

# Reflectance spectrum of crystalline and vitreous SiO<sub>2</sub> at low temperature

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The vacuum ultraviolet reflectance spectrum of crystalline and vitreous SiO<sub>2</sub> has been measured at low temperature. We find only minor differences between the room-temperature and 5-K spectra of both crystalline and vitreous SiO<sub>2</sub>. These observations impose restrictions on the models to explain the electronic structure of the ordered as well as the disordered phase of SiO<sub>2</sub>. The electronic structure of both forms of SiO<sub>2</sub> is mainly determined by the short-range structure of the SiO<sub>4</sub> tetrahedra. The strong reflectance band at 10.3 eV is described as an excitonic resonance in interaction with a background of interband transitions and with optically forbidden exciton states.

The optical properties of crystalline and amorphous SiO<sub>2</sub> in the vacuum ultraviolet spectral region have been discussed in a number of experimental<sup>1-5</sup> and theoretical<sup>6-8</sup> papers. Their striking similarity demonstrates that the electronic transitions in SiO<sub>2</sub> are rather insensitive to the long-range structural order and are essentially determined by the electronic properties of the SiO<sub>4</sub> tetrahedra. Nevertheless, conflicting interpretations of the observed reflectance spectra have been proposed in terms of excitons, interband transitions, and combinations of both.<sup>7</sup> Only recently, photoconductivity and photoluminescence measurements<sup>9-11</sup> together with band-structure calculations that include a treatment of the electron-hole interaction<sup>12,13</sup> have led to the identification of the observed reflectance peaks with excitonic resonances. We report here measurements of the reflectance of crystalline and vitreous SiO<sub>2</sub> at liquid-helium temperature in the range from 7.5 to 11.5 eV. The observed temperature dependence confirms the interpretation proposed by Pantelides<sup>12</sup> and by Laughlin<sup>13</sup> but differs from the one predicted by Mott on the basis of a different model.

The vacuum ultraviolet spectrometer used for the measurements has been described in detail elsewhere.<sup>14</sup> In the case of crystalline quartz, virtually identical spectra were obtained from clean, naturally grown, and mechanically polished surfaces. Figure 1 shows the reflectance spectra of a z-cut na-

tural quartz crystal for unpolarized light at near-normal incidence. At low temperature we expected a narrowing of the exciton line at 10.4 eV with a simultaneous increase of the peak reflectance. Surprisingly, the low-temperature reflectance of quartz is practically unaltered as compared with the room-temperature spectrum. This observation

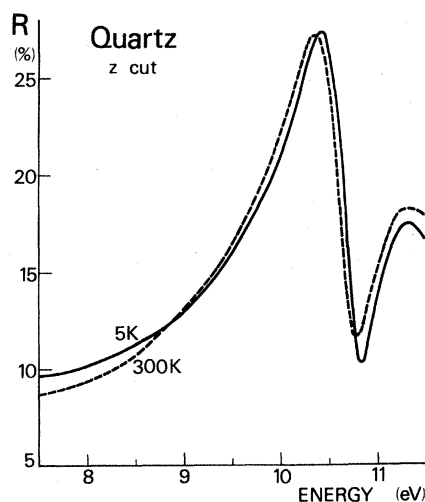


FIG. 1. Reflectance spectra of a z-cut quartz crystal at room temperature and at 5 K. The measurements were taken in an oil-free vacuum ultraviolet spectrometer.

has considerable impact on the model of the electronic structure of crystalline  $\text{SiO}_2$ , and will be discussed later.

The spectra of silica (Suprasil) are shown in Fig. 2. No essential changes in the line shapes were expected to occur for vitreous  $\text{SiO}_2$  upon cooling. This assumption is confirmed by the experimental results of Fig. 2. Our room-temperature data in the fundamental absorption region are in good agreement with those published by other workers.<sup>1-5</sup> In the transparency range below 7.5 eV the reflectance varies from sample to sample and the differences were attributed to impurity bands below the gap, luminescence from defects, and to a minor extent to reflections from the back surface of the sample.

