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Temperature dependence of the absorption properties of silanol groups in amorphous SiO₂: Are silanol groups organized in clusters?

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1. Introduction

Silanol groups (Si–OH) are one of the most common impurities in amorphous silicon dioxide (*a*-SiO₂). Their presence in the network affects many of the physical properties of this material. In particular Si–OH groups improve the radiation hardness in the UV spectral region by favoring the structural relaxation of the matrix. This makes *a*-SiO₂ materials having high silanol group contents (*wet a*-SiO₂) to be widely employed as optical components in devices such as ArF excimer lasers or UV light sources. On the other hand silanol groups are known to reduce the vacuum UV (VUV, $\lambda < 190$ nm, E > 6.5 eV) near-edge transmission of *a*-SiO₂ [1–6] and can, thus, be detrimental in appliances like the F_2 excimer laser ($\lambda = 157$ nm, E = 7.9 eV) optics. The growing attention to this kind of devices makes the issues related to the *a*-SiO₂ optical transparency and radiation toughness in the VUV spectral region particularly interesting.

The vibrational activity of silanol groups in a-SiO₂ is well characterized by the infrared (IR) absorption band at \sim 3670 cm⁻¹. This asymmetrical band is ascribed to the OH-stretching vibrational mode in Si–OH groups [7] and it is generally considered as the overlap of several different components related to the absorption of silanol groups in different bond configurations [2,8–14]. However, the problem of the decomposition of the band into sub-bands

ABSTRACT

We present a study on the vacuum-ultraviolet (VUV) and infrared (IR) absorption of silanol groups in amorphous silicon dioxide (a-SiO₂) in the range of temperature from 4 to 300 K. The observed temperature induced modifications of IR and VUV absorption spectra are interpreted as due to a process of conversion of free into H-bonded silanol groups. The changes of the amplitude of the VUV absorption spectra are shown to be linearly correlated to the changes of the IR absorption of free Si–OH groups. This point together with the evidence that the shape of the Si–OH VUV absorption does not depend on temperature demonstrates that the different silanol group sub-species have different VUV absorption properties, being only the free Si–OH groups responsible for the near-edge VUV absorption. A rough estimation of the percentage of free Si–OH groups (\sim 43%) converted into H-bonded ones by cooling *a*-SiO₂ down to 4 K is provided as well. A possible model for the interpretation of the observed experimental evidences is proposed: we suggest silanol groups to be arranged in clusters in the amorphous SiO₂ network.

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is tricky, because the profile of the band at room temperature is the same irrespective of the kind of materials and of their silanol group concentration [6,11]. In the studies where the problem of the identification of the sub-bands of the Si-OH IR absorption band was coped with, such a decomposition was proposed in order to account for the asymmetry of the band [8] or for the observed changes of the band profile induced by temperature [5,14] or by hydration treatments [15]. Although the results reported in the literature led to slightly different identifications and assignations of the components, there is agreement around some basic conclusions: the region of the band from \sim 3680 to \sim 3730 cm⁻¹ is associated to the vibrational activity of free Si-OH groups, i.e., those whose H atom is bonded only to one O atom; whereas the region from \sim 3500 to \sim 3680 cm⁻¹ is generally described as the sum of three different components ascribed to distinct species of hydrogen bonded Si-OH groups, i.e., those bound via hydrogen bond to the O atom either of another Si-OH group or of Si-O-Si linkages [5,8,10,11,14].

In this context an important and still missing piece of information is that related to the electronic transition of silanol groups in a-SiO₂. In particular, even if it is now well established that Si–OH groups contribute to the absorption in the spectral region close to the intrinsic absorption edge, i.e., at around 8 eV [1–6,16–20], the question concerning the sub-species responsible for this absorption has not been addressed yet. The present paper focuses on the study of the temperature dependence of both the IR and the VUV absorption features of silanol groups in a-SiO₂, with the aim of isolating the sub-species responsible for the near-edge absorption. A model describing silanol groups as arranged in clusters in



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 Si-OH concentrations ([SiOH]) as experimentally estimated from room temperature IR absorption spectra.

