Electronic Spectra of Si Nanocolloids in 2-Propanol

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The ultraviolet (UV) and visible spectra of Si nanocolloids in 2-propanol were measured. In UV region, we have found, for the first time, the electronic transition at about 3.5 eV being superimposed by fine structures. The fine structures with the energy spacing around 1000 cm^{-1} can be related to IR absorption spectra which are assigned to Si-O-Si stretching vibration.

Recently, a great deal of research effort has been focused on nanometer-sized particles made of indirect-gap semiconductors such as Si[1-3] because of fundamental and technical importance. Although much progress has been made in the past on the properties of them, there were not so many reports on their optical spectra. It is still open question what is the real chemical structure of the particle surface layer and how it affects on optical absorption. In this letter, we report a new finding of fine structures on the UV/visible spectra of Si nanocolloids in 2-propanol.

Sample was prepared by an Ar ion sputtering method in a home made apparatus which is designed in a new sputtering way to get nanocolloids.[4] 2-propanol is located in a separated stock bottle from the discharge zone to avoid the reaction against Si particles. The Si target was of 6N purity and the background vacuum was 8Pa. The sputtering gas was Ar at the pressure of 80Pa. After the sample preparation, we measured the IR and UV/visible spectra (sample s1). In order to examine size effect, the sample s1 was filtered by the filter paper with 1 μm pore size (sample s2). The effluent was filtered again with the filter paper of 0.3 μm (sample s4). The residue on the 0.3 μm paper was washed by 2-propanol (sample s3). Therefore, the sample s3 contains particles in the size range 1-0.3 μm, s2 less than 1 μm and s4 less than 0.3 μm. In transmission electron microscope (TEM) observation, the size of the most particles of the sample s4 were found to be less than 100nm.

UV/visible absorption spectra were measured with a Hitachi U-3210 spectrophotomter. Figure 1 is a spectrum of Si nanocolloids in 2-propanol of sample s4 in whole wavelength region from 900 nm to 200 nm. We should note that there is small hump at 350 nm the intensity of which is about 0.5% of the main peak at 210 nm. This peak is known as due to interband transition. Figures 2a to 2c emphasize fine structures of samples s1, s3 and s4 in the wavelength region from 330 nm (3.8 eV) to 400 nm (3.1 eV). It is very clear that 5 major peaks appeared in Figure 2a and 2c but absent in Figure 2b. As the peak profiles are most clear in s4 (smallest particles), we discuss hereafter only on this sample. The peak positions are 390, 373.2, 360, 347.6 and 334.8 nm, the wavenumbers of the difference between neighboring two peaks are 1154, 982, 991 and 1100 cm^{-1} from low energy to high energy side. At the moment, no other fine structure was found in the samples.

IR absorption spectra were measured in Horiba FT-210 Fourier Transform Infrared Spectrophotometer. Figure 3a and 3b show the IR spectra of the samples s3 and s4 separately, the wavenumber is from 700 to 1300 cm^{-1} which is in the Si-O-Si stretching bands region. Comparing our results with the reported spectra,[5] the surfaces of our Si particles can be said to be oxidized due to the low background vacuum. It was confirmed by TEM and energy dispersive X-ray analyses (EDX) that the particles are composed of Si crystal core covered by oxidized shell. There are four major peaks in the sample s4 (the first one is around

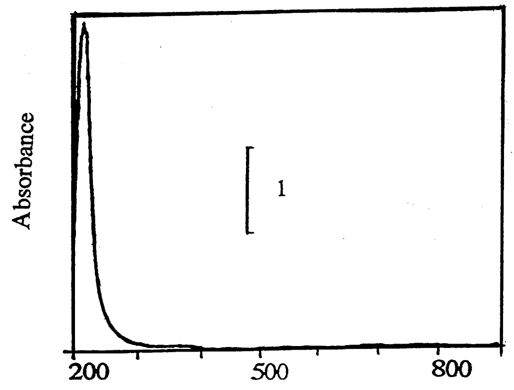

Figure 1. A typical UV/visible spectrum (sample s4). Inserted scale bar shows optical density.

