

Vacuum-ultraviolet absorption of amorphous SiO₂: Intrinsic contribution and role of silanol groups

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We present a study on the vacuum-ultraviolet (VUV) absorption properties of amorphous SiO₂ (*a*-SiO₂) with high concentrations of silanol groups (Si-OH). We found that the absorption spectra are made up of a couple of exponential profiles. The first, in the range from ~ 7.5 to ~ 8.1 eV, was attributed to Si-OH group absorption, while the second, in the range from ~ 8.1 to ~ 8.25 eV, was ascribed to the intrinsic absorption. The VUV absorption cross section of Si-OH groups in *a*-SiO₂ was determined as well. The intrinsic absorption was found to be affected by the Si-OH concentration: high silanol group contents allow lower values of the Urbach energy. This result is interpreted in terms of a reduction in the degree of disorder in wet materials.

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I. INTRODUCTION

Amorphous silicon dioxide (*a*-SiO₂) is a key optical material in the ultraviolet (UV) and vacuum-ultraviolet (VUV) ($\lambda < 190$ nm, $E > 6.5$ eV) spectral regions. Thanks to its high transparency up to 8 eV, it is used as component of UV and VUV light sources such as Xe₂ excimer lamps ($\lambda = 172$ nm) $E = 7.2$ eV and ArF ($\lambda = 193$ nm, $E = 6.4$ eV) and F₂ ($\lambda = 157$ nm) $E = 7.9$ eV excimer lasers. The latter, in particular, has recently become leading in the optical lithography of semiconductor technologies. In order to employ *a*-SiO₂ in these devices, an understanding of the factors controlling its optical transparency and its radiation hardness is crucial.

The VUV transmission of *a*-SiO₂ is mainly limited because of its intrinsic absorption edge. The presence of impurities and structural point defects may reduce the VUV transmission as well. A careful analysis of both effects is required to control the transmittance losses in the VUV spectral region.

In the intrinsic absorption spectral region, from ~ 8 to ~ 9 eV, the absorption spectra of *a*-SiO₂ are well described by the equation,

$$\alpha(E) \propto \exp\left(\frac{E - E_g}{E_u}\right), \quad (1)$$

known as the *Urbach law*.^{1,2} $\alpha(E)$ is the absorption coefficient, E_g is the optical energy gap, and E_u is called Urbach energy and depends on temperature. High values of E_g and low values of E_u are associated with a high transparency in the VUV spectral region and with a steep absorption edge, while materials showing less transmission in the Urbach region are characterized by high E_u and low E_g values, respectively. There are several evidences³⁻⁷ that structural disorder affects the characteristics of the Urbach tail and, in particular, the E_u value. For this reason, the Urbach energy is generally considered as an indicator of the disorder degree of an amorphous structure. In order to clarify the mechanisms through which the physical disorder of the network influences the VUV transmission of *a*-SiO₂, it is useful to examine another parameter usually related to structural disorder: the fictive temperature (T_f). T_f is defined as the temperature

at which the amorphous network is frozen in, which is the temperature at which the actual structural disorder would be in equilibrium.⁸ It is widely accepted that the main structural modification associated with changes in T_f is the variation of the average Si-O-Si bond angle, and, in particular, it has been shown that an increase in the fictive temperature corresponds to a decrease in the value of the average Si-O-Si bond angle.⁹

The VUV transmission of *a*-SiO₂ is affected by the presence of impurities as well. In particular, several experimental results suggest that one of the most common impurities in *a*-SiO₂, silanol group (Si-OH), contributes to the absorption in the spectral region close to the intrinsic absorption edge.¹⁰⁻¹⁹

Silanol groups in *a*-SiO₂ are well characterized from infrared (IR) spectra. It is well known that the IR absorption band at ~ 3670 cm⁻¹ is associated with the stretching vibrational mode of Si-OH groups,²⁰ and, in particular, this band is generally considered as the overlap of several subbands due to the absorption of silanol groups in different bond configurations.^{12,21-26} The two main bond configurations are the free Si-OH groups, i.e., those whose H atom is bonded only to one O atom, and the H-bonded Si-OH groups, i.e., those bonded via hydrogen bond to another Si-OH group.