Samples	[SiOH] (cm ⁻³)
S1 SG-A SG-B	$\begin{array}{c} 6.2 \times 10^{19} \\ 4.7 \times 10^{19} \\ 3.2 \times 10^{19} \end{array}$

the a-SiO₂ network is suggested, in order to account for the set of experimental evidences.

2. Experimental procedure and samples

We report here the results obtained on two sets of optically polished samples of two different materials: a Suprasil 1 (S1) and a sol-gel (SG) material. In the following we will refer to the different samples with the nicknames put in brackets. The S1 material is a trademark by Heraeus Co.¹ and is produced by hydrolysis of SiCl₄ in a H₂/O₂ flame, while the SG material was produced by Degussa Novara Technology by the SiVARA sol-gel process. The main difference between these two kinds of materials lies in the highest temperature reached during their synthesis: the former is obtained via high temperature manufacture processes (typically at ~1700 °C), while the latter by production techniques characterized by lower temperatures (generally equal or lower than ~1400 °C). Both materials belong to the category of *wet a*-SiO₂, i.e. having a high content of silanol groups, typically > 10¹⁹ cm⁻³.

IR and VUV temperature-controlled absorption measurements in the range from 4 to 300 K were carried out using a continuous liquid helium flow cryostat (Optistat CF-V; Oxford instruments) and a two stage rotary/turbomolecular pump (Leybold Vacuum PT 50, base pressure $\sim 10^{-6}$ mbar). Thermal equilibrium within 1 K at the working temperature was achieved by an Oxford-ITC503 instrument, controlling the He flow. Along the direction of the transmitted beam the cryostat mounted two MgF₂ or two CaF₂ windows for the VUV and IR absorption measurements respectively.

VUV absorption spectra were obtained by an ACTON singlebeam spectrophotometer (mod.SP150), working in N₂ flux (typically 80 l/min), and equipped with a 30 W D₂ lamp and with two identical monochromators (1200 lines/mm, stray light $< 5 \cdot 10^{-4}$). The second monochromator filters the light coming out from the sample chamber and it is necessary in order to reduce stray light and possible luminescence emissions. These effects could, indeed, be particularly detrimental for the measurements in the spectral region we are interested in, because the transmitted light is very low. Measurements were performed with a bandwidth (FWHM) of 0.4 nm. Experimental spectra were corrected for the photomultiplier dark current and surface reflections. The latter were estimated using literature data [21] of the refractive index in *a*-SiO₂. Optical densities lower than ~2.7 could be measured with an accuracy of ± 0.03 .

IR absorption spectra were measured by a Bruker Vertex 70 Fourier Transform IR single-beam absorption spectrometer, operating in the medium IR range by a light globar source. Spectra were acquired with a spectral resolution of 1 cm⁻¹. To avoid the effects of water in air, the absorption spectrum of the empty beam line was subtracted from every spectrum after suitable normalization. The errors on the determination of the position and the intensity of the IR bands of our interest are ± 0.5 cm⁻¹ and less than 1% respectively.



Fig. 1. IR absorption spectra of the S1 sample in the region from 3500 to 3800 cm⁻¹, temperature ranging from 4 to 300 K: (a) absorption spectra and (b) difference spectra relative to the absorption spectrum at room temperature. The arrows show the increase of temperature from 4 to 300 K.

3. Results

In the present work we report the results obtained on three different samples, one of the S1 material and two of the SG material. This choice allowed to carry out our analysis over a set of samples differing both for the production method and for the silanol group concentration, thus accounting for the possible differences between distinct materials. We first estimated the Si-OH group concentration of each sample of each material from the amplitude of the band at \sim 3670 cm⁻¹ at room temperature. We used the value 77.5 $l \text{ mol}^{-1} \text{ cm}^{-1}$ for the molar extinction coefficient [10]. As it has been already reported [6,11], the profile of the band at \sim 3670 cm⁻¹ at room temperature is the same in every sample regardless of the overall Si-OH group concentration. If the band at \sim 3670 cm⁻¹ originates by the overlap of components associated to the vibrational activity of different sub-species, then this datum implies that the pristine distributions of the several sub-species are the same in all samples. Table 1 reports the silanol group contents of the three samples we studied.

