is favored by the presence of open channels. It was found that the conductivity is highly anisotropic, since values measured perpendicular to the optical axis are at least two orders of magnitude lower.[14]

In this work, we have extended ac conductivity studies to amorphous silicon dioxide, both in bulk and in thin film form thermally grown on a silicon substrate. Our aim was to investigate the role of the amorphous structure in modifying the transport parameters of the residual alkali impurities, which are known to be mobile; moreover, we wanted to verify whether an intrinsic ionic conductivity contribution, possibly due to oxygen-related defects such as oxygen vacancies and peroxy linkages, could be put into evidence as well. Complex impedance measurements were used to avoid polarization and electrode effects, and were carried on in a wide temperature range. The results are also discussed in comparison with those already obtained for crystalline quartz.

II. EXPERIMENTAL CONDITIONS

Two types of bulk silica were examined, both produced from natural quartz: (i) Pursil K, a dry silica with an OH content less then 20 ppm purchased from Electro Quartz (Nemours, France); and (ii) Herasil, a wet silica with an OH content of approximately 130–180 ppm purchased from Heraues (Hanau, Germany). Samples of these two types are characterized by a content of metallic impurities of approximately 10–50 ppm of aluminum ions and about 1–3 ppm of alkali ions (data supplied by the producers). For the imped-
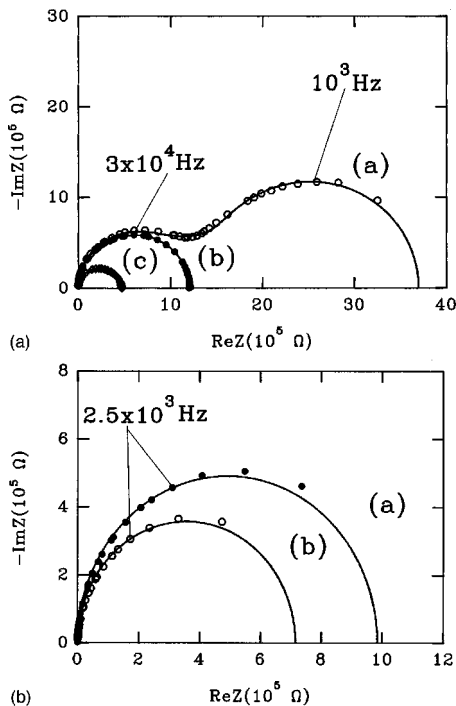
FIG. 1. (a) Complex impedance spectra of Pursil K at T = 970 K performed in different conditions: (curve a), 5-mm thickness, unmetallized surfaces; (curve b), 5-mm thickness, Cr-metallized surfaces; (curve c), 2-mm thickness, Cr-metallized surfaces. Continuous lines: numerical fits of the experimental data. (b) Complex impedance spectra of thin thermal films performed at 830 K (curve a), 13 420-Å-thick sample; (curve b), 8360-Å-thick sample. Continuous lines: numerical fits of the experimental data.

ance measurements, both bare and Cr-coated surfaces were used.

Thin films of SiO_2 were provided by ST-Microelectronics, (Agrate Brianza, Italy): they were thermally grown on a silicon substrate, of two different thicknesses, 13 420 and 8360 Å (this lower thickness was obtained by etching originally 13 420-Å-thick oxides with HF at 1:10 concentration). Both dry (grown at 1100 °C) and wet (grown at 920 °C) samples were examined, and aluminum dots (2-mm diameter) were used as electrodes. The technology used for their growth is in accordance with Ref. 18, and so these layers are characterized by an alkali concentration (mainly sodium) lower than 10^{-1} ppm.

Complex impedance measurements were performed in a homemade condenser kept in vacuum atmosphere (10^{-5} torr) in the temperature ranges 700–1400 and 570–830 K for bulk silica and thin films, respectively, by a Hewlett-Packard 4284a impedance bridge (frequency interval 20 Hz–1 MHz). The electrodes were 1-mm-thick tungsten plates; the metallic coatings on the samples had the beneficial effect of eliminating the surface contributions, as will be commented upon in Sec. III. The overall sensitivity of the apparatus, taking into account both the sensitivity of the impedance bridge and the presence of temperature dependent leakage components of the measurement condenser, was evaluated to be better than $10^{-8}\ \Omega^{-1}$ up to 800 K, being reduced to approximately $10^{-7}\ \Omega^{-1}$ at higher temperatures.

