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ABSORPTION EDGE AND BAND GAP OF SiO_2 FUSED SILICA GLASS

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ABSTRACT

The presence of OH at 0.1 % levels in fused silica leads to a decrease in the deep ultraviolet (DUV) absorption. In fused silica prepared with appreciable dissolved oxygen and OH levels below 5 ppm (Suprasil W1), an absorption edge tail, extending from 7.65 eV, is seen and produces the additional absorption seen in the DUV. This tail, modeled as an indirect band gap, leads to a decrease in the band gap energy from 7.21 eV for silica with 1200 ppmw OH (Suprasil 1) to 6.31 eV for Suprasil W1 silica with dissolved oxygen and less than 5 ppmw OH. At the same time, the direct gap energy is seen to increase from 7.78 eV to 8.01 eV with decreasing OH content and increasing dissolved O_2.

Raman scattering measurements to investigate possible changes in the the Si-O-Si bond angle distributions, the glass fictive temperature and the relative populations of regular 4 fold and planar 3 fold ring defects in the glass have been performed to determine if glass structural changes are associated with the measured DUV absorption in the high oxygen, low OH glass. The bond angle distributions in Suprasil 1 and W1 are found to be identical with in the accuracy of the measurement, as are the fictive temperatures determined from Raman spectroscopy. Both glasses exhibit a similar number of 4 and 3 fold ring defects even though there is a slight change in the ratio of these defects among the two glasses. From this Raman characterization of the glass structure, no appreciable difference in the glass structure is found. These findings support the conclusion that the additional DUV absorption found in Suprasil W1 arises from extrinsic absorption of the dissolved excess oxygen introduced in the glass during synthesis. The Si-O bond length distribution is not well determined using Raman spectroscopy, and a 0.07 Å increase in this bond length distribution could lead to the 0.2 eV change in the band gap energy of low and high OH fused silica. The mechanism for this could arise from the atomic structure and relaxation of the $\equiv Si - OH$ species.

INTRODUCTION

Fused silica is used as a substrate for photomasks in integrated circuit (IC) lithography, and with the current focus in conventional optical lithography to move from visible exposure wavelengths to deep ultraviolet (DUV) sources, the DUV properties of fused silica are gaining renewed importance. The DUV absorption of ultrahigh purity fused silica is found to increase in glasses with very low OH concentrations. This is in direct contradiction to what is observed in the IR for fused silica used for optical waveguide communications where even extremely low concentrations of OH have a deleterious effect on transparency due to the presence of the OH vibrational absorptions in the IR. For DUV applications of fused silica, the presence of OH in the glass leads to increased transparency. The synthetic fused silica studied here is Suprasil 1 and W1, where the low OH glass is synthesized in an oxygen plasma torch. In recent work of Awazu and Kawazoe[1], studying glasses they prepared, they show that an absorption edge tail appears in glasses which contain excess dissolved oxygen. Our goal is to find if the DUV absorption in Suprasil fused silica with low OH is comparable to the excess O_2 absorption reported by Awazu, and to determine if their are other structure related changes in the absorption edge of these glasses. We have used UV and vacuum ultraviolet (VUV) spectroscopy to probe the DUV absorption and the fundamental absorption edge arising from the band gap transitions along with Raman spectroscopy to determine if their are changes in the glass structure of the high and low OH containing Suprasil glasses, 1 and W1.

SiO_2 glass has wide spread technological applications in optics, including optical lenses, optical fiber waveguides and photomasks. It therefore has been the focus of much fundamental research to understand its electronic structure, bonding, defects and properties[2,3,4]. This has included band structure calculations of crystalline and amorphous SiO_2[5,6,7,8] including the work of W. Y. Ching, and recently there has been extensive work on using band structure calculations to study the physical properties of crystalline forms SiO_2 and their pressure induced amorphitization.[9,10,11,12,13]. Experimentally the interband electronic structure of silica has been studied using optical techniques, with some studies extending up to 50 eV [14,15,16,17,18,19,20,21,22,23,24] and two studies reporting the temperature dependence of the absorption edge[25,26]. In addition photoemission[27,28] and electron energy loss[29] methods have also been applied to the study of the intrinsic electronic structure. There is a very extensive literature studying the effects of irradiation on the intrinsic defects and extrinsic impurities and their optical properties in the UV which is not so relevant to our present discussion but does demonstrate the large number of possible sources of DUV absorption in glass.[30,31]

