Mechanism of Intrinsic Si E'-Center Photogeneration in High-Purity Silica

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(Received 25 January 1988; revised manuscript received 6 June 1988)

Permanent Si E' centers with concentrations as high as 10^{17} spins/g induced in high-purity SiO_2 by sub-band-gap (6.4 eV) light were studied by electron-spin resonance. Although an electron-trap nitrogen center has been reported as the dominant defect induced by 7.9-eV photons in Suprasil 1 silica, its absence in the present experiment is evidence that free carriers are not produced by 6.4-eV photons. The E'-center concentration increased as the square of 6.4-eV laser power, confirming the efficacy of two-photon processes for producing point defects in silica with sub-band-gap light. Our evidence supports the view that E' centers are generated by nonradiative decay of neutral excitons.

PACS numbers: 61.70.At, 61.80.Ba, 76.30.Mi

Since the first Si E' center was reported in irradiated silica by Weeks[1] in 1956, much effort has been directed towards characterization and understanding of the formation mechanism(s) of this fundamental defect. Several variants have been identified,[2] and it is now well accepted that at least one of these is due to hole trapping at the site of a neutral oxygen vacancy[3,4] which either preexists in the SiO_2 network or is created by the radiation itself. For incident photons of energy greater than 100 keV, a Compton electron can displace an oxygen out of its lattice site by the knock-on process,[4,5] resulting in simultaneous creation of oxygen vacancies and hole trapping to form E' centers in high-purity silica. In general, this latter process can result in much larger E'-center concentrations than would be the case for hole trapping on preexisting defects.

However, large concentrations of Si E' centers have also been induced in high-purity silica by soft x-rays with insufficient energies (0.4–3.9 keV)[6] to cause knock-on displacements. Moreover, as reported by Stathis and Kastner,[7] both E' centers and oxygen hole centers can be generated in high-purity, *low-water* (<5 ppm OH) silica (Suprasil W) by irradiation with uv laser light of photon energies ranging from 5 to 7.9 eV. But when high-purity, *high-water* (1200 ppm OH) silica (Suprasil 1 or 2) was exposed to 7.9-eV laser light, the oxygen hole center was not induced; rather the Si E'-center spectrum and a three-line signal with magnetic field spacing of about 1.8 mT were observed.[7] The latter spectrum was attributed to a defect involving a nitrogen impurity,[7] and has been characterized in detail by Tsai, Griscom, and Friebele.[8]

E' centers induced by sub-band-gap uv light have also been studied in thermal oxides grown on silicon[9] and in substoichiometric bulk synthetic silicas.[10] Devine, Fiori, and Robertson[11] reported the temperature dependence of E'-center production in Suprasil W under 5-eV laser irradiation. Imai *et al.*,[10] found the formation efficiency and the stability to be strongly dependent on the OH concentration and oxygen stoichiometry; the latter dependence would suggest that many of the observed defects were due to ionization of preexisting oxygen vacancies. Imai *et al.* also demonstrated that E' centers are induced by ArF laser light by a two-photon process.

One of the proposed generation mechanisms for the Si E' center involves the nonradiative decay of self-trapped excitons.[4] Experimental evidence for *transient* defect formation by this mechanism was reported by Hayes *et al.*[12] and Tanimura, Itoh, and Itoh.[13] However, little direct experimental evidence linking the production of *permanent* E' centers to the decay of excitons has been given. The strongest indication to date for a possible excitonic mechanism of permanent defect production has been the observation by Devine, Fiori, and Robertson that E'-center generation by 5-eV light is quenched below ≈ 170 K in anticorrelation with the radiative decay time of the exciton.[13] We present here an entirely separate line of evidence leading to the conclusion that permanent oxygen vacancies indeed must be created in silica by nonradiative decay of excitons. We argued in Ref. 8 for the existence of a positively charged precursor for the uv-induced "nitrogen center"[7] in Suprasil 2. We now propose that these precursors can serve as probes of defect-generation processes in silica: If the defect generation involves free conduction electrons, the nitrogen precursors in the glass will act as electron scavengers. If, on the other hand, electrons and holes should be trapped pairwise through the decay of neutral excitons, no nitrogen centers would be observed.

To understand how defect centers are formed during energetic particle or high-energy photon irradiations is difficult because of the multiplicity of possible radiation-induced electronic processes. In contrast, sub-band-gap uv light is much more selective in terms of the possible channels by which defects can be produced.[11] In this Letter, we report our preliminary understanding of the defect-center formation mechanisms in stoichiometric, high-purity silicas exposed to 6.4-eV uv light of an ArF excimer laser.