The characterization of the VUV absorption of silanol groups is more difficult because of the experimental difficulties of the study of this spectral range. Although several studies addressed the problem of their electronic transition in *a*-SiO₂, this is still debated. In this context, it is useful to mention three of the works where this issue was dealt with. First,¹⁰ the VUV absorption cross section of Si-OH groups in *a*-SiO₂ was estimated as the difference between the absorption spectrum of a wet material (i.e., having a high content of silanol groups, in this case, [SiOH] $\sim 6.6 \times 10^{19}$ cm⁻³) and that of a dry one (with a negligible Si-OH concentration, [SiOH] $< 10^{17}$ cm⁻³), under the assumption that the differences between the spectra of the two samples in the region from 7 to 8 eV are due to the different Si-OH contents only. This hypothesis, however, is questionable and it was not supported by concurrently measuring the Urbach energy. In a latter study,¹² the VUV absorption cross section of silanol groups was determined from the variation of the absorption spectrum of a wet sample ([SiOH] $\sim 10^{20}$ cm⁻³) after a ther-

mal treatment at 1273 K for 50 h in vacuum. This estimate is based on the hypotheses that the thermal treatment reduces the Si-OH content without affecting any other structural feature and that in the spectral region $E > 7.4$ eV, the absorption is only due to these centers. In particular, it was suggested that the free Si-OH groups only are responsible for the near-edge absorption, while the absorption due to the H-bonded ones must be located at higher energy regions. In a more recent paper,¹⁸ finally, the cross section was obtained assuming that the absorption in the range from 7.5 to 8 eV could be entirely ascribed to silanol groups, and this hypothesis was verified in two different kinds of material.

The studies just reported were carried out over a limited variety of materials. Besides, the cross sections were determined by comparing the spectra of materials, which differ either in the production procedure or in the undergone treatments. In particular, they were obtained by neglecting the structural differences in the network, possibly leading to different features of the intrinsic absorption edge. Finally, no correlation was observed between the Si-OH concentration and the VUV absorption of α -SiO₂.

In this paper, we will report a study of the near-edge spectral region on a wide variety of α -SiO₂ materials. We analyzed the features of their VUV spectra distinguishing the intrinsic absorption contribution from the Si-OH one and checking the disorder degree of the network by evaluating the values of the fictive temperature and the Urbach energy. We found that the contribution of Si-OH groups to the VUV absorption of α -SiO₂ is described by an exponential law whose parameters show a good correlation with the silanol group concentration. Besides, we identified the VUV absorption cross section of Si-OH groups.

II. EXPERIMENTS

A. Experimental procedure and samples

Three types²⁷ of wet α -SiO₂ glass were studied: (a) type II (natural wet) Homosil (HM), Herasil 1 (H1); (b) type III (synthetic wet) Suprasil 1 (S1), Suprasil 311 (S311), Corning 7940-5F (CNG5F); and (c) sol-gel (SG). A dry material, Suprasil F300 (F300), was also examined for comparison. In the following, we will refer to the different materials with the nicknames set in brackets. The materials HM, H1, S1, S311, and F300 are trademarks by Heraeus Co,²⁸ while CNG5F was supplied by Corning, Inc.²⁹ The SG samples were produced by Degussa Novara Technology by the SiVARA sol-gel process. For every material, we used a set of optically polished samples with $5 \times 5 \times 0.15$ or $5 \times 5 \times 0.5$ mm⁻³ in size. The samples used for IR and VUV measurements were, respectively, 0.5 and 0.15 mm thick. The sample thickness of 0.15 mm allows us to measure the values of the VUV absorption coefficients as high as $\alpha(E) \sim 650$ cm⁻¹; this condition sets the upper limit of the investigated spectral range up to ~ 8.3 eV ($\lambda \sim 149$ nm). This range is wide enough to evidence the exponential region of the absorption edge and to measure E_u .