To be able to clearly identify changes in the absorption edge and band gap as arising from OH or nonstoichiometry and not from transition metal impurities, it was very important to choose high purity SiO_2 with identical

impurity contents. Transition metal impurities in SiO_2 can produce strong DUV absorption below the band gap, so impurity content must be controlled. We have chosen two fused silica materials from Heraeus Amersil[32] which are grade 1 Suprasil, among the highest purity and most homogeneous commercial materials. They are synthesized from high purity starting materials, and contain less than a total of 1 ppmw metallic impurities. The type 1 grade of Suprasil is essentially isotropic for index variations. The only difference between Suprasil 1 and W1 is the fabrication method of the glass from the synthetic starting materials[33]. Suprasil 1 is made using a flame torch, which leads to an OH content in the final glass of 1200 ppmw, while Suprasil W1 is "water free" because it is made in a oxygen plasma torch and therefore has an OH content below 5 ppmw. Suprasil W1 may have 40 to 50 ppmw of Cl and also residual dissolved O_2 from the oxygen plasma, in addition its fusion temperature is higher than the flame torch used to produce Suprasil 1. After fusion both materials undergo the same high temperature annealing schedule to improve index of refraction homogeneity.

In the 80's, the important role of oxygen nonstoichiometry in producing DUV absorption centers such as non-bridging oxygens, oxygen vacancies, or interstitial oxygen had gained importance.[34] Most of this work centered on oxygen deficient and OH containing glass and the role of these nonstoichiometry related defects on optical absorption and luminescence properties of fused silica.[35,36,37,38,39] In addition extensive studies by Hama et al[40,41] and Awazu and Kawazoe[42,43] have focused on the non-stoichiometric defects and their optical and ESR properties.

There have been two previous studies to specifically address the changes in the DUV absorption and fundamental absorption edge of low and high OH content fused silica. In 1978, Kaminow, Bagley and Olson [44] reported VUV absorption measurements on two high OH fused silicas (Suprasil 2 and Spectrosil A[45]) and two low OH fused silicas (Suprasil W2 and Spectrosil WF). They report absorption coefficient values (α) up to 40 cm^{-1}. For the low OH water-free fused silica they found both an absorption edge peak centered at 7.5 eV with a prominent tail extending to lower energies and a shift of the fundamental absorption edge to higher energy by 0.1 to 0.2 eV. They speculated that these two absorption edge changes probably arise due to the differences in OH content of the glasses, either from an optical transition which is suppressed in OH containing glass, or the presence of possible structural or electronic defects in the low OH containing fused silica.

Awazu and Kawazoe[1] have recently published an extensive study of 9 types of synthetic fused silica, including samples made by the VAD soot method, in a conventional flame torch and in oxygen and oxygen/argon plasma torch. they report absorption coefficients for these glasses up to 10 cm^{-1}. In glasses synthesized in a high oxygen pressure, they observe the 7.5 eV shoulder and associated DUV absorption tail reported by Kaminow for low OH content glass. By comparing the wavelength of this absorption tail with the known Schumann-

Runge bands[46] of O_2 molecules in the VUV, they attribute this absorption edge tail to dissolved oxygen in the glass. In addition using an ArF excimer laser they are able to transform the dissolved O_2 into O_3 molecules with an associated absorption appearing at 4.8 eV, the Hartley bands[47] of the gaseous species. In their paper they are most concerned with the optical absorption arising from the nonstoichiometry associated defects present in the fused silica, but do show that the high OH containing silica does exhibit a red shift of the fundamental absorption edge which is seen at energies higher than the dissolved O_2 absorption edge tail. They reference unpublished work of H. Imagawa for this shift to higher energies of the band gap or fundamental absorption edge of low OH containing fused silica. Imai identified they band gap shift as arising directly from OH related species [38] by observing its dependence on OH content. Still no direct atomic and electronic mechanism is given for the role of OH in increasing the band gap of low OH containing fused silica.

BAND GAP AND GLASS STRUCTURE

It is known that the presence of OH in fused silica strongly effects the melt viscosity[48,49]. This OH induced decrease in the melt viscosity leads to a reduction of the fictive temperature[50,51] of the glass, the temperature at which the glass structure is frozen into the solid state. Therefore one may expect that the OH containing glass, with its lower fictive temperature, will possess a more ideal glass structure with a narrower distribution of Si-O bond lengths or Si-O-Si bond angles. Still for the Suprasil materials, they are both extensively annealed after synthesis, which may lead to similar glass structures and fictive temperature independent of the OH induced viscosity changes during fusion. Because of these arguments we wish to determine if the effect of OH on the band gap and fundamental absorption edge energy arises due to some modification of the intrinsic glass structure.

Raman spectroscopy has proven to be a useful probe of glass structure,[52] and we use Raman measurements to determine if there are any observable characteristics of the glass structure which produced the electronic structure changes responsible for the unexplained increase of the fundamental absorption edge and band gap in low OH containing fused silica. The Raman spectra can give information on the Si-O-Si bond angle distribution from the width of the broad peak, ω_1, centered near 446 cm^{-1} . This peak has has been interpreted in the central-force network model of Sen and Thorpe[53] as extended by Galeener[54] as arising from a maximum in the Raman matrix element at the low-frequency edge of a band growing out of the A_1 breathing mode of the SiO_4 molecule, which is drastically broadened by the coupling with the network that occurs when the intertetrahedral angle θ is larger than 90°. Making the simplifying assumptions that the force constants do not vary with θ, and that non-central forces can be neglected, the width of this band is proportional to the spread $\Delta\theta$ in the intertetrahedral angle. In addition the Raman spectra are observed to shift with the fictive temperature of the glass and to change with the presence of higher

energy structures present in the glass.[55] The fictive temperature of the glass is seen to correlate with the frequency of the first peak, ω_1, and with the four other Raman peaks associated with normal network vibrations, ω_3, ω_4(LO) and ω_4(TO). Two other peaks in the Raman spectra, D_1 and D_2, are believed to arise from the existence of regular four-fold and planar threefold ring defects in the glass, which are high energy structures representative of a more disordered glass structure typically associated with a higher glass fictive temperature.

Insight into how glass structure may change the band gap energy of fused silica is given by the work of W. Y. Ching who has calculated band structures for a family of crystalline SiO_2 compounds including the variation of the the band gap energy with variations of the structural parameters such as the Si-O bond length and the Si-O-Si bond angle.[56] In these crystalline structures the bond lengths vary from 1.55 to 1.65 Å while the Si-O-Si bond angles vary from approximately 136 to 180° and these changes are found to correlate to changes in the band gap energy from 8.4 to 11 eV. These results correspond to band gap dependences on the Si-O-Si bond angle of 0.065 eV/° and -35 eV/Å for the Si-O bond length. Ching has also done band structure calculations of amorphous silica based on the continuous random network glass structural model of Bell and Dean (BD)[57] and has found that one of the major characteristics of the amorphous state of silica is band tailing into the band gap region.[58] In a band structure study of both the Bell and Dean model, and a molecular dynamics (MD) model of fused silica by Gupta[59], a reduction in the band gap energy is reported in the amorphous state, from 8.4 eV for crystalline α quartz, to 7.5 eV for BD and 7.2 eV for the MD model. The MD model exhibited large distortions (+/- 15% of 1.62 Å) in the Si-O bond lengths compared to the BD model, and in both cases changes in the amorphous SiO_2 structure produce decreases in the band gap energy. In a similar band structure study of compressed forms of fused silica, Ching reports changes in the band gap energy from 8.47 to 8.13 as the density increases from 0 to 20%.[60] Their study of compressed forms of SiO_2 found that the band gap decrease is associated with changes in the spread of the Si-O bond lengths from 1.62 +/- 0.016 Å to 1.62 +/- 0.005 Å at 20 % compression and also changes in the Si-O-Si bond bangle from 147.4° to 133.7°. These results demonstrate that changes in the glass structure can lead to changes in the band gap energy and fundamental absorption edge of fused silica.

EXPERIMENTAL TECHNIQUES

Samples

The Suprasil 1 and W1 samples used are 1.27 cm (1/2") disks, 0.067 cm thick, and were optically polished on both sides using colloidal silica by the manufacturer. Two samples of each Suprasil grade were studied, with identical results found for each type.

Optical Spectroscopy

The optical spectroscopy measurements were taken using two spectrophotometers, a Perkin Elmer Lambda 9 in the NIR, visible and UV and a UV, VUV spectrophotometer using a laser plasma light source, which is discussed in detail elsewhere.[61] Reflectance and transmission were measured at all wavelengths and the absorption coefficient calculated taking into account the effects of second surface reflections which arise in the transparent regions of the sample.[62]

To characterize the various absorption edge structures observed, band gap energies were determined by fitting the absorption edge using either direct or indirect band gap models. A band gap energy is determined using a direct gap model using a linear fit in the region of interest to a plot of α^2E^2, where α is the absorption coefficient in cm^{-1} and E is energy in eV. A band gap energy for an indirect band gap model is determined by linear fitting to $\alpha^{1/2}$. Formally direct and indirect band gap models do not apply to amorphous materials such as glass, due to the loss of long range periodicity in the material, and the consequent destruction of the Brillouin zone construct used for band structure analysis. Here we are using the direct and indirect models only as a tool to characterize the complex absorption edge behavior of these samples, and draw on the crystalline band gap models because the shape of the absorption edges measured are reminiscent of those found in crystalline materials.[63] The direct and indirect gap fitting has been used previously for characterizing the changes in the absorption edge in amorphous materials such as silicon[64] and other amorphous semiconductors [65] and has been found useful to characterize the observed changes in the electronic structure.