We performed IR absorption measurements in the range of temperatures from 4 to 300 K. Fig. 1 (panel a) shows the IR absorption spectra of the S1 sample in the range from 3500 to 3800 cm^{-1} at all the examined temperatures. On lowering temperature the amplitude of the low wavenumber side of the band increases, whereas the amplitude of the high wavenumber side of the band decreases. These changes produce a significant increase of the overall area of the band. In Fig. 1 (panel b) the spectra of the S1 sample obtained as difference between spectra at each temperature and the spectrum at 300 K are reported in the range from 3500 to 3800 cm⁻¹. The difference spectra clearly evidence the existence of an isosbestic point at \sim 3680 cm⁻¹. The decreasing contribution is peaked at \sim 3700 cm⁻¹, whereas the increasing one has a maximum at \sim 3615 cm⁻¹. The inspection of difference spectra shows, besides, that the increasing contribution is asymmetric; this effect is especially evident at high temperatures. Finally, a further decreasing contribution, whose peak is at \sim 3740 cm⁻¹, is observed. The changes induced by temperature are reversible. In both SG samples analogous behaviors of the band at \sim 3670 cm⁻¹ were observed as a function of temperature, although having different extents of the variations.

The asymmetrical deformation of the silanol group band observed by cooling samples supports the hypothesis of the presence of several components related to different species of Si–OH groups. Actually the presence of more than two components is likely because of the existence of a negative contribution at high wavenumbers and because of the asymmetry of the positive

¹ Heraeus Quartzglas, Germany, catalog POL-0/102/E.



Fig. 2. VUV absorption spectra of the SG-A sample. Temperature ranges from 4 to 300 K. The dashed line is guide to the eye evidencing the exponential profile. On the *y*-axes breaks at around 7.7 eV are present: below the break the scale is linear, above it is logarithmic.

contribution in the difference absorption spectra, as evident in Fig. 1 (panel b).

Let us now describe the effects of lowering temperature on the VUV absorption of silanol groups. We performed VUV absorption measurements on the S1 and SG samples in the range of temperatures from 300 to 4 K. Fig. 2 shows the near-edge absorption spectra of the SG-A sample. It is known that in wet materials the absorption in the spectral region from \sim 7.5 to \sim 8 eV is due to silanol groups, whereas the intrinsic exponential absorption, known as *Urbach tail*, starts being relevant for energies >8 eV [6], being negligible for lower energies. It was shown [6] that the VUV absorption by Si–OH groups has an exponential profile, which, using a procedure which was discussed in detail in previous works [6,22], was described as follows:

$$Y = Y_0 + A_0 \exp\left(\frac{E - 8eV}{A_1}\right) \tag{1}$$

 A_0 is the value of the absorption coefficient at 8 eV due to the silanol group contribution only and at room temperature it was shown to be linearly correlated to the total silanol group concentration as measured from IR absorption spectra [6], whereas A_1 is the slope of the Si–OH exponential in a semi-logarithmic scale. Y_0 is a parameter introduced to describe the profile of the absorption spectra in the range <7.5 eV. The particular expression of Eq. (1) is just a suitable form for an exponential profile and the value 8 eV represents only a reference point for the absorption. All the conclusions drawn in the present study do not depend on this arbitrary choice. A quick inspection of spectra in Fig. 2 suggests that the effect of decreasing temperature on the Si–OH contribution is to reduce its amplitude without affecting its slope. A similar trend was observed also in the S1 material.