IR absorption spectra were obtained by using a Bruker Vertex 70 Fourier transform IR single-beam absorption spectrometer, equipped with a medium-IR light global source.

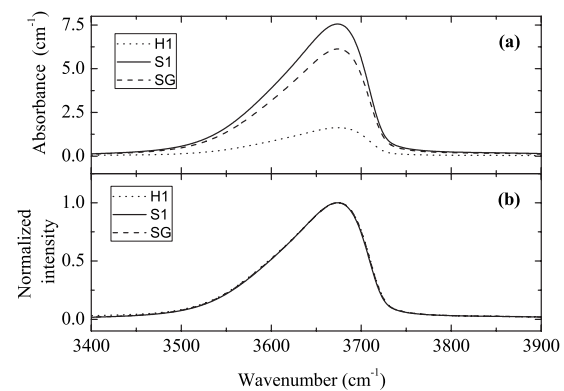


FIG. 1. IR absorption spectra in the region from 3400 to 3900 cm⁻¹. The three materials are representative of each examined material type (H1 natural, S1 synthetic, and SG sol-gel) (a) as measured and (b) normalized spectra.

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 beamline was subtracted from every spectrum after suitable normalization. The errors associated with the determination of the position and the intensity of the IR bands of our interest are ± 0.05 cm⁻¹ and less than 1%, respectively.

VUV absorption spectra were measured at room temperature by an ACTON single-beam spectrophotometer (model SP150) working in N₂ flux (typically 80 l/min). The spectrophotometer is equipped with two identical monochromators (1200 lines/mm, stray light of $< 5 \times 10^{-4}$). The first monochromator selects the light going into the sample chamber, while the second filters the light coming out from it and it is necessary in order to reduce stray light and possible luminescence emissions. The filtering action is needed especially in the high absorption region because the transmitted light is very low. The light source is a 30 W D₂ lamp. Measurements were carried out with a bandwidth (full width at half maximum) of 0.4 nm. For a reliable measure of the Urbach edge, experimental spectra were corrected for the photomultiplier dark current and surface reflections. The latter were estimated by using the literature data³⁰ of the refractive index in α -SiO₂. Optical densities lower than ~ 2.7 could be measured with an accuracy of ± 0.03 . The experimental setup and the analysis procedure allow a reliable estimate of E_u within 10% for values of the Urbach energy as low as ~ 45 meV. This was verified by measuring the absorption edge in a sample of crystalline quartz: the obtained value of E_u (48 ± 4 meV) is in fair agreement with the literature data.³¹

B. Experimental results

We first estimated the Si-OH concentration and the fictive temperature of the different materials from their IR absorption spectra as discussed in the following. Figure 1(a) shows as an example the IR absorption spectra of three of the examined materials, one for each of the considered α -SiO₂ types (natural, synthetic, and sol-gel), in the range from 3400 to 3900 cm⁻¹. The peak at ~ 3670 cm⁻¹ is attributed to the stretching vibrational mode of the Si-OH groups.²⁰ From its

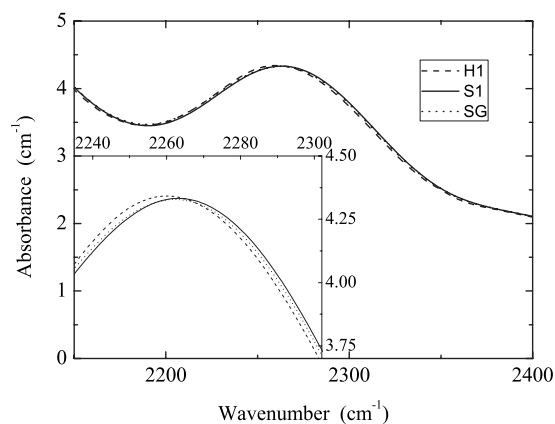


FIG. 2. IR absorption spectra in the range from 2100 to 2400 cm^{-1} . The reported spectra are representative of each of the three examined $\alpha\text{-SiO}_2$ types. In the inset, an enlargement of the peak of the bands is shown.

