Selective Generation of Oriented Defects in Glasses: Application to SiO_2

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The use of polarized light to generate oriented paramagnetic centers in glass is discussed. Analytic expressions are derived for the resultant EPR line shape, and are compared to experimental results obtained for *a*-SiO_2. Analysis of the EPR anisotropy provides information concerning the formation mechanism of the paramagnetic center and about the degree of lattice relaxation following the formation of the center.

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The nature of point defects in glasses, and their generation mechanisms, is an important problem which has received considerable attention recently.[1] Glasses, or more generally amorphous materials, are crucial ingredients in electronics (SiO_2 for integrated circuits, *a*-Si and Si_3N_4 for thin-film transistors) and in light-wave communications (silicate and fluoride glasses for optical fibers). Electron paramagnetic resonance (EPR) spectroscopy has been one of the most powerful experimental tools for the identification and study of point defects in insulators and semiconductors, both crystalline and amorphous. Paramagnetic defects, if not present in the as-grown material, may be introduced by various perturbations such as irradiation by ions, neutrons, electrons, or photons. In crystalline materials the defects tend to be oriented so that their axes of symmetry are along the crystal axes, and by observation of this orientation much information can be gained about the structure and properties of the defect. In glasses and amorphous solids, on the other hand, the defects assume a random orientation because of the inherently random structure of the host material. Instead of observing discrete, angle-dependent EPR lines corresponding to defects with specific orientations, one observes a "powder pattern," corresponding to an angular average over all orientations. While the three principal values of the **g** tensor can in principle be extracted from the powder pattern, other factors, such as disorder-induced broadening, sometimes make it difficult to do so in a reliable fashion.

Starting from such a random arrangement, various experimental techniques may be applied in order to induce some preferential orientation among the defects. For example, it is well known that polarized light may be used to selectively bleach, or reorient, color centers in alkali halides.[2] More recently, the same technique has been applied[3] to the formyl radical (HCO) which is produced[4] in certain types of synthetic fused silica by x irradiation. Defect alignment may also be induced by unaxial stress, a technique which has successfully been applied to studies of defects in crystalline silicon.[5]

The purpose of this paper is to present a novel approach in which paramagnetic centers are *created* directly in an aligned state. By use of a selective generation mechanism, the paramagnetic centers are created with a preferential orientation along some externally defined axis. For example, a unaxial stress applied to the sample during irradiation might either inhibit or enhance the creation of paramagnetic defects oriented parallel to the stress axis. In the example to be described in this paper, the centers are created by optical excitation. In this case the use of *polarized* light makes certain defect orientations more favorable than others. This may arise for example when the formation mechanism of the paramagnetic center involves the ionization of a localized defect state, with an electron being excited from a localized *p* orbital into an *s*-like band state. Then the transition matrix element will be proportional to the cosine of the angle between the polarization direction and the axis of the *p* orbital. In contrast to an optical bleaching or reorientation experiment, which furnishes information regarding excited states of an existing radical or defect, the sort of experiment described here provides information concerning the generation mechanism of the paramagnetic center, and the subsequent fate of the center as the lattice relaxes around it.

In this paper I demonstrate the use of polarized light to produce oriented paramagnetic centers in amorphous SiO_2 (*a*-SiO_2). First I derive expressions for the expected line shapes for centers produced by polarized excitation, under certain assumptions of symmetry. These results apply to the case of unaxial stress as well. I then describe and discuss the experimental results for *a*-SiO_2.

The EPR spectrum of an isolated point defect is described (in the absence of hyperfine interactions) by three parameters, g_1, g_2, and g_3, the diagonal components of the **g** tensor. The resonance condition is $\hbar\omega = \beta|\mathbf{H}\cdot\mathbf{g}|$ where ω is the microwave frequency, β is the Bohr magneton, and $\mathbf{H}$ is the applied magnetic field. There is thus an angle-dependent g value, given in the case of axial symmetry by

$$g = ([g_\parallel^2 - g_\perp^2]\cos^2\theta + g_\perp^2)^{1/2},$$

where $g_\perp = g_1 = g_2$, $g_\parallel = g_3$, and θ is the angle between **H** and the unique axis of the defect. In a powder or a glass all orientations are equally probable, leading to the distribution $P(\theta) \propto \sin\theta$, from which one obtains a corresponding probability distribution for g, which is the absorption powder pattern

$$P(g) = P(\theta) \, | \partial\theta / \partial g | .$$

In the case of generation by polarized light two simplest cases may be distinguished, depending on whether the resulting paramagnetic centers are produced with their unique axes along the electric vector of the light (case I), or perpendicular to the light (case II). Of course, any other orientation is possible, including random, if there is large lattice relaxation accompanying the formation of the center, or if the center results from free-carrier trapping. Indeed, by analysis of the resulting anisotropy of the EPR signal it will be possible to gain some insight into the exact formation mechanism.