Fig. 3 (panel a) shows the temperature dependence of the variation of the A_0 parameter at each examined temperature in respect to that at 4 K ($A_0(T) - A_0(4 \text{ K})$) as determined by fitting VUV spectra of S1 and SG samples. In all specimens the value of A_0 decreases by lowering temperature in the range from 300 to \sim 100 K and it remains constant for lower temperatures. As for the A_1 values, they do not change in the whole examined range of temperatures, remaining constant at (180 ± 5) meV in all samples. The temperature dependence of the A_0 and A_1 parameters gives us information about the VUV absorption cross-section of silanol groups as a function of temperature. With regard to the A_1 behavior, this implies that the shape of the Si-OH VUV absorption cross-section does not change with lowering temperature. As to the A₀ values, a few remarks are required. The exponential character of the VUV silanol group contribution and the expression we have chosen to describe it (Eq. (1)) do not allow to distinguish between a reduction of the



Fig. 3. Temperature dependence (a) of the variation of the A_0 parameter (see Eq. (1)) at each examined temperature in respect to that at 4 K ($A_0(T)$ – $A_0(4 K)$) as determined by fitting the VUV spectra; (b) of the absolute value of the amplitude of the peak at ~3700 cm⁻¹ in the IR difference spectra (Fig. 1 panel b). In both panels: S1 (filled circles), SG-A (filled diamonds) and SG-B (empty circles) samples.

amplitude and a rigid shift of the exponential itself. This means that the decrease in the A_0 parameter with lowering temperature (Fig. 3 panel a) cannot be straightforwardly interpreted in terms of a reduction of the concentration of the species responsible for the VUV absorption. Data reported in the following will help to clarify this aspect.

Let us compare these results with those concerning IR spectra. As it is possible to see from Fig. 1, the contributions decreasing with temperature are those located at the high wavenumber side of the band. The absorption in the region of wavenumbers > 3720 cm⁻¹ is generally attributed to the vibrational activity of H₂O related species [15], which are beyond the aims of the present study. Thus, neglecting the changes regarding the high wavenumber band wing, the only component decreasing its amplitude with lowering temperature is that at \sim 3700 cm⁻¹, which, as mentioned before. is attributed to free silanol groups [5.8.10.11.14]. Our purpose is now to verify whether the amplitude of this contribution to the IR absorption band can be connected to the silanol group related absorption in the VUV region as measured by the values of the A_0 parameter. In this context it is useful to consider the variations induced by temperature on both the A_0 values and the amplitude of the peak at $\sim 3700 \text{ cm}^{-1}$ as obtained by the IR difference absorption spectra (see Fig. 1 panel b). Fig. 3 (panel b) reports the absolute value of the amplitude of the peak at \sim 3700 cm⁻¹ in the IR difference spectra of Fig. 1 (panel b) as a function of temperature for every examined sample. Data in Fig. 3 (panel b) show a trend very similar to that of the variation of the A_0 parameter at each examined temperature in respect to that at 4 K $(A_0(T) - A_0(4 \text{ K}))$ as determined by VUV spectra (see Fig. 3 panel a), that is, they decrease in the range from 300 to \sim 100 K, remaining approximately constant for lower temperatures. In Fig. 4 the values of the difference between $A_0(T)$ and $A_0(4K)$ are reported as a function of the absolute value of the corresponding amplitude of the peak at \sim 3700 cm⁻¹ in the IR difference spectra (Fig. 1 panel b). These two quantities show a very good linear correlation. The straight line reported in Fig. 4 was obtained by linear fitting of data; the value of its slope is 32 ± 5 .

4. Discussion

The purpose of the experiments discussed in the present work is to identify the silanol group sub-species responsible for the near-edge VUV absorption in a-SiO₂. In previous studies we characterized the VUV absorption profile of Si–OH groups in a-SiO₂ [6] and we clarified the structural role of silanol groups in



Fig. 4. Variation of the A_0 parameter at each examined temperature in respect to that at 4 K ($A_0(T)$ – $A_0(4$ K)) versus the absolute value of the amplitude of the peak at \sim 3700 cm⁻¹ in the IR difference spectra (Fig. 1 panel b) in the S1 (filled circles), SG-A (filled diamonds) and SG-B (empty circles) samples. The solid line was obtained by linear fitting of data.

the material as evidenced by the features of the Urbach tail in wet a-SiO₂s [22]. Here we focus on the temperature dependence of the VUV absorption of silanol groups with the aim of isolating the sub-species responsible for this contribution. Indeed, while the temperature induced modifications of the IR absorption band were already discussed in the literature [5,14], to the best of our knowledge a linear correlation between the temperature induced changes of IR and VUV spectra has never been observed.

