10. Electronic Properties of Amorphous Silicon Dioxide

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We have discovered that exposure to below-bandgap (i.e., weakly absorbed) photons changes the charge state of some or all of the intrinsic defects in amorphous SiO_2. This change is manifested in several ways: (a) a mid-gap absorption band (4.8 eV); (b) a large enhancement of the intensity of the 1.9 eV photoluminescence band; and (c) the appearance of an electron-spin-resonance (ESR) signal. The discovery of photoinduced ESR in a-SiO_2 is the most significant development. ESR provides a local probe of the structure of the defects which is complementary to the optical probes (absorption, luminescence). Experiments now in progress will enable us to correlate the photoinduced ESR and photoinduced optical effects, giving us specific information about the structure and properties of the defects intrinsic to SiO_2. Although similar studies have been performed in the past to correlate the ESR and optical measurements, with some success, these studies have relied on ionizing radiation (gamma or x-ray) to generate significant numbers of paramagnetic centers from the normally diagmagnetic ground state of the intrinsic defects. Photoinduced ESR has the advantage of providing another parameter, namely the photon energy. This gives us a new spectroscopic tool which we are using to measure the energy needed to ionize the intrinsic defects in SiO_2.

By changing the photon energy and annealing temperature we have been able to resolve the photoinduced ESR into several components. We have found that at the highest photon energy currently available to us, 7.9 eV, the ESR spectrum is very similar, although not identical, to that observed after gamma irradiation, and that $10^{16}-10^{17}$ paramagnetic centers per cubic centimeter can be photogenerated, the same number as produced by gamma rays. When lower photon energies are used, the relative intensities of the components are changed. Paramagnetic centers can be generated by photon energies at least as low as 5 eV, corresponding to roughly half the band-gap. The centers responsible for the 1.9 eV luminescence are also created by these lower photon energies, but the centers giving the mid-gap absorption are not. We also found that the photoresponse of a–SiO_2 depends markedly on the amount of OH present in the material. SiO_2 which is specially prepared in a way which prevents the incorporation of OH is much more sensitive to ultraviolet light than material containing ~1200 ppm OH impurity.