If we assume a "$\cos^2$" (electric dipole) probability for conversion of a diamagnetic precursor to a paramagnetic state, the paramagnetic centers will be arranged according to one of the following probability distributions: case I,

$$D(\theta) = \cos^2\theta;$$

case II,

$$D(\theta) = \tfrac{1}{2} \sin^2\theta,$$

where in the present case θ is defined with respect to **E**. The probability distribution for θ is now the product of $D(\theta)$ and $P(\theta)$, and so the desired expression for the "polarized powder pattern"

$$P(g) = P(\theta) D(\theta) \, | \partial\theta / \partial g |$$

is obtained simply by our expressing $D(\theta)$ in terms of g and multiplying by the expression for the standard axial pattern. Note that for noncoparallel orientations of **E** and **H** it is necessary to express $D(\theta)$ in the coordinate system defined by **H**. Such expressions depend on the azimuthal angle ϕ, but since g is assumed to be axial it is independent of this angle which can therefore be averaged out.

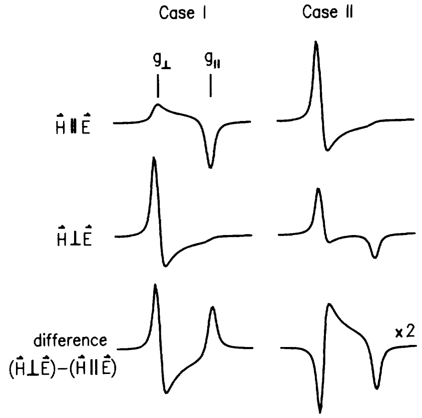

FIG. 1. Theoretical predictions for powder patterns produced by polarized light, for centers of axial symmetry. The bottom two curves are the predicted polarization-induced anisotropy.

The resulting expressions for the powder patterns, for **H** either parallel or perpendicular to **E**, are, for case I, (A) **H**∥**E**,

$$P(g) = g(g^2 - g_\perp^2)^{1/2} / (g_\parallel^2 - g_\perp^2)^{3/2},$$

(B) **H**⊥**E**,

$$P(g) = \frac{g}{2} \, \frac{g^2 - g_\parallel^2}{g_\perp^2 - g_\parallel^2} \, \frac{1}{\{(g^2 - g_\perp^2)(g_\parallel^2 - g_\perp^2)\}^{1/2}};$$

for case II, (A) **H**∥**E**, same as case I(B), (B) **H**⊥**E**, $\frac{1}{2}$ [case I(A) + case I(B)].

The upper four spectra in Fig. 1 are the predicted polarized powder-pattern derivative spectra, computed from the above expressions for the absorption line shapes with $g_\perp > g_\parallel$ and convolved with a Lorentzian function whose width is one-tenth of the anisotropy. In the more general case where $g_1 \neq g_2 \neq g_3$ it is not possible to derive a closed-form expression for the powder pattern, even for a uniform distribution, and one must resort to numerical techniques.[6]

As a test of these ideas I have carried out a series of experiments using sub-band-gap ultraviolet light to generate paramagnetic centers in a-SiO$_2$.[7-9] The output from an ArF excimer laser (6.4 eV) was polarized by means of Brewster-angle reflection from LiF plate. A sample of Suprasil-W[10] was exposed at room temperature to a dose of $\sim 10^{20}$ photons cm^{-3}. EPR measurements were performed at room temperature with a Varian model E-9 spectrometer equipped with a TE$_{011}$ cylindrical cavity operating at ~ 10 GHz.

The orientation dependence of the polarized-light–induced EPR is shown in Fig. 2. In order to produce

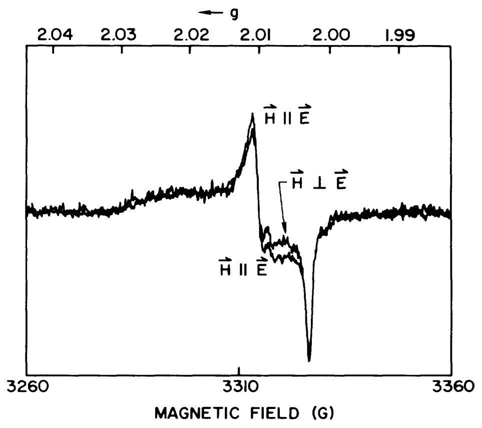

FIG. 2. Orientation dependence of the EPR induced in Suprasil-W by polarized 6.4-eV light.

these data the sample, which had been previously exposed to the polarized 6.4-eV light, was mounted in the microwave cavity such that the axis defined by the polarization vector of the excitation light, **E**, lay in a horizontal plane. The magnetic field was then rotated in the same plane, so that the field was either parallel or perpendicular to this axis. It can be seen that there is a distinct, although small, orientation dependence.

To check for systematic effects the sample was also mounted so that the polarization axis was vertical, perpendicular to the rotation plane of the magnetic field. In this case rotating the magnet had no measurable effect.