amplitude, we estimated the Si-OH concentration of each sample of each material by using the value of $77.5 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the molar extinction coefficient.²¹ In the dry material F300, the band at $\sim 3670 \text{ cm}^{-1}$ was not detectable ($[\text{Si-OH}] < 10^{17} \text{ cm}^{-3}$). As it is possible to see from Fig. 1(b), the band at $\sim 3670 \text{ cm}^{-1}$ has the same profile regardless of the Si-OH group concentration. This band is considered as the overlap of several subbands ascribed to different bond configurations of the Si-OH groups.^{12,21–26} In this context, the normalized spectra of Fig. 1(b) show that the ratios between the various subspecies do not depend on the Si-OH concentration. As consequence, the experimental results reported in the following cannot be accounted for as the effect of different percentages of the Si-OH subspecies in the various materials. To this end we notice that this evidence weakens the attribution of the IR absorption band to different subspecies.

In Fig. 2 the IR spectra of the same materials of Fig. 1 in the range from 2100 to 2400 cm^{-1} are reported. The band at $\sim 2260 \text{ cm}^{-1}$ is the overtone of the IR structural absorption band at $\sim 1120 \text{ cm}^{-1}$, which is attributed to the stretching vibrational mode of the Si-O-Si bridges.³² It was shown³³ that the peak position of the band at $\sim 2260 \text{ cm}^{-1}$ is related to T_f through the following equation:

$$\nu = 2228.64 + \frac{43\,809.21}{T_f}, \quad (2)$$

where ν is the frequency of the peak of the band. We used Eq. (2) in order to determine from the IR absorption spectra the fictive temperature of the examined materials. In Table I, the values of the Si-OH group concentration and of the fictive temperature as determined from the IR spectra of each sample are reported. The results in Table I require a few remarks. We note first that the set of the examined materials have values of the silanol group content encompassing the whole typical range of concentrations in wet $\alpha\text{-SiO}_2$. Besides, it is important to underline that the samples of the same SG material show quite different Si-OH group concentrations. These samples were produced via the same proce-

TABLE I. Si-OH concentration ($[\text{SiOH}]$), fictive temperature (T_f), Urbach energy (E_u), and A_1 [see Eq. (3)] as experimentally determined from IR and VUV absorption spectra of every examined sample. Labels A, B, etc., used for the materials CNG5F and SG indicate samples of the same material showing slight different Si-OH contents. The errors on E_u and A_1 are 5 and 10 meV, respectively.

Materials	$[\text{SiOH}]$ (cm^{-3})	T_f (K)	E_u (meV)	A_1 (meV)
H1	1.3×10^{19}	1420 ± 20	61	170
HM	1.3×10^{19}	1400 ± 20	60	170
S311	2.6×10^{19}	1250 ± 10	68	180
S1	6.2×10^{19}	1570 ± 30	66	180
CNG5F-A	7.2×10^{19}	1240 ± 10	55	160
CNG5F-B	7.8×10^{19}	1220 ± 20	55	170
SG-A	3.2×10^{19}	1290 ± 20	55	180
SG-B	3.9×10^{19}	1290 ± 20	55	160
SG-C	4.7×10^{19}	1300 ± 20	55	170
SG-D	6.1×10^{19}	1290 ± 20	55	170

dure. This circumstance allowed us to use the samples with the same structural features but with different Si-OH group concentrations. The fact that the SG samples have the same structural characteristics is proved from the values of their fictive temperature as well: $\sim 1300 \text{ K}$ for all the considered samples.