In order to obtain complementary information on the behavior of OH groups in wet bulk silica, optical-absorption
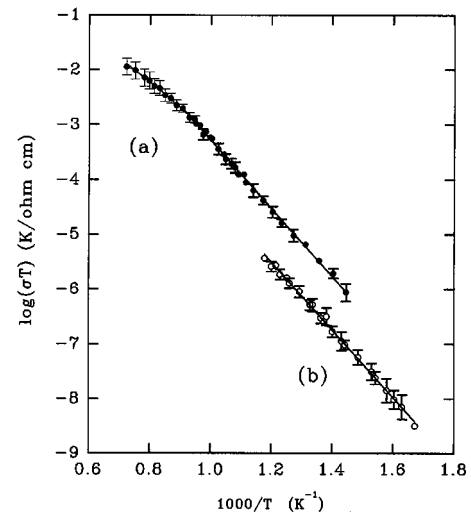

FIG. 2. Arrhenius plot of the ionic conductivity of (a) bulk fused silica and (b), thin thermal films. Continuous lines: numerical fits of the experimental data.

measurements were also performed at room temperature, by a Cary 2300 spectrophotometer, in the wave-number range 3250–4250 cm^{-1}.

III. RESULTS AND DISCUSSION

Figure 1(a) displays impedance spectra of a Pursil K sample at 970 K obtained in different experimental conditions, i.e., with a 5-mm sample thickness and unmetallized (curve a) or Cr-metallized (curve b) surfaces, and with 2-mm thickness [metallized surfaces, curve c]: in a complex impedance plane, each parallel RC circuit gives rise to a semicircle, the value of the resistance being evaluated by the intersection with the real axis.[19] The bulk component could be well fitted by a single RC element at all the investigated temperatures. The influence of the RC element due to surface contributions is evident in curve a, where, besides the semicircle due to the bulk of the sample, an additional impedance component is also present at low frequencies. The frequencies corresponding to the maxima of the semicircles of curve a, for which the condition $2\pi\nu = (RC)^{-1}$ holds, are also reported. Figure 1(b) displays impedance spectra of thin films of 13 240 (curve a) and 8360 Å (curve b), obtained at 830 K: in this case, only the high-frequency portion of the bulk semicircle is detected in the available frequency window.

In Fig. 2 we show the temperature dependence of the conductivity of fused silica (curve a) and of thin films (curve b): the variation of the conductivity extends over several decades in the investigated temperature ranges, with a monotonically decreasing slope at high temperatures observable in bulk material. The error bars evaluated at each temperature by considering several measurements are also displayed. It is important to remark that no significant variations were observed by considering wet and dry samples, indicating that hydrogen impurities do not play a direct role as charge carriers at least in this temperature region; thus this figure is well representative of the behavior of both wet and dry samples. In order to investigate possible modifications of hydrogen content as a consequence of the thermal treatment during conductivity measurements, the concentration of hydrogen impurities in wet samples was monitored by infrared-absorption spectroscopy performed on fused silica before and after a conductivity run performed in vacuum up to 1400
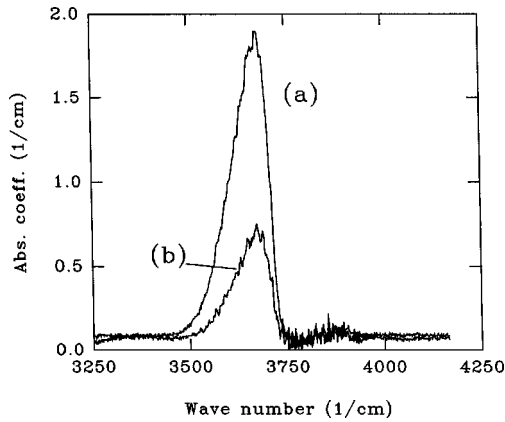
FIG. 3. Optical-absorption spectra of wet fused silica performed at room temperature: (curve *a*) as-received sample; (curve *b*) after a conductivity run up to 1400 K and lasting 10 h.