It may be seen that the theoretical spectra of Fig. 1 do not bear a strong resemblance to the experimental spectra shown in Fig. 2. This stems from the fact that some components of the EPR spectra are unpolarized. Since the excitation is below band gap, the mechanism for producing the paramagnetic centers is almost certainly one involving the ionization of native defects, with subsequent trapping of the ionized electron or hole at a second site.[8,9] This trapping process should not depend on the polarization of the exciting light, and so at least half of the centers are expected to be unpolarized. Close inspection shows that the spectra are composed of at least two distinct centers, and it is in fact possible to separate these components by their annealing behavior.[9,11] Furthermore, the centers, even if initially created with maximum polarization, may have partially relaxed and randomized before the EPR was measured. Indeed, the EPR was remeasured after allowing the sample to anneal at room temperature for a period of one week and it was found that the anisotropy had relaxed somewhat.

Because only a fraction of the centers are polarized even under the best conditions, it is more meaningful to look at the polarization-induced anisotropy, i.e., the difference between the EPR spectra measured with the magnetic field perpendicular and parallel to the polarization direction. This difference is shown in Fig. 3, and is to be compared with the theoretical predictions shown in the lower portion of Fig. 1. The experimental spectrum resembles quite closely the prediction for case II, in which the symmetry axis of the centers is oriented preferentially normal to the polarization direction. Note in particular the agreement in the relative magnitudes of the two minima (indicated by arrows). Of course the difference spectrum is rather noisy, and is not in precise agreement with the theoretical prediction, e.g., in the region between the two minima. Such discrepancies in the exact shape of the spectra may result from the assumption of perfect axial symmetry in the theoretical spectrum. This assumption could be relaxed in a numerical calculation.

It may seem at first sight that the EPR spectrum under consideration here (Fig. 2) could not possibly be described as having axial symmetry, i.e., characterized by only two g values. For example, there is clearly a third g value giving rise to the low-field shoulder which extends roughly to $g=2.03$. However, from previous work[9,11] it is known that the features at g values of approximately $g_{\parallel}=2.0025$ and $g_{\perp}=2.01$, which are found here to exhibit the polarization-induced anisotropy, correspond to an EPR line which has nearly axial symmetry, with possibly a narrow distribution of small splittings of the perpendicular g components. These features anneal at a lower temperature than does the low-field shoulder, which is therefore not part of the same EPR line. Moreover, if there were an additional nonaxial component, it would show up as another feature in the orientational anisotropy (Fig. 3), although perhaps more weakly because of a distribution in g_3 values.

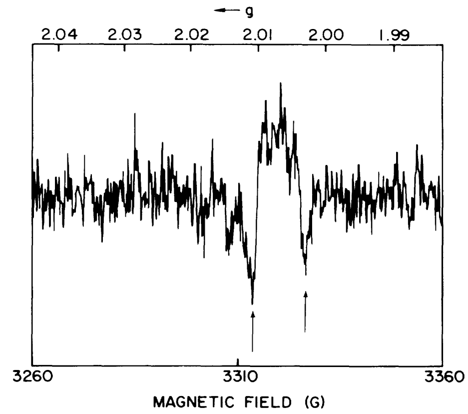

FIG. 3. Polarization-induced anisotropy, i.e., the difference $(\mathbf{H}\perp\mathbf{E})-(\mathbf{H}\parallel\mathbf{E})$ of the two spectra in Fig. 2. This figure is plotted with a gain of 5 relative to Fig. 2.

In this paper I have demonstrated that it is possible to obtain anisotropic EPR spectra in glassy materials by using an anisotropic generation mechanism. Analysis of the EPR anisotropy can then provide information concerning the formation mechanism of the paramagnetic center, e.g., whether the center results from ionization of a localized defect or from the trapping of a mobile carrier, and about the degree of lattice relaxation following the formation of the center. In the example given of paramagnetic centers in a-$\mathrm{SiO_2}$, both polarized and unpolarized components of the EPR are seen, in agreement with expectations since some of the centers are formed by trapping of photoexcited electrons or holes. Of the centers which do exhibit a polarization-induced anisotropy, the anisotropy is fairly weak indicating some random lattice relaxation following the formation of the center. This conclusion is further supported by the observation that the anisotropy decreases even further after room-temperature annealing for several days. The data show that the photoinduced centers discussed in this paper possess axial symmetry with $g_{\perp}\cong 2.01$ and $g_{\parallel}\cong 2.0025$, and are produced with their axes of symmetry oriented perpendicular to the polarization direction of the excitation light.

While the theoretical line shapes given here are limited to cases of axial symmetry, solutions for lower symmetry can easily be obtained numerically, as was done by Bohandy *et al.* in their analysis of bleaching.[3] The experimental technique described in this paper should be useful for the study of defects in many other material systems as well, both crystalline and amorphous. For example, the use of polarized excitation light could help to elucidate the generation mechanism of the photoinduced defects seen in amorphous silicon.[12,13]

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