Figure 3 shows the VUV absorption spectra of two samples: a wet one (S1) and a dry one (F300). The S1 sample has quite a high Si-OH group concentration ($\sim 6.2 \times 10^{19} \text{ cm}^{-3}$). Its spectrum is essentially characterized by two different regions, both approximately linear in a semi-logarithmic scale, but with different slopes: the first from ~ 7.5 to $\sim 8.1 \text{ eV}$ and the second from ~ 8.1 to $\sim 8.25 \text{ eV}$. We found that the VUV spectra of all the examined wet materials have the same features. On the contrary, the spectrum of the F300 sample can be represented as a single exponential in the region from ~ 7.7 to $\sim 8.25 \text{ eV}$. The low energy contribution to the VUV absorption of wet materials

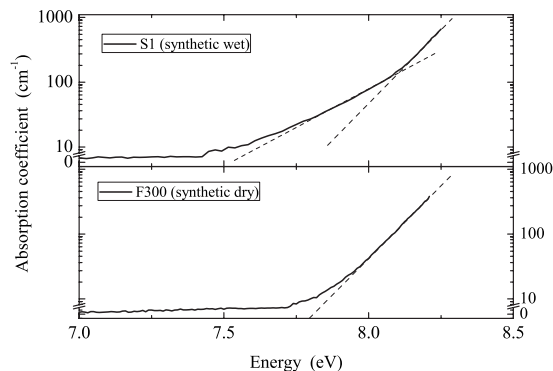


FIG. 3. VUV absorption spectra of one of the wet materials (S1) and of the dry material (F300) chosen for comparison. The thicknesses of the two samples are ~ 0.15 and $\sim 0.2 \text{ mm}$, respectively. Dashed lines are a guide for the eye.

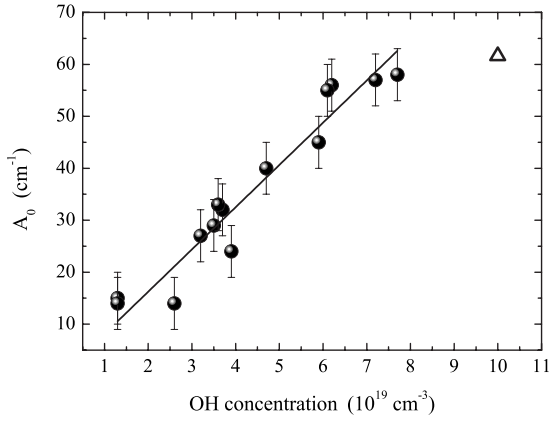


FIG. 4. Plot of the parameter A_0 , contribution of Eq. (3) to the absorption coefficient at 8 eV, versus the Si-OH group concentration in the wet samples (filled symbols). The line is obtained by linear fit of the data. The value of the absorption coefficient at 8 eV versus the Si-OH group concentration, as reported in Ref. 18, is also shown for comparison (open symbol).

is guessed being related to the Si-OH groups. As it is possible to see from the spectrum in Fig. 3, it can be described as another exponential contribution over at least a decade of the absorption coefficient. Thus, we fitted the VUV spectra of all the wet samples by the sum of the two functions,

$$Y = A_0 \exp\left(\frac{E - 8 \text{ eV}}{A_1}\right), \quad (3)$$

$$Y = Y_0 + 100 \exp\left(\frac{E - E_0}{E_u}\right). \quad (4)$$

In Eq. (3), A_0 is the value of the absorption coefficient at 8 eV due to the low energy contribution only and A_1 is the slope of this low energy exponential in a semilogarithmic scale. We have chosen the particular expression of Eq. (3) to improve the fitting procedure. If this contribution is due to the VUV absorption of the Si-OH groups, then A_0 is expected to be linearly correlated with the Si-OH concentration and A_1 must have comparable values in all the wet materials. The high energy region, from ~ 8.1 to ~ 8.25 eV, may be described by Eq. (4), which is a convenient expression of the Urbach law [Eq. (1)]: E_0 is the energy value at which the contribution of the Urbach tail to the absorption coefficient is 100 cm^{-1} , E_u is the Urbach energy, and Y_0 is a parameter introduced to describe the profile of the absorption spectra in the range of < 7.5 eV. In Table I, the E_u , A_0 , and A_1 values as determined from the fits on the VUV absorption spectra are reported.