K, and lasting 10 h. Optical-absorption spectra are displayed in Fig. 3: the intensity of the strong and composite band around 3700 cm^{-1} (due to OH stretching vibrations[20]) shows a marked decrease following the thermal treatment during measurement, suggesting that desorption of hydrogen impurities possibly occurred, as already observed in crystalline quartz: however, no significant changes of the conductivity in the wet samples during subsequent measurements were observed, at variance with the results previously obtained on crystalline quartz, which showed a strong conductivity increase as a consequence of hydrogen desorption.[17]

In analogy with the results already obtained for crystalline quartz, it is proposed that alkali ions act as charge carriers in the silica forms under investigation. As already mentioned in Sec. I, in that case a strong dependence of the alkali conductivity upon the hydrogen content was observed, and the results were interpreted by considering the presence of two interacting dissociation reactions, of the aluminium-alkali ($[AlO_4-M]^0$) and aluminium-hydrogen ($[AlO_4-H]^0$) centers. Conversely, no significant conductivity differences were observed in the amorphous silica forms with different hydrogen content considered in this investigation. Thus at a first approximation a simpler approach can be used, with the assumption that only $[AlO_4-M]^0$ centers can be considered, and that the conductivity is governed uniquely by the dissociation of alkali ions (M) from these centers, according to the reaction
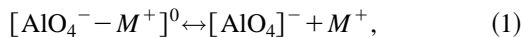
$$[AlO_4{}^- - M^+]^0 \leftrightarrow [AlO_4]^- + M^+, \qquad (1)$$

and their subsequent migration. The temperature-dependent concentration of free alkali ions can be derived by the mass-action relation of Eq. (1),[14]

$$\frac{[AlO_4]^-[M]^+}{[AlO_4-M]^0} = K(T) = \exp(-E_D/k_bT), \qquad (2)$$

where $[AlO_4]^-$, $[M]^+$ and $[AlO_4-M]^0$ are the atomic fractions, relative to silicon atoms, of dissociated aluminium ions, alkali ions, and associated pairs, respectively, E_D is the dissociation energy of the $[AlO_4-M]^0$ center, and k_b is Boltzmann's constant. Since in the present picture $[AlO_4]^-$ and $[M]^+$ are formed together, their concentrations can be taken as equal. By using the symbol m to denote the concentration of dissociated $[AlO_4]^-$ and $[M]^+$, and m_0 to denote the total atomic fraction of $[AlO_4-M]^0$ centers prior to dis-

sociation, $K = \exp(-E_D/k_bT)$, Eq. (2) can be written as $m^2 = (m_0 - m)K$ which can be easily solved with respect to m in order to obtain

$$m(T) = -K/2 + [(K^2/4) + Km_0]^{1/2}. \qquad (3)$$

The conductivity $\sigma(T)$ can be written as

$$\sigma(T) = m(T)Ne\mu(T), \qquad (4)$$

where e is the electric charge, N is the number per unit volume of silicon atoms, and μ is the mobility defined as

$$\mu(T) = \frac{\mu_0}{T}\exp(-E_M/k_bT) = \frac{er^2\nu}{k_bT}\exp(-E_M/k_bT). \qquad (5)$$

In this expression, r represents the jump distance, ν is the vibration frequency, and E_M is the migration energy. In the absence of a periodical structure, the E_M value can be interpreted as representative of a mean potential barrier experienced by the alkali ions during their motion in the amorphous matrix.

By taking into account Eqs. (3)–(5), the conductivity can be finally expressed as

$$\sigma(T) = \left[-\frac{K}{2} + \left(\frac{K^2}{4} + Km_0\right)^{1/2} \right] \frac{Ne^2r\nu}{T}\exp(-E_M/k_bT). \qquad (6)$$

Numerical fits of the conductivity curves of bulk silica were performed on the basis of Eq. (6): due to the high number of parameters involved, satisfactory independent evaluations were hard to obtain. However, by considering, at a first approximation, realistic values for m_0 ($\approx$1 ppm) and for the jump distance ($\approx$1 Å), the dissociation and migration energies turned out to be 1.3 and 0.6 eV, respectively. The vibration frequency resulted to be of the order of 10^{13}–10^{14} s^{-1}. The numerical fit obtained under these assumptions is shown in Fig. 2: both the single exponential dependence detected below 1000 K and the monotonic slope decrease shown in the higher temperature region are well fitted. We admit the qualitative character of this numerical evaluation: however, the present analysis is supported by the similarity between the value of the dissociation energy of the $[AlO_4-M]^0$ center obtained here and the value found in crystalline quartz; moreover, the migration energy value here found is coherent with that obtained in previous investigations concerning the mobility of sodium ions in thin SiO$_2$ layers.[21–23] The higher value of the migration energy here obtained with respect to that found in crystalline quartz [0.25 eV (Ref. 16)] is in accordance with the absence, in the amorphous structure, of migration paths (channels) present in the crystalline form along the c-axis direction.