Suprasil 2 and Suprasil W rods 4 mm in diameter and

20 mm in length were mounted on a liquid-nitrogen-cooled metal plate with their axes perpendicular to the direction of the incident unfocused beam of a multigas excimer laser model (EMG103 MSC, Lambda Physik) with ArF as the lasing medium. *X*-band ESR spectra ($\nu \approx 9.4$ GHz) were obtained with a Bruker model ER 200D-SRC spectrometer employing 100-kHz field modulation. The temperature of the samples during the laser-light exposure was measured with a thermocouple to be less than 400 K.

Figure 1 shows the concentrations of the E' centers in Suprasil 2 and Suprasil W as functions of the number of laser pulses. The concentrations of uv-induced E' centers averaged over the entire illuminated volumes range as high as 10^{17}/g (or 10 ppm Si). However, it can be shown that the silica rods focus the laterally impinging uv light into a limited volume of the sample where the local defect concentrations certainly must be higher. The high power density (estimated to reach 120 mJ/cm^2 per pulse) in the focused region undoubtedly led to a higher energy deposition than was achieved by Imai *et al.*[10] and is likely to be responsible for our observations of average spin densities up to an order of magnitude higher than reported by those authors. Indeed, we observed much lower spin densities when we eliminated the focusing effect by irradiating a set of control samples end on. For comparison, in order to induce an E'-center concentration of 10^{17}/g with ^{60}Co γ rays, a dose $\approx 10^8$ rads is required.[4] Such high observed E'-center concentrations are generally believed to exceed the population of preexisting oxygen-vacancy precursors in bulk stoichiometric silica, such as Suprasil. [Note also in Fig. 1 that the E'-center production efficiency in *high-water* silica (Suprasil 2) is 5–10 times of that in *low-water* silica (Suprasil W), in agreement with the results of Imai *et al.*[10]]

In Suprasil 2, the positively charged nitrogen precursors may trap conduction electrons induced by x or γ irradiation, becoming "nitrogen centers," which are easily observed at room temperature.[8] The fact that this defect was not observed in our 6.4-eV photon-irradiated Suprasil 2 samples is strong evidence that free conduction electrons are not generated by the absorption of 6.4-eV light. We conclude therefore that the observed E' centers are not generated by photoionization of preexisting oxygen vacancies. The fact that the concentrations of laser-induced E' centers in both low-OH and high-OH silica do not appear to saturate even at levels $\approx 10^{17}$ spins/g (see Fig. 1) also supports this conclusion. Thus, an excitonic process must be considered. The most likely candidates for the neutral excitons in low-dielectric-constant silica are Wannier excitons (strongly bound electron-hole pairs having significant mobilities.[4,14]

Since the band gap of silica is about 9 eV and the exciton binding energy is ≈ 1.3 eV,[12] the self-trapped excitons necessary for E'-center formation with 6.4-eV photons are expected to be induced through multiphoton absorption processes. We confirm this expectation in Fig. 2 by showing that the concentration of Si E' centers increases as the square of laser pulse energy (for equal irradiation times).

The differences in the defect centers induced in Suprasil 2 by 7.9-eV (Ref. 7) or by 6.4-eV photons (this work) can be understood in the following way: Since the maximum pulse power density of the 7.9-eV photons generated by an F_2 excimer laser is more than 1 order of magnitude smaller than that possible with 6.4-eV ArF photons, it seems likely that the defect centers reported[7] to be induced by the higher-energy photons were the result of one-photon-absorption processes. We note that

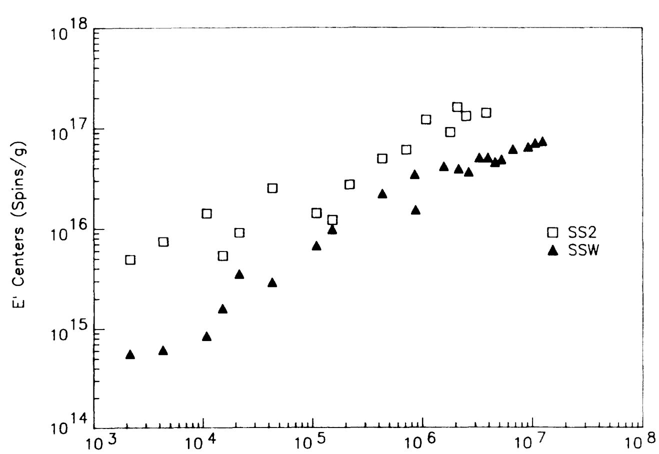

FIG. 1. The concentrations of Si E' center in Suprasil 2 (SS2) and Suprasil W (SSW) as functions of 6.4-eV photon fluence with average pulse energy of 40 mJ/cm^2.