Raman Spectroscopy

The Raman measurements were made using 514.5 nm light from an Ar^+ laser and a double-grating spectrometer with 1 cm^{-1} resolution. As shown by Shuker and Gammon[66], the measured intensity $I(\omega)$ can be described by

$$I(\omega) = C(\omega)G(\omega)\frac{n(\omega)+1}{\omega} \quad (1)$$

where $C(\omega)$ is the matrix element, $G(\omega)$ is the density of states, and $n(\omega)$ is the boson occupation. The raw data have therefore been multiplied by $[n(\omega)/(n(\omega)+1)]$ so that the reduced intensity $I_r(\omega) = C(\omega)G(\omega)$.

RESULTS

The transmission of Suprasil 1 and W1 is shown in Figure 1, where the x axis is plotted on a log energy scale to show both the NIR absorption due to the OH present in Suprasil 1, and the VUV transmission cutoff. The transmission in the region from 1.5 to 7.65 eV is higher for the OH containing Suprasil 1 sample, and this demonstrates that Suprasil 1 has increased DUV transparency.

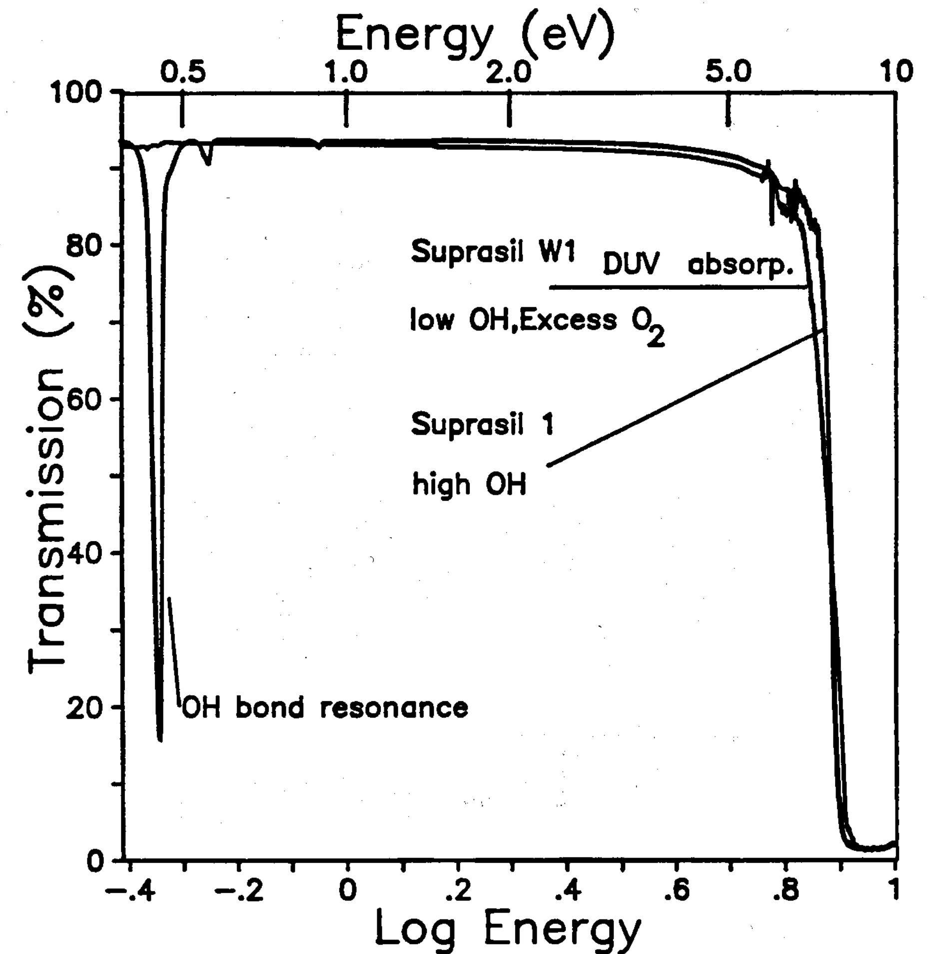

Figure 1. The transmission of Suprasil fused silica from the NIR to the VUV, spanning the NIR bond resonance of OH up to the fundamental absorption edge in the VUV arising from electronic transitions. The x axis is plotted as a function of Log energy, values of energy are shown on the top axis.