Only a single exponential behavior is observed in the conductivity of thin films, due to the more limited temperature interval in which they were investigated: in this temperature region, the association of $[AlO_4-M]^0$ centers is still almost complete,[14] so that $m_0 - m \cong m_0$ and the atomic fraction of free alkalis can be written as

$$m(T) = (m_0)^{1/2}\exp(-E_D/2k_bT). \qquad (7)$$

By taking Eq. (5) into account, the conductivity can be written as

$$\sigma(T) = 1/T \, (m_0/2)^{1/2}\mu_0 \exp(-E_A/k_bT), \qquad (8)$$

where E_A is the total activation energy for the transport process, defined as

$$E_A = 1/2 \, E_D + E_M. \qquad (9)$$

The total activation energy E_A of the conduction in thin films was evaluated, and turned out to be 1.2 eV. This value is in agreement with total activation energies obtained in the literature in bulk silica in a purely single exponential analysis.[4,9–11] As can be seen from Fig. 2, the slopes of the curves of bulk silica and thin films are very similar in their common temperature interval, so that this activation energy actually also governs the ionic conductivity of our bulk silica samples in the lower-temperature region up to approximately 1000 K, where the approximation $m_0 - m \cong m_0$ also holds; as expected, according to Eq. (9), its value is compatible with those of E_D (1.3 eV) and E_M (0.6 eV) obtained here by the complete fit of the conductivity curve of bulk silica up to 1400 K.

From the pre-exponential term of Eq. (8), and by considering a jump distance of 1 Å in μ_0 and a vibration frequency of the order of $10^{13} - 10^{14} \text{ sec}^{-1}$ as in bulk silica, a concentration of alkali ions in thin films of the order of $10^{-1} - 10^{-2}$ ppm can be derived, in accordance with alkali concentrations in these layers. It is worth remarking that, besides alkalis, the presence of aluminium impurity in complementary metal-oxide-semiconductor technology is also frequently observed due to different processes as ion implantation and cleanings.[24] Moreover, on the basis of thermally stimulated ionic current measurements, it was suggested that the limiting step in the release of Na^+ ions in Al-SiO$_2$-Si structures may be the diffusion of Al in the SiO$_2$ layer, and the subsequent reaction with Na to form substitutional $[AlO_4 - Na]^0$ centers.[25] Evaluations of ion trap depths led to values in the interval 0.8–1.6 eV, depending upon the ion considered (mainly Na^+ and K^+) and the applied electric field.[25–27]

The comparison between conductivity and infrared-absorption measurements indicates that hydrogen is incorporated into the silica structure without any significant formation of $[AlO_4 - H]^0$ centers, but mainly in other configurations like, for example, Si-OH and Si-H groups.[28,29]

As already mentioned above, the strong conductivity variations observed in crystalline quartz during high-temperature treatments were attributed to the interaction between $[AlO_4 - H]^0$ and $[AlO_4 - M]^0$ centers, and to the gradual reduction of the former because of hydrogen desorption. Due to the different incorporation of hydrogen impurities in the amorphous structure, hydrogen desorption (evidenced by the lowering of the broad IR band) has no effect on the alkali transport. In literature, controversial results were found concerning the influence of hydrogen impurity on alkali conduction in amorphous silicon dioxide: by tracer diffusion studies, a role similar to that shown in the conductivity of crystalline quartz was found,[5] while from impedance spectroscopy data different effects were found in silicas grown by different preparation methods.[9,12] Thus it appears that the presence of high concentrations of hydrogen is not sufficient to determine an influence of this species on alkali transport: rather, the key factor in this respect is the type of local compensation of this impurity in the structure, possibly driven by specific conditions of the material preparation process.

In conclusion, an accurate analysis of the high-temperature conductivity of both bulk silica and thin films was performed and compared with analogous previous results obtained in crystalline quartz: the overall picture calls for an interpretation based on the dominant presence of extrinsic mechanisms in the ionic transport, related to the presence of alkali charge carriers, and no intrinsic process was put in evidence in spite of the good purity of the materials. The good correspondence between results obtained by impedance spectroscopy technique and other electrical techniques suggests that this kind of investigation can be a useful tool in monitoring alkali dynamics in thin dielectric layers with very low impurity contents.

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