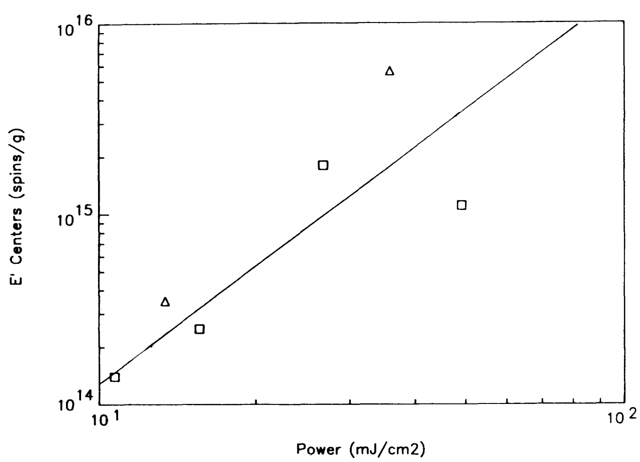

FIG. 2. Concentrations of Si E' centers induced in Suprasil 2 by 6.4-eV photons as a function of the average pulse energy generated by an ArF excimer laser. Irradiation times were held constant. Squares and triangles are two different irradiations. The line with slope of 1.9 ± 0.7 is a linear regression fit of our data.

7.9-eV photons can excite one of the spin-paired electrons from an Si—Si bond into the conduction band of silica in the schematic energy diagrams for optical transitions associted with oxygen vacancies proposed by Robertson[15] and confirmed recently by Imai and coworkers[10,16] and by Nagasawa *et al.*[17] This conduction electron may then transport and become trapped at a positively charged nitrogen precursor, converting it to a paramagnetic nitrogen center.[7,8] The remaining unpaired electron in the Si—Si bond will localize on one of the Si atoms, forming an Si E' center after asymmetric relaxation at the Si $\cdots$ Si site.[3] Accordingly, the concentrations of E' and nitrogen centers should be about equal, and indeed, we estimate the concentrations of both E' and nitrogen centers to be $\approx 10^{14}$ spins/g for a fluence of about 30 J/cm^2 from the data of Stathis.[18]

In our case, a single 6.4-eV photon does not have enough energy to promote an electron from an Si-Si precursor site into the conduction band, and so this single-photon-absorption process cannot occur. Moreover, the majority of events for two-photon-absorption processes involve the excitation of the valence-band electrons because of the much higher electron concentration here than in Si-Si bonds. The excited electron in the conduction band is strongly bound to the hole in the valence band (because of the low dielectric constant of silica), forming an exciton. Since these excitons are neutral and have small dipole moments, they cannot be attracted by the relatively small number ($\approx 10^{13}$/g)[8] of positively charged nitrogen precursors. The absence of nitrogen centers in our 6.4-eV irradiated Suprasil 2 samples supports this picture.

In summary, we found that the concentration of Si E' centers induced by 6.4-eV photons can be as high as 10^{17} spins/g in high-purity *stoichiometric* silicas of both high and low water contents, suggesting that these E' centers are not induced through charge trapping at preexisting oxygen-vacancy sites. This result extends previous work by Imai *et al.*[10] where mainly oxygen-deficient silicas were studied and lower photon intensities were employed, and it complements the studies of Devine, Fiori, and Robertson who focused on low-water Suprasil W. The Coulombic explosion mechanism[19] for defect production can be ruled out in all cases involving excimer laser irradiation since the uv photons do not have enough energy to ionize the core levels of constituent atoms of silica. The absence of electron-trap nitrogen centers in our 6.4-eV photon-irradiated Suprasil 2 samples strongly suggests that E' centers are induced via the nonradiative decay of neutral excitons. The present observation that the concentration of E' centers grows as the square of the 6.4-eV laser pulse energy confirms that these defects result from two-photon-absorption processes. The prior report of nitrogen centers induced by 7.9-eV photons[7,18] in Suprasil 1 can be explained by the generation of conduction electrons via single-photon-absorption processes involving the ionization of preexisting Si—Si bonds. We note that nitrogen centers are not observed in Suprasil W nor in more recently purchased samples of Suprasil 1,[8] presumably because of the absence of the nitrogen precursors. However, the similar power-squared growth dependences and high concentrations of E' centers induced by 6.4-eV irradiations are strong evidence for the exciton model of E'-center formation in these materials as well. More work, including the use of $\approx$4-eV (XeCl laser) photons to probe the threshold production energy of excitons, is clearly needed to understand fully the defect generation mechanisms in silica; further investigations are in progress at this laboratory and will be presented in future publications.

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