We analyzed two kinds of wet materials, S1 and SG, differing for both the manufacture procedure and the silanol group concentration. This circumstance is relevant because it allows to evidence possible effects due to structural properties, which can be different in materials produced by distinct methods.

The changes induced on the Si-OH group band shape by cooling samples can be interpreted as a consequence of the presence of different contributions constituting the band itself. Changes of the shape of the band at \sim 3670 cm⁻¹ upon different treatments (hydration treatments [15] or irradiation either with a Xe₂ discharge lamp or with a F₂ excimer laser [3,5,17,18,23]) have been reported in the literature and interpreted as an evidence of the existence of different sub-bands. In our case the main evidence supporting the existence of several components is the presence of a clear isosbestic point at \sim 3680 cm⁻¹ in difference spectra (see Fig. 1 panel b). This point was already reported in the literature in the same range of temperature [5,14]. The existence of an isosbestic point can be considered as consequence of a process of conversion between the different sub-species. In this scheme the fact that with lowering temperature the overall area of the band increases can be explained hypothesizing that the different species have distinct molar extinction coefficients. As it was mentioned before, the low wavenumber side of the band at \sim 3670 cm⁻¹, i.e. the region from \sim 3500 to \sim 3680 cm⁻¹, is generally ascribed to the absorption of Si-OH groups involved in hydrogen bonds, while the absorption in the high energy side of the band, i.e. the region from \sim 3680 to \sim 3520 cm⁻¹, is considered as due to the absorption of free silanol groups [5,8,10,11,14]. Thus, attaining to the assignations already proposed in the literature, present data point out that the temperature decrease induces a conversion of free into H-bonded species.

As far as the effects of lowering temperature on VUV spectra are concerned, we observed that in all samples the A_1 values are not affected by the decrease in temperature. As we mentioned, this point suggests that the profile of the VUV absorption crosssection of silanol groups does not change in the examined range of temperatures.

Fig. 4 clearly shows that the different sub-species have distinct VUV absorption properties. As it can be seen, in all samples

the variations of the A_0 parameter between 300 and 4 K show a very good linear correlation with the absolute value of the amplitude of the peak at \sim 3700 cm⁻¹. This result provides a natural interpretation of the strong temperature dependence of the A_0 values. In particular, the decrease in the A_0 values by lowering temperature (see Fig. 3 panel a) can be considered as a consequence of a reduction of the concentration of the species responsible for the VUV absorption, as it is linearly correlated to the variations of the peak at \sim 3700 cm⁻¹, which are in turn evidence of a decrease of the concentration of free Si-OH groups due to a conversion process of one species into another. This point alone actually does not allow to exclude that another sub-species, together with free Si-OH groups, contribute to the VUV absorption. Indeed, the linear correlation between the changes of the value of the A_0 parameter in the VUV spectra and the variations of the amplitude of the peak at \sim 3700 cm⁻¹ as reported in Fig. 4 would be observed anyway even if two sub-species were related to the VUV absorption, only one of which changing its concentration with temperature. Nevertheless, the fact that the VUV silanol group exponential absorption does not change its profile (i.e. its slope in a semi-logarithmic scale) with lowering temperature allows us to reject this possibility and to conclude that only free Si-OH groups are related to the near-edge VUV absorption, being the contribution of the other silanol group sub-species only marginal. It is worth noting that this conclusion was drawn without introducing any a priori hypothesis for the description of the overall profile of the band. Indeed, no arbitrary decomposition of the IR band into sub-bands was carried out, whereas only difference spectra were used to interpret data.

One may wonder where the absorption of hydrogen bonded species is set. This could be guessed to be located at energies >8 eV and thus not detectable in VUV absorption spectra because of its overlap with the intrinsic absorption. This blue-shift of the electronic transition of hydrogen bonded silanol groups could be the effect of different causes: it could be due to the hydrogen bonding lowering the vibrational levels in the ground electronic states together with a modification of the excited electronic state, which, being more spatially extended, is more affected by the presence of surrounding atoms.

