

SOFT X-RAY EMISSION STUDIES OF THE ELECTRONIC STRUCTURE IN SILICON NANOCLUSTERS

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INTRODUCTION

The discovery of visible photoluminescence in ultra fine Si particles has lead to tremendous interest in their electronic and optical properties [1]. It is generally agreed that quantum confinement caused by the restricted size of the nanometer scale silicon particles is essential for the light-emitting properties[2]. A prediction of the quantum confinement model is that the energies of the valence band (VB) and conduction band (CB) edges are shifted relative to the bands of bulk silicon. Silicon nanocrystals were synthesized by thermal vaporization of Si in an Argon buffer gas follow by exposure to atomic hydrogen to passivate the surface. Synthesis techniques have been reported in detail earlier [3,4]. The electronic structure of the Si cluster is then investigated in-situ using x-ray absorption (XAS) and soft x-ray fluorescence (SXF) spectroscopies. SXF and XAS measurements were performed on beamline 8.0 at the Advanced Light Sources. Characterization of the size and morphology of the Si clusters was done ex-situ using atomic force microscopy.

RESULTS

Two Si cluster samples were grown by evaporation of Si at 1700•C in an argon buffer gas of 40 and 80 mