

# 15. Electronic Properties of Amorphous Silicon Dioxide

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Amorphous  $\text{SiO}_2$  (a- $\text{SiO}_2$ ) is one of the most important materials for electronic and optical applications. The thermal oxide which provides high electrical insulation and dielectric strength for integrated circuits and most other Si devices is a- $\text{SiO}_2$ . One might say, therefore, that the entire electronic revolution rests on a thin layer of a- $\text{SiO}_2$ . The newest revolution in the technology of communication, optical fibers, also depends on a- $\text{SiO}_2$ , for this material is the low-loss medium of which the fibers are made.

It is surprising, therefore, how little is really understood about the optical and electronic properties of this very important material. The paucity of understanding does not reflect a lack of effort. On the contrary, there is a long history of experiments, dating back at least to the mid 1950's, and a good deal of factual information is available. However, very few of the simplest fundamental issues have been resolved. For example, the magnitude of the energy gap between valence and conduction bands is not completely agreed upon.

The difficulty in deciding such fundamental points in the case of a- $\text{SiO}_2$  arises from two of its properties. First, the band gap of a- $\text{SiO}_2$  is very large which means that vacuum ultraviolet excitation is needed for optical experiments, making some of them quite difficult. Second, the fact that the material is amorphous allows for a wide variety, and greater number, of atomic-scale defects than would be accommodated by the ordered structure of a crystal. As a result, many of the optical and electronic properties of a- $\text{SiO}_2$  are dominated by these defects which have, therefore, been the focus of much of the research on this material. The defects may be extremely important, by the way, in both electronic and optical applications of a- $\text{SiO}_2$ . Defects in thermal oxides on Si devices, especially if charged, can influence carrier mobilities near the surface as well as the threshold of field-effect transistors. Defects in optical fibers may limit the ultimate optical attenuation either by absorption or scattering.

It is because we have had some success in understanding the electronic and optical properties of

defects in other glasses, that we have been emboldened to attack the problem of defects in a-SiO<sub>2</sub>. In the chalcogenide glasses, sulfur, selenium or tellurium takes the place of oxygen as the two-fold coordinated element which forms the backbone of the glass network structure. These glasses have much narrower band gaps (1-2 eV) than SiO<sub>2</sub> so that they can be photoexcited with visible lasers and a wide variety of experiments can be carried out. We have found<sup>1</sup> that the response of the chalcogenide glasses to pulsed laser excitation provides a wealth of new information about their electronic structure. The experiments that have provided great insight are time-resolved photoluminescence, photoconductivity, and photoinduced optical absorption.

Our study of photoluminescence in a-SiO<sub>2</sub> began with experiments using a continuous and weak excitation source, a H<sub>2</sub> discharge lamp. These early experiments proved very informative. We found<sup>1</sup> that a-SiO<sub>2</sub>, like the narrower-gap glasses, has a photoluminescence (PL) band peaked near mid-gap when excited in the region of the optical absorption edge. By showing that the PL band increases in intensity after neutron-irradiated, we demonstrated that the PL band increases in intensity after neutron irradiation and that crystalline SiO<sub>2</sub> shows<sup>2</sup> no PL until it is neutron-irradiated, we demonstrated that the PL centers are defects, as is thought to be the case in the other glasses. Furthermore, the temperature dependence of all the glasses could be explained in a simple way,<sup>3</sup> which indicates that the nonradiative mechanism in all the glasses, including a-SiO<sub>2</sub>, have a common origin.

In the past two years we have begun time-resolved experiments on the PL of amorphous and neutron-irradiated crystalline SiO<sub>2</sub>. The high power of our pulsed F<sub>2</sub> laser allowed us to see<sup>4</sup> PL bands which were buried in noise when using the H<sub>2</sub> lamp.

The time evolution of the PL spectrum is not yet understood. Part of the problem is that the various bands we observe may arise from electronic transitions at several different types of defect. The question of which PL bands come from the same defect will be partly resolved by comparing glasses prepared in different ways. However, a discovery we have made in the past few months may provide a breakthrough in our ability to study the PL processes.

The results of our measurements with the continuous excitation source led us to believe that only vacuum-ultraviolet excitation had adequate photon energy to excite the photoluminescence. We have found, however, that near-ultraviolet excitation with high-power excimer laser lines can also excite the PL. We are now trying to determine whether this is a one- or two-photon process. In any event, excitation in the near-ultraviolet can be made tunable, and we have found tunable excitation indispensable in our studies of narrower-gap materials. Furthermore, near-ultraviolet excitation would allow us to dispense with the high-vacuum requirements which have made our measurements arduous.

Our long-term effort will take two directions. First, we hope by improving our experiment to be able

to decide which PL bands arise at particular defects. In addition, we will begin to study the PL bands in a-SiO<sub>2</sub> thermally grown on Si surfaces and in optical fibers. Second, we will explore the possibility of measuring transient photocurrent and photoinduced optical absorption, two experiments which have provided great insight into the nature of defect states in the narrower-gap glasses.

#### References

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