It is finally worth noting that the slope (32 ± 5) of the line reported in Fig. 4 represents the ratio between the free silanol group absorption cross-section at 8 eV and their IR absorption cross-section at ~3700 cm⁻¹.

Present data also allow a rough estimation of the percentage of free Si–OH groups converted into hydrogen bonded ones by cooling samples down to 4 K. Relying on the evidence that the A_0 parameter is linearly related to the concentration of centers responsible for the absorption [6], the ratio $(A_0(300 \text{ K})-A_0(4 \text{ K}))/A_0(300 \text{ K})$ roughly represents the percentage of free Si–OH groups converted into hydrogen bonded ones, the results being \sim (43 ± 5)% in all the examined materials.

As it was anticipated, the silanol group related band at \sim 3670 cm⁻¹ has the same shape in all samples. This implies that the pristine distribution of the several sub-species of silanol groups is the same in materials having strongly different structural features. In this regard a few comments are required. The room temperature pristine distribution of the different silanol group sub-species should be that corresponding to the equilibrium distribution of the various sub-species in the material. Lowering temperature alters this distribution, in particular inducing a conversion from free to H-bonded Si-OH. This datum suggests silanol groups to be close to each other in the material. Besides, it is important to underline that the conversion process is not caused by a compaction of the material. It was observed, indeed, that the thermal expansion coefficient of a-SiO₂ is negative for temperatures lower than 200 K [24]. A hypothesis that could be guessed to explain these evidences as a whole is that silanol groups do not distribute uniformly through the whole vitreous matrix, but, on the contrary, tend to concentrate in some confined regions, thus characterized by a silanol group concentration higher than the average measured value, surrounded by regions where the Si-OH content is much lower. In other words, silanol groups are proposed to be arranged in *clusters* in the *a*-SiO₂ network. In this scheme the conversion of free silanol groups into H-bonded ones can be explained as caused by a local compaction, i.e. a compaction of the clusters of Si-OH groups, which is not necessarily accompanied by a compaction of the material as a whole. This model could explain also the fact that at room temperature the Si-OH related band has the same profile regardless of the manufacture procedure of different materials and of their total silanol group content. The room temperature pristine distribution of the different silanol group sub-species should be that corresponding to the equilibrium distribution of the high Si-OH content regions. From this point of view, this distribution should be thought as a property of such clusters more than a feature of the network as a whole and this can be the reason why the silanol group absorption band is actually not affected by the characteristics of the vitreous matrix of different materials. Finally, it has to be noticed that it was observed that the main contribution to the \sim 3670 cm⁻¹ band is given by H-bonded species [14]. In such a scheme this point is straightforward, because the very high concentration of silanol groups in these Si-OH soaked regions should favor the formation of H-bonds between pairs of silanol groups.

5. Conclusions

We studied the effects of lowering temperature from 300 to 4 K on the IR and VUV absorption of silanol groups in *a*-SiO₂. The temperature induced modifications of the Si–OH group IR absorption band are interpreted as due to a process of conversion of free into H-bonded silanol groups. As for the VUV absorption of Si–OH groups, we described it as having an exponential profile in the range from ~7.5 to ~8 eV. We found that the slope in a semilogarithmic scale of this exponential profile does not change with lowering temperature, while its amplitude decreases in the range for lower temperatures. We observed moreover that the changes of the amplitude of the VUV exponential absorption of silanol groups show an excellent linear correlation with the changes of the high wavenumber component of the IR band associated to free Si–OH groups. This point together with the evidence that

the shape of the Si–OH VUV absorption does not depend on temperature demonstrates that the different silanol group subspecies have different VUV absorption properties, being only the free Si–OH groups responsible for the near-edge VUV absorption. The percentage of free Si–OH groups converted into H-bonded ones by lowering temperature down to 4 K was estimated to be \sim (43 ± 5)%. Finally, in order to explain the observed evidences, i.e. the conversion process together with the fact that the room temperature equilibrium distribution of the various sub-species is the same in different materials, silanol groups are proposed being arranged in clusters in the *a*-SiO₂ network.

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