The first reflectance peak in both crystalline and vitreous  $\text{SiO}_2$  is only weakly dependent on the temperature. This is unusual for an exciton if compared to the excitonic structures observed in the spectra of other wide-band-gap solids, e.g., the alkali halides.<sup>15</sup> In quartz (Fig. 1) the peak shifts from 10.38 eV at room temperature to 10.45 eV at liquid-helium temperature. The linewidth does not change appreciably and the  $V$ -like antiresonance on the high-energy side of the peak becomes slightly sharper at 5 K. In silica (Fig. 2) the changes are similar: The peak shifts upon cooling from 10.22 eV to 10.28 eV.

Mott elaborated in a recent review article<sup>7</sup> on the interpretation of the optical spectrum of crystalline and vitreous  $\text{SiO}_2$ . In his model the band gap is estimated at 10.6 eV, and the reflectance peak at 10.4 eV is assigned to a Frenkel exciton on the ox-

ygen sites. In *vitreous*  $\text{SiO}_2$  the structural disorder breaks the  $k=0$  selection rule and optical transitions to exciton states of any  $k$  vector should become allowed, at least to some extent. This explains the large linewidth of the reflectance band. The peak at 10.22 eV corresponds to the maximum density of states in the exciton band. Therefore, we expect only a weak, if any, temperature dependence of the reflectance. In *crystalline*  $\text{SiO}_2$  at room temperature the first peak has approximately the same width as in the glass. It is then assumed that exciton-phonon scattering is sufficiently strong to limit the exciton mean free path  $L$  to a distance  $L \approx a$ , where  $a \approx 2$  Å is the separation between sites for the exciton (oxygen atoms). In this case the  $k$ -selection rule will also break down. At low temperatures one expects the phonons to freeze out and therefore (in the crystal but *not* in the glass) the exciton line to narrow. Figure 1 shows that this is not the case and that a different model is required to explain the low-temperature data.

The work of Pantelides<sup>12</sup> and more recently of Laughlin<sup>13</sup> has led to a different interpretation. Laughlin calculates the imaginary part of the dielectric constant  $\epsilon_2$ , starting from a tight-binding Hamiltonian and including electron-hole interactions (and thus excitonic effects) through a Green's-function formalism. The model is rather insensitive to the long-range order and is independent of the network structure as long as the integrity of the basic  $\text{SiO}_4$  tetrahedra is preserved, and should therefore apply to both crystalline and amorphous  $\text{SiO}_2$ . With the band gap (not necessarily a direct gap) fitted at 8.9 eV in agreement with photoconductivity<sup>9</sup> and absorption<sup>16</sup> measurements, the four peaks in the reflectance spectrum below 20 eV are associated with excitonic resonances. These resonances occur in a region where the joint density of states for interband transitions, calculated in the one-electron approximation, does not vanish. The calculations also predict the existence of optically forbidden exciton states above 8.4 eV. Similar conclusions were reached by Trukhin on the basis of photoluminescence measurements.<sup>11,17</sup>

In summary, the reflectance spectra of the ordered and disordered form of  $\text{SiO}_2$  exhibit only minor differences between room temperature and 5 K. We suppose that the reflectance band at 10.4 eV can be described as an excitonic resonance. The exciton interacts with a background of interband transitions and with optically forbidden exciton states. The large width of the excitonic band

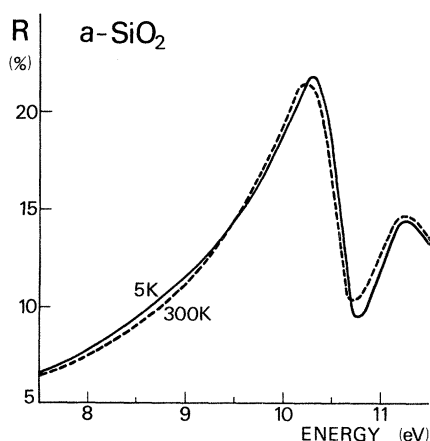


FIG. 2. Reflectance vs photon energy of silica (Suprasil) at room temperature and at 5 K.

is caused mainly by the interactions with the background, which is expected to be only weakly dependent on the temperature, in accordance with the observations.

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