In Fig. 4 (filled symbols), the values of A_0 obtained from VUV spectra are reported as a function of the Si-OH group concentrations as estimated from the IR spectra. A_0 shows a good linear correlation with the Si-OH group concentration. The slope of the linear correlation was determined via a linear fit and it is $(8.1 \pm 0.8) \times 10^{-19} \text{ cm}^2$.

Finally, Fig. 5 shows the VUV absorption cross section of Si-OH groups in the range from ~ 7.5 to ~ 8.1 eV. We determined it as difference between the spectra of the SG-D

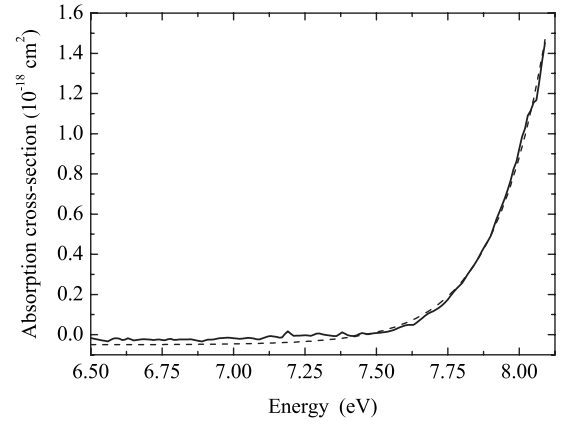


FIG. 5. VUV absorption cross section of Si-OH groups in $a\text{-SiO}_2$. The dashed line is obtained via an exponential fit of the cross-section curve.

and SG-A samples. These samples differ for their Si-OH group content only, but not for their T_f value. In Fig. 5, an exponential fit of the cross-section profile is shown as well.

III. DISCUSSION

The A_0 parameter as obtained from the VUV absorption spectra shows a good linear correlation with the Si-OH concentration as estimated from the IR absorption spectra. This result strongly supports the hypothesis that the absorption contribution in the region from ~ 7.5 to ~ 8.1 eV can be ascribed to the VUV absorption of the Si-OH groups. This outcome is relevant for several reasons. First, the linear correlation was verified over a broad set of wet materials which were produced via different methods and which have silanol group contents that encompass the whole typical range of Si-OH concentrations in $a\text{-SiO}_2$. Moreover, the correlation reported in Fig. 4 does not rely on any arbitrary assumption concerning the features of the intrinsic absorption because it was obtained in experimental conditions in which both the intrinsic and the Si-OH contributions are detectable and it was thus determined including the intrinsic absorption contribution in the analysis of VUV absorption spectra. Finally, in order to further point out the accuracy of our analysis, we also determined the VUV absorption cross section of Si-OH groups in the range from ~ 7.5 to ~ 8.1 eV as the difference between the spectra of two samples that were different in their Si-OH group content only, but not in their T_f value. We underline that the slope of the linear correlation between the A_0 and the Si-OH concentration data provides an estimate of the absorption cross section of silanol groups at 8 eV, $\sigma(8 \text{ eV}) = 8.1 \times 10^{-19} \text{ cm}^2$, which is in fair agreement with that independently obtained by the cross-section profile in the range from ~ 7.5 to ~ 8.1 eV. In Fig. 4, the value of the absorption coefficient at 8 eV versus the Si-OH group concentration as determined in Ref. 18 is reported for comparison (open symbol). Although the order of magnitude of the data already available in literature¹⁸ is consistent with our analysis, the graph in Fig. 4 makes the improved accuracy of the present results evident.

As for the A_1 values, we observed that they are comparable in all the examined materials. This point actually sustains our description of the VUV cross section of silanol groups as an exponential. Moreover, our results show that the values of both the parameters A_0 and A_1 are not affected by the disorder degree of the network, at least in the range of values of T_f examined in this study, and thus they can be accounted for only depending on intrinsic properties of Si-OH groups in α -SiO₂.

