15. Electronic Properties of Amorphous Silicon Dioxide

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Since last January a number of significant changes and advancements have taken place in our investigation of defects in amorphous SiO_2 (a–SiO_2). These advancements have been facilitated by a move to a larger lab and the acquisition of several new pieces of equipment.

Although the initial plan was to probe the intrinsic defects using photoluminescence, this has been superceded, for the time being, as a result of a remarkable discovery. We have found that the charge state of some of or all of the intrinsic defects in a–SiO_2 is changed, in a metastable way, by exposure to sub–bandgap ultraviolet light. 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 perhaps 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 instrinsic to SiO_2. Although similar studies have been performed in the past to correlate 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 spectroscopic tool which we are using to measure the energy needed to change the charge state of the defect.

By changing the photon energy we have been able to resolve the 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 part of the spectrum is absent, and the relative intensities of other 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.

Our investigation of the photo-generation of the 4.8 eV absorption and the 1.9 eV luminescence centers has been accepted for publication. We demonstrated that these two optical transitions arise at different types of defects, belying previous speculations that a single defect was responsible. 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.

During this past year we also initiated experiments to study electrical transport in SiO_2. These experiments use the phenomenon of internal photoemission to inject electrons or holes into the conduction or valence band of thin SiO_2 samples, where their subsequent transport and interaction with traps can be studied using the time-of-flight technique.