The absorption coefficient α in units of cm^{-1} for the two Suprasil samples is shown in Figure 2 in the region of the fundamental absorption edge. The absorption is dramatically decreased below 7.65 eV for Suprasil 1 fused silica. In addition, at 7.65 eV, the absorption edges of Suprasil 1 and W1 cross,

with Suprasil W1 exhibiting lower absorption above 7.65 eV. This demonstrates the two different effects that are present in these samples: there is increased absorption in Suprasil W1 at 7.65 eV and below, while the fundamental absorption edge and band gap of Suprasil W1 in simultaneously increased. In Table 1 the results of band gap fitting are summarized, including the direct gap fits at higher energy and both direct and indirect gap fits in the lower energy region of the fundamental absorption edge.

The Raman spectra taken on the two samples are shown in Figure 3, and fits to the spectra, made using an asymmetric lorentzian lineshape are given in Table 2.

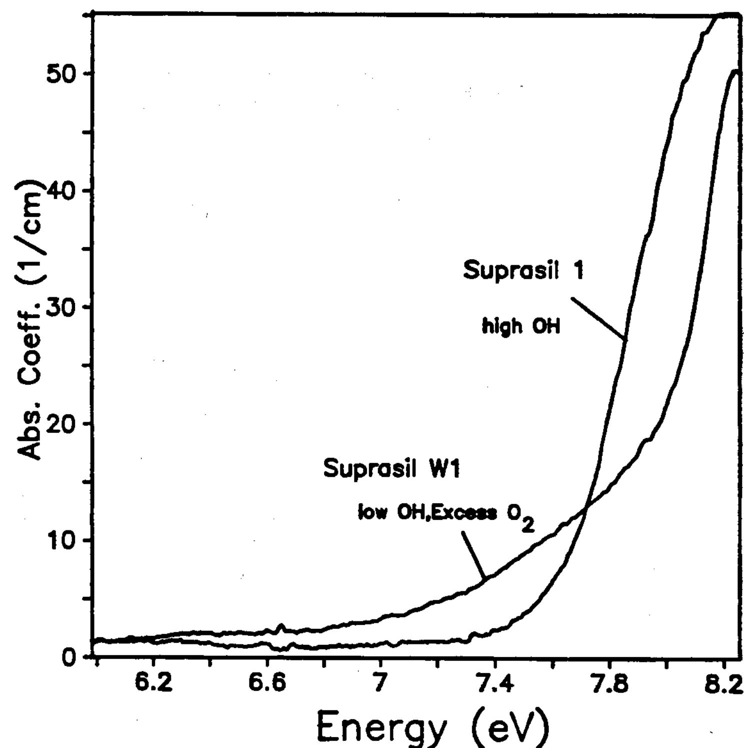

Figure 2. The fundamental absorption edge of fused silica samples with low OH and excess O_2 (Suprasil W1) and high OH content (Suprasil 1). The absorption coefficient (α), in units of cm^{-1}, is plotted versus energy. The Suprasil W1 sample exhibits a large direct gap energy, but a prominent tail extends to low energy. This tail, arising from excess dissolved O_2, in the low OH sample produces a higher absorption coefficient in Suprasil W1 below 7.65 eV, which extends through the DUV to the visible.

Table 1. Results of band gap fitting of the VUV absorption edge of Suprasil fused silica. At higher energy a direct gap model has been used to fit the absorption edge in the range of α from 26 to 47 cm^{-1}, while at lower energy on the absorption edge both direct and indirect band gap models are used to determine band gap energies for α in the range from 2.4 to 14 cm^{-1}. The accuracy of the fits was +/- 0.05 eV.

Sample	α = 2.4-14 cm^{-1} Indirect Gap Fit	α = 2.4-14 cm^{-1} Direct Gap Fit	α = 26-47 cm^{-1} Direct Gap Fit
Suprasil 1 High OH	7.21 eV	7.52 eV	7.78 eV
Suprasil W1 Low OH	6.31 eV	7.19 eV	8.01 eV

Table 2. Fit parameters to the Raman features of Suprasil 1 and Suprasil W1, with all units in cm^{-1}. The peak labeling as per Galeener. Peak heights are normalized to the measured height of ω_1.

Peak	Center S1	Center SW1	Height S1	Height SW1	Width S1	Width SW1	Asym. S1	Asym. SW1
ω_1	447.3	446.9	1	1	200.5	198.6	-0.422	-0.408
D_1	491.2	492.7	0.432	0.439	25.99	29.98	0.067	-0.011
D_2	600.8	597.0	0.145	0.172	70.8	57.3	0.325	0.3936
ω_3	801.8	803.17	0.371	0.357	81.24	84.65	0.128	0.072
ω_4(TO)	1061.1	1054.0	0.158	0.140	58.29	72.97	-0.197	0.201
ω_4(LO)	1191.3	1207.5	0.099	0.092	88.01	86.67	0.093	-0.0298

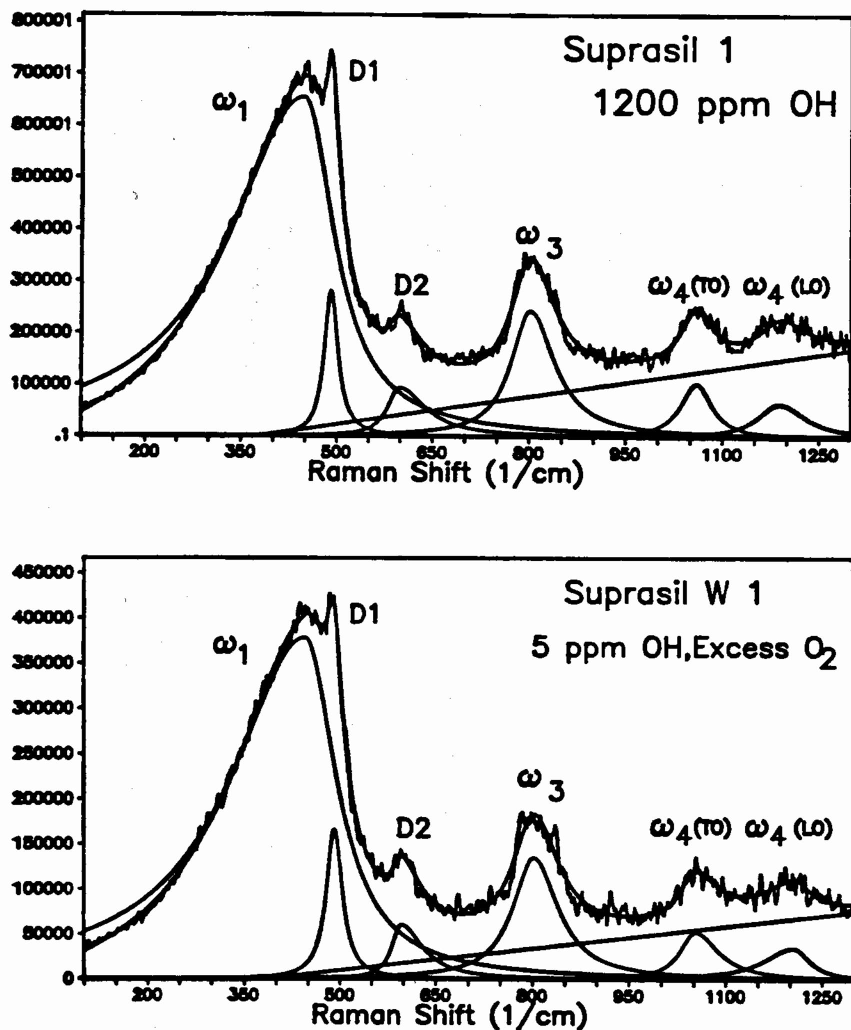

Figure 3. Raman spectra, and Lorentzian fits for a)Suprasil 1 and b)Suprasil W1, showing the peaks, labeled as per Galeener, used for glass structure data.

DISCUSSION

In the range of OH and dissolved O_2 content studied in Suprasil 1 and W1, increased OH and decreased O_2 content decreases the DUV absorption of fused silica. In the low OH fused silica, the increase in the DUV absorption arises from the introduction of a tail to the fundamental absorption edge which starts at 7.65 eV and extends to 1.5 eV. This change in the absorption edge shape can be seen in the band gap fits performed in the lower energy part (below α=10cm^{-1}) of the edge. As reported by Awazu[1], Suprasil W1 appears to have excess dissolved O_2 which gives rise to the DUV absorption edge tail. The introduction of OH to the 1200 ppmw level, and removal of O_2, in fused silica leads to a dramatic increase in the energy of the absorption edge tail evaluated in this lower energy region, from 6.31 to 7.21 eV, or using a direct gap fitting the energy increases from 7.19 to 7.52 eV. This increase in the indirect gap energy below 7.65 eV with increased OH and decreased dissolved O_2 is directly responsible for the decrease in the DUV absorption of fused silica. Imai[38] believes that the incorporation of excess oxygen in low OH fused silica, such as Suprasil W1, occurs through the presence of peroxy linkages, $\equiv Si-O-O-Si\equiv$, as first reported by Friebele[67], instead of dissolved molecular oxygen. Awazu's identification of the observed absorption as comparable to the Schumann-Runge bands of O_2 appears to contradict the assignment of the VUV absorption edge tail to peroxy linkages. But either of these species can react with OH to produce a substantial quantity of $2\equiv Si-OH$ as recently discussed by Griscom.[34] This Si-OH group may play an important role in the change in the direct band gap energy of low and high OH containing fused silica as discussed below.