In Table I, the values of E_u are reported. E_u has substantially the same value in all the considered wet materials. In particular, it does not depend on the material type, natural, synthetic, or sol-gel. It is important to note that the Urbach energy we have previously measured in dry materials is generally higher: typically >70 meV. This information may explain the fact that the E_u values are comparable among wet materials produced via different methods. It is indeed known from several effects^{34–36} that a significant concentration of Si-OH groups favors the structural relaxation of the α -SiO₂ network and this may affect the degree of structural disorder of the system. In this context, our results suggest that the role of Si-OH groups can be important for the features of the VUV absorption spectra of α -SiO₂ both because of their contribution to the absorption in the spectral region from ~ 7.5 to ~ 8.1 eV and because of their influence on the intrinsic absorption characteristics, in particular, allowing the lower values of the Urbach energy. This can be interpreted in terms of a reduction in the disorder degree in wet materials.

The exponential character of the VUV absorption of Si-OH groups requires a few remarks. Actually, the description of this contribution as an exponential might be merely considered as a convenient representation of a limited part of a more complicated spectrum: from this point of view, this representation is useful because it offers a reliable tool for the analysis and description of VUV spectra of α -SiO₂. However, it is necessary to mention different interpretations possibly explaining the observed exponential absorption spectrum. First, the VUV absorption of silanol groups may be related to processes requiring an activation energy, such as, for example, a transient photodissociation. Alternatively, it can be argued that Si-OH groups may themselves induce a class of localized states determining a second Urbach edge. Admittedly, the experimental data reported here do not allow us to explore the reliability of these possible interpretations.

Our work does not address the question concerning the subspecies of Si-OH groups responsible for the VUV absorption. It has been suggested that the free Si-OH groups only are responsible for the observed VUV absorption.^{12,14} We found that all the examined wet materials show the same features of the VUV absorption spectra and that they have the same ratio between the concentrations of the several subspecies. This information does not allow us to identify the

subspecies responsible for the VUV absorption. From this point of view, the absorption cross section we have obtained may be affected by the presence of several subspecies of silanol groups only because of a constant factor depending on the ratio between the concentration of the subspecies responsible for the VUV absorption and the total content of silanol groups.

IV. CONCLUSIONS

The VUV absorption spectra of amorphous silicon dioxide with high concentrations of silanol groups (Si-OH) were studied. A scheme for the description of the VUV absorption spectra was obtained. These can be represented in terms of two exponential profiles. The low energy (from ~ 7.5 to ~ 8.1 eV) exponential [Eq. (3)] is ascribed to the absorption of Si-OH groups because a good correlation between the A_0 parameter (i.e., the contribution of this exponential to the absorption coefficient at 8 eV) and the Si-OH concentrations, as determined by infrared absorption measurements, was found. The high energy exponential profile (from ~ 8.1 to ~ 8.25 eV) [Eq. (4)] is due to the intrinsic absorption. Our results suggest that its features are affected by high Si-OH concentrations as well. In particular, it appears that Si-OH groups, favoring structural relaxation, allow lower values of the Urbach energy. This can be interpreted in terms of a reduction in the degree of disorder in wet materials.

Finally, the absorption cross section of silanol groups in α -SiO₂ in the range from ~ 7.5 to ~ 8.1 eV was determined. This result is particularly important because it was obtained without doing any special hypothesis. We derived it from the difference between the spectra of two samples produced via the same procedure and thus have the same average structural features. This is also confirmed by the fact that the two samples show comparable values of the fictive temperature. Moreover, this procedure assures that the intrinsic absorption contribution is correctly taken into account.

Further experimental study is required in order to address the issue concerning the role of the different subspecies of Si-OH groups. This can be done by analyzing, for example, the effects of irradiation and of temperature both on the IR and VUV absorption contributions of silanol groups in α -SiO₂. Work is in progress in this direction.

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