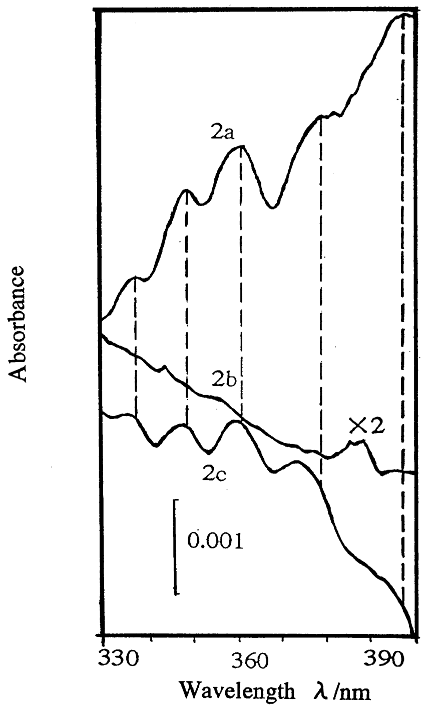

Figure 2. Fine structure of UV/visible spectra (2a: sample s1, 2b: sample s3, 2c: sample s4). Inserted scale bar shows optical density. The broken lines are for eye-guide.

900 cm^{-1}, the second one is around 970 cm^{-1}, the third one is around 1080 cm^{-1} and the forth is around 1150 cm^{-1}) while a single peak (around 1100 cm^{-1}) in the sample s3 compatible with the profiles in UV/visible spectra. The same feature was also found in samples s1 and s2 with a single broader peak around 1000 cm^{-1}.

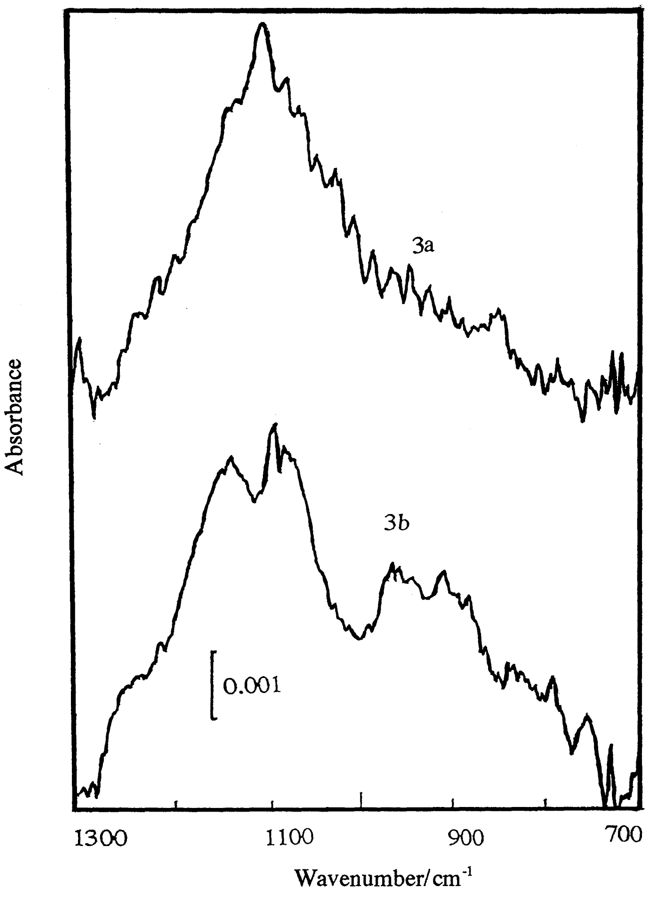

Figure 3. IR spectra (3a: sample s3, 3b: sample s4). Inserted scale bar shows optical density.

From the results of UV/visible spectra, we can see the fine structures depending on the size of colloid such as a difference in Figures 2b and 2c. The IR spectra also depend on the colloid size which could be caused by chemical structures of the colloid surface layer, since the oxidation rate depends on the size of the Si particles. It was reported that the IR peak shapes and positions of Si-O-Si stretching vibration are different for different oxidation condition and for different SiO_x samples.[6,7] Comparing the results of UV/visible spectra with IR spectra, peaks for the fine structure were clear for the sample with the clear IR peaks. When the fine structure was not clear, the IR peak was not clear too. These indicate the fact that the fine structures have close relation to Si-O-Si stretching vibration and depend on the size of particles. In our knowledge, optical absorption of Si above 3 eV is associated with direct transition. In the region of 330-400 nm, there is a direct gap of $\Gamma_{25'} \rightarrow \Gamma_{15}$, therefore, we can say roughly, the fine structures is the electronic transition at 3.5 eV (bulk value) superimposed by Si-O-Si stretching vibration. In order to clarify the mechanism of the appearance of fine structures, the more detail work is in progress in our laboratory.

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