The presence of OH and O_2 leads to another change in the fundamental absorption edge which is seen at energies above 7.65 eV or at values of the absorption above 11 cm^{-1}. Above this point the difference between these two materials is reversed, the absorption edge is seen to shift to lower energy with the increased OH content of Suprasil 1, as reported by Kaminow. This is seen in the values of the direct gap energy fitted in this region where the band gap of SiO_2 decreases from 8.01 to 7.78 eV with increased OH content. Except for the fact of the additional effects of the dissolved O_2, this inversion in the absorption edge behavior might be considered to arise from the f sum rule and the conservation of transitions. In Suprasil W1, oscillator strength or interband transitions would therefore be considered to shift from higher energy and redistributed at lower energy giving rise to the DUV absorption.

The properties of these two Suprasil fused silicas are very similar, no change in the density, index, or birefringence are reported by the manufacturer. Other than the OH and O_2 content, the only observed property difference is a reduction in the homogeneity achievable in the low OH silica Suprasil W1, whose index uniformity is reported as 10 x 10^{-6} as opposed to 8 x 10^{-6} for the high OH Suprasil 1. This index inhomogeneity does support the idea that there are structural difference between these two materials. Hama et al[41] mention that low

OH fused silica with excess O_2 can exhibit regions which have oxygen excess and at the same time have regions where oxygen vacancies occur; this might be the source of the index nonhomogeneity in Suprasil W1. Another possible cause of the inhomogeneity arises from the fact that the melt viscosity of the low OH silica is much higher than the high OH silica and this, coupled with the higher fusion temperature of the oxygen plasma torch used to synthesize Suprasil W1, may produce changes in the glass structure, giving rise to the greater index nonhomogeneity in Suprasil W1. But by the findings of Ching, increased structural disorder as demonstrated by index nonhomogeneity, in Suprasil W1 would lead to a decrease in the band gap energy in this material, in contradiction to what is found. A structural mechanism involving some of the extrinsic or nonstoichiometric defects in fused silica will be required to explain the observed results.

The Raman measurements give us access to some characteristics of the glass structure. From Table 2, the width of the ω_1 peak is identical, within measurement accuracy, demonstrating no appreciable difference in the Si-O-Si bond angle distributions for these glasses. This bond angle distribution is one of the most easily varied aspects of glass structure and we had expected to see the structural difference appear in the bond angle distribution. The center energy of the ω_1 peak is found to be related to the fictive temperature, but here again these glasses, which have been extensively annealed after formation, show no appreciable difference in the fictive temperature of the structure determined in this manner. The relative amounts of four and three fold ring structures, which are characteristic of a more distorted glass structure, can be determined by comparing the relative intensities of the D_1 and D_2 peaks. The total areas of these defect structures in the glass are comparable, with only a slight difference in the relative quantity of the four or three member rings in the two silicas. This difference in the glass structure does not appear to be sufficient to give rise to the fundamental band gap change we observe in the low OH silica.

From the band structure calculations, a much greater dependence on the Si-O bond length (-35 eV/Å) is found than on the Si-O-Si bond angle distribution (0.065 eV/°). In the BD glass structure model, the distribution of Si-O bond lengths is 1.62 Å +/- 0.162 Å. A decrease in the band gap of SiO_2 arising from variation of the Si-O bond length requires an increase in the Si-O bond length. A change in the direct gap energy from 8.01 to 7.78 eV, i. e. 0.23 eV, would require an increase in the Si-O bond length distribution of the high OH silica 0.07 Å. The Raman vibrational modes are insensitive to the Si-O bond length due to the relative flatness of the vibrational potential with bond length. Yet the band gap and absorption edge is very sensitive to the Si-O bond length. With these considerations, we suggest that a structural difference between fused silica synthesized under low and high OH conditions might arise from a change in the Si-O bond length distribution. Still the argument of variation in the stoichiometric and intrinsic glass structure determining the change in the band gap energy from 7.78 to 8.01 eV is not satisfying. The low OH glass (Suprasil W1) is expected to be more structurally disordered, which would be expected to decrease, not increase, the band gap energy of the material.

