

Photoinduced paramagnetic defects in amorphous silicon dioxide

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(Received 17 April 1984)

Several paramagnetic defects are photoinduced in amorphous SiO_2 by sub-band-gap light. The resulting EPR spectrum changes dramatically as the excitation energy is varied, and is sensitive to the OH content of the material. A three-component resonance seen in high-OH-content SiO_2 is ascribed to a nitrogen-impurity-related defect.

One of the most powerful experimental tools for investigation of defects in amorphous silicon dioxide ($a\text{-SiO}_2$) is electron paramagnetic resonance (EPR) (for a review see Ref. 1). Although annealed $a\text{-SiO}_2$ is not paramagnetic, defects containing unpaired spins can be produced by ionizing radiation such as γ or x rays. Similarly, for the semiconducting chalcogenide glasses the most direct evidence for the structure of defects has come from EPR.^{2,3} However, in the latter materials the paramagnetic states were induced by visible or infrared light. There is an important potential advantage in using light to induce paramagnetic states, since the excitation energy can be varied. In this paper we report the first observation of paramagnetic defects induced by light in $a\text{-SiO}_2$.

We have exposed both Suprasil (~ 1200 ppm OH) and Suprasil W ("water-free," ~ 5 ppm OH) samples⁴ to the unfocused beam from a multigas excimer laser (Lumonics). Photon energies of 5.0, 6.4, and 7.9 eV were obtained using KrF, ArF, and F_2 , respectively, as the lasing medium. For the 7.9-eV excitation the samples were held in an evacuated chamber flanged directly to the output window of the laser. The samples are polished plates of 3-mm thickness, and were exposed over an area of about 0.5 cm^2 . For the weakly absorbed 5.0- and 6.4-eV light the sample volume is thus $\sim 0.15 \text{ cm}^3$. For 7.9-eV photons the absorption coefficient is $\sim 20 \text{ cm}^{-1}$ in Suprasil W (Ref. 5), giving an active sample volume of 0.025 cm^3 . The data of Ref. 5 do not accurately show the absorption coefficient of Suprasil at this energy, but it is approximately 2 or 3 times that of Suprasil W. In all cases the absorbed dose of photons is a few times 10^{19} ; data given by Greaves⁶ were used to estimate the number of absorbed photons at the lower photon energies. EPR measurements were carried out at room temperature using a Varian E-9 spectrometer equipped with a TE011 cylindrical cavity operating at $\sim 9.41 \text{ GHz}$ and 0.2-mW microwave power.

The EPR spectra are displayed in Fig. 1. There are striking differences between Suprasil and Suprasil W, and in the Suprasil W spectra at different excitation energies. We will discuss the Suprasil W spectra first. The resonance at $g \approx 2.001$, seen in all of the spectra, is the well-known E' center, which is a silicon dangling bond.⁷⁻⁹ This resonance is easily recognized from the form of its g tensor and by its saturation properties.¹⁰ In all of the spectra displayed, the E' resonance is saturated and is not well resolved because it is narrower than the modulation amplitude of 3.2 G. This means that the absolute number density of E' centers cannot be extracted from the spectra. Nonetheless, trends in this density are apparent. Most striking is the larger

number of E' centers induced by 5.0-eV light than by 6.4-eV light.

The spectrum observed in Suprasil W after 7.9-eV excitation closely resembles that which has been previously observed in this material after gamma irradiation.¹¹ However, the presence of several sharp features between $g = 2.01$ and $g = 2.00$ in these room-temperature spectra is surprising since such structure is only resolved in the γ -irradiated samples when measured at low temperature. A distinguishing feature of this spectrum is the shoulder extending to $g \approx 2.065$. This shoulder has been identified as part of the resonance of a peroxy radical.^{11,12} The shoulder disappears upon lowering the excitation energy to 6.4 eV.