A distinct mechanism, considering the extrinsic (such as OH) or non stoichiometric (such as excess oxygen) defects, is needed to understand the measured properties of these samples. First let us discuss the possible effects of the oxygen nonstoichiometry related defects. Hama [41] in his discussion of low OH, oxygen excess, fused silica discusses two methods by which the oxygen excess can be accommodated. One, first suggested by Friebele et al, involves the presence of peroxy linkages of the form $\equiv Si-O-O-Si\equiv$, while the other is simple interstitial, or dissolved, molecular oxygen which is not incorporated in the glass structure. The peroxy linkage, the precursor to the formation of the peroxy radical defect, is the species which holds interest for explaining the increase in the direct band gap energy of low OH, excess O_2 fused silica. The presence of these species could give rise to the observed increase in the band gap energy. These types of linkages do not represent a simple change in the structure of the glass but instead involve an increased oxidation state of the silicon atoms involved in the peroxy linkage. To shift the band gap 0.2 eV to higher energy requires removing the lowest lying Si derived conduction band states and the highest lying O 2p lone pair states at the top of the conduction band. The oxidation state represented by $\equiv Si-O-O-Si\equiv$ suggests such a "super oxidation" of the silica. From this point of view, the absorption edge of the high OH silica would be the intrinsic band gap of SiO_2 , while the presence of excess O_2 modifies this fundamental band gap, removing states from the intrinsic band gap to form the excess oxygen absorption edge tail. This perspective, of the intrinsic band gap of stoichiometric SiO_2 fused silica being 7.78 eV, is not supported by findings of other researchers.

Griscom,[34] based on work of Imai[68] and Awazu,[69] instead reports that the fundamental absorption edge seen in the Suprasil W1 at 8.01 eV is the intrinsic edge of SiO_2 and that the shift to 7.78 eV in high OH silica arises from the the additional band edge absorption arising from the presence of $\equiv Si-OH$. In Suprasil 1 these species would be present at the level of 1200 ppm, quite a high concentration, well able to lead to the levels of absorption reported here. For these hydroxyl species to produce the 0.2 eV decrease in the direct band gap energy, they would need to give rise to a 0.07 Å increase in the Si-O bond length of these $\equiv Si-OH$ defects so as to push states below the band gap edge of intrinsic low OH silica. Accurate information on the atomic structure and bond lengths of these hydroxyl species could elucidate the atomic and electronic mechanism of this band gap change.

CONCLUSIONS

The presence of OH at 0.1 % levels in fused silica leads to a decrease in the deep ultraviolet (DUV) absorption. In Suprasil W1 fused silica prepared with OH levels below 5 ppm, and excess dissolved O_2, an absorption edge tail, extending from 7.65 to 1.5 eV, is seen and produces the additional absorption seen in the

DUV. This tail, modeled as an indirect band gap, leads to a decrease in the band gap energy from 7.21 eV for Suprasil 1 fused silica with 1200 ppmw OH to 6.31 eV for silica with less than 5 ppmw OH and excess dissolved O_2. This absorption edge tail has been shown by Awazu and Kawazoe to arise from dissolved oxygen in the fused silica. Suprasil W1 is prepared in an oxygen plasma torch and the absorption edge tail we observe below 7.65 eV is consistent with the reported properties of dissolved excess O_2.

The direct gap energy, measured above 7.65 eV, is seen to increase from 7.78 eV for high OH Suprasil 1 to 8.01 eV in oxygen excess, low OH Suprasil W1 fused silica. The mechanism for this change in the band gap energy could arise from the effect of OH on glass viscosity and fictive temperature, leading to changes in the structure of fused silica synthesized under conditions of low OH content. To pursue this we performed Raman scattering measurements to investigate possible changes in the the Si-O-Si bond angle distributions, the glass fictive temperature and the relative populations of regular 4 fold and planar 3 fold ring defects in the glass. The bond angle distributions in low and high OH content silica are found to be identical with in the accuracy of the measurement, as are the fictive temperatures determined from Raman. Both glasses exhibit a similar number of 4 and 3 fold ring defects even though there is a slight change in the ratio of these defects among the two glasses. From this Raman characterization of the glass structure, no appreciable difference in the glass structure is found.

From band structure calculations for crystalline phases of SiO_2 and of various glass structure models a strong dependence of the band gap energy on the Si-O bond length is found, while the Si-O bond length does not strongly affect the Raman vibrational parameters. A slight change in the Si-O bond length distribution between low and high OH fused silica may be responsible for the observed absorption edge and band gap changes.

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