By double integration of the 7.9-eV-induced spectrum and comparison with the Varian weak-pitch standard we find that there are $\sim 2.5 \times 10^{17}$ spins/ cm^3 . In contrast, the spectra obtained from the lower photon energies correspond to

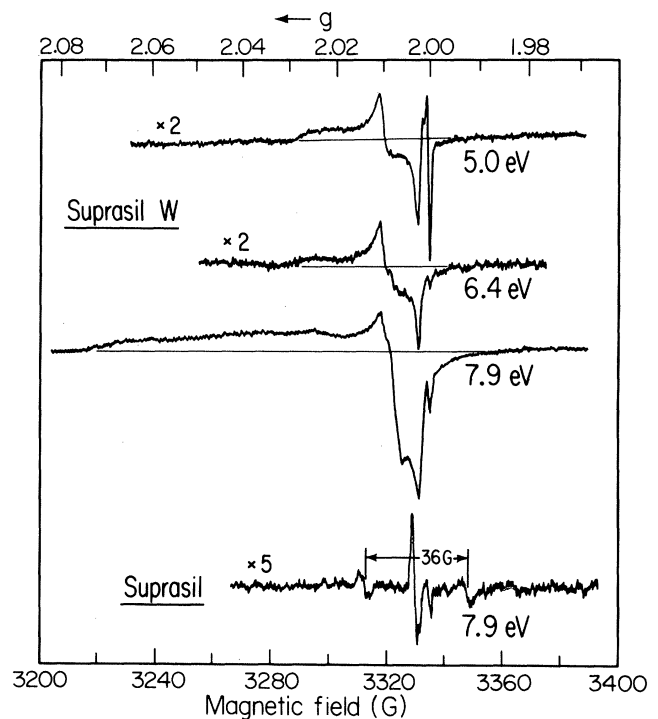


FIG. 1. Photoinduced electron paramagnetic resonance derivative spectra (X band) in amorphous SiO_2 . Upper three curves: Suprasil W (OH free), spectra resulting from three different excitation photon energies. Lower curve: Suprasil (1200 ppm OH), 7.9-eV excitation.

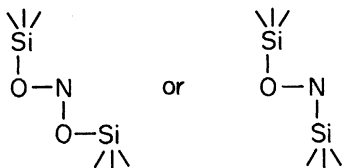
only $\sim 2 \times 10^{15}$ spins/cm³ (not counting the E' centers).

The predominant changes observed in going from 7.9 to 6.4 eV excitation are the loss of the low-field shoulder and of the sharp minimum at 3324 G. Other features of the spectrum remain relatively unchanged: a shoulder at $g \approx 2.025$, a maximum at $g = 2.011$ and a minimum at $g = 2.003$. The only unambiguous difference between the 6.4- and 5.0-eV spectra is the change in E' intensity; enough sample-to-sample variation was observed, both in the shape of the low field shoulder and in the region between the two extrema, to account for the smaller differences. There seem to be contributions from several overlapping resonances, so that small variations in the relative intensities of these components could lead to substantial changes in the appearance of the spectrum.

The spectrum obtained in Suprasil is strikingly different. Here, we observe a narrow resonance at $g = 2.004$ in addition to the E' resonance. Symmetrically placed about the new resonance and separated from it by approximately 18 G are two hyperfine lines. The hyperfine lines are smaller in amplitude (by about a factor of 4) but wider (by about a factor of 2), so that the number of spins in each of the three lines is the same. Such a three-component spectrum is characteristic of an electron or hole undergoing a hyperfine interaction with a single nucleus of spin 1. The different linewidths of the three components could result from a hyperfine anisotropy which is greater than the g -factor anisotropy. For the simplest case of an isotropic g tensor and an axial A tensor the resonance condition to first order is¹³

$$\hbar\omega = g\beta H + m_l(A_{\parallel}^2 \cos^2\theta + A_{\perp}^2 \sin^2\theta)^{1/2} \quad (1)$$

Since the observed spectrum in the glass corresponds to an angular average of Eq. (1), the lines corresponding to $m_l \neq 0$ will be broadened by the hyperfine anisotropy, whereas the central $m_l = 0$ line will not. Another explanation is that there may be a distribution of hyperfine coupling constants because of disorder. From the data alone we cannot rule out the possibility that the nuclear spin is greater than one; the width of the lines is proportional to $|m_l|$, so the lines with $|m_l| \geq 2$ would have amplitude smaller than the noise. A mixture of integer and half-integer spin isotopes in the right ratio is also possible, for example, spin-zero plus twice as many spin $\frac{1}{2}$. However, there is only one element whose natural isotopic abundances are consistent with the observed spectrum, and that is nitrogen (99.3% $I = 1$, 0.7% $I = \frac{1}{2}$). We therefore ascribe this resonance to a nitrogen-impurity-related defect. Strong supporting evidence for this identification comes from the magnitude of the hyperfine interaction. The radial NF₂ exhibits a hyperfine splitting of 17 G (Ref. 14) which is nearly identical to that (18 G) observed in Suprasil (Fig. 1). In NF₂ the unpaired electron is in a three-atom π^* orbital formed from the dangling nitrogen bond and a lone-pair orbital on each of the fluorine atoms. A similar electronic state, and consequently a similar hyperfine splitting, could result if the fluorine were replaced by oxygen. Possible candidates for the structure of this paramagnetic center are thus



The density of these nitrogen-associated centers is approximately 7×10^{14} cm⁻³, if we take the absorption coefficient of the 7.9-eV light in Suprasil to be 50 cm⁻¹. We have not observed this resonance in Suprasil W, but it may be obscured by the other resonances.

None of the broad resonances seen in Suprasil W are observed in Suprasil, but the behavior of the E' resonance as a function of excitation energy is similar in the two types of α -SiO₂. Differences in the photosensitivity of Suprasil and Suprasil W have been noted previously.¹⁵ After 7.9-eV excitation an absorption band centered at 4.8 eV is induced only in Suprasil W, and although 1.9-eV radiative-recombination centers are induced in both materials only a fraction of them are stable at room temperature in Suprasil. Since the major difference between these materials is the amount of OH present it seems reasonable to ascribe these effects to the presence of hydrogen, which may act to tie up dangling oxygen bonds and relieve strains in the glass network.

In an attempt to separate the various components of the Suprasil W EPR spectra, and to correlate the photoinduced EPR with the photoinduced optical effects, we are carrying out isochronal annealing experiments. We have found that for the 7.9-eV-induced EPR the total integrated intensity anneals quite gradually, reaching the half-intensity point at 400°C and annealing completely by 700°C. However, different components of the spectrum anneal at different temperatures. Details of this work will be published at a later date.

It is noteworthy that the EPR spectra induced in Suprasil W by the lower photon energies resemble the spectra observed in x-irradiated alkali-silicate glasses.¹⁶ These spectra have been interpreted as nonbridging oxygens with nearby cations. Thus, it may be that the centers induced by the lower photon energies are associated with residual metallic impurities in the material. Certainly the density of these spins ($\sim 10^{15}$ /cm³) is not inconsistent with the density of impurities (~ 0.1 ppm alkali) in these materials. However, it must be kept in mind that absolute spin-density calibrations are susceptible to a number of errors, and that we do not yet know if the number of photoinduced centers has saturated. If the broad resonance is associated with alkali-related centers then it is difficult to understand the difference between Suprasil W and Suprasil, since the metallic impurity levels in these materials are believed to be quite comparable. Further work, such as the annealing studies and an investigation of less pure samples is needed to resolve this issue.

It is interesting to speculate on the relationship of the observations described here to the photoinduced EPR in the chalcogenide semiconductors. Because α -SiO₂ and the chalcogenide glasses are all lone-pair materials it has often been suggested that the intrinsic defects in these materials should be similar, although the details are a matter of controversy.^{6,17,18} In the chalcogenides the EPR spectra are very similar for x-irradiated material and for samples excited with Urbach-tail light.¹⁹ Similarly we observe in Suprasil W an EPR spectrum quite similar to the γ -induced spectrum when we excite with 7.9-eV light, which is in the exponential absorption region of α -SiO₂. In the chalcogenides the photoinduced spins are only stable at low temperature. In α -SiO₂ we observe photoinduced EPR at room temperature, but it can be completely annealed by raising the temperature to 1000 K. The difference can be ascribed to the difference

in the relevant energy scales (band gaps or bond strengths) for the two types of materials.

In summary, we have observed that metastable paramagnetic defects are created in a -SiO₂ by sub-band-gap light with photon energies at least as low as 5 eV. In Suprasil we observe a new defect which we attribute to nitrogen impurity. The highly anisotropic spectra previously associated with dangling oxygen bonds are observed only in Suprasil W, which does not contain large amounts of hydrogen. These spectra resemble those observed in a -SiO₂ after γ or x irradiation, but the differences between the photoinduced and the radiation-induced EPR may be as important as the simi-

larities in terms of understanding the interaction of radiation with a -SiO₂. In particular, we have found that the photoinduced EPR changes as the excitation energy is varied. This provides a new spectroscopic tool for studying defects in a -SiO₂. It is hoped that further study may provide insight into the nature of the diamagnetic precursor defects and of the excitation process whereby they are converted into paramagnetic centers.

This work is supported by the Joint Services Electronics Program through contract No. DAAG-29-83-K-0003.

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⁴Suprasil and Suprasil W are trade names for synthetic fused silica made by Heraeus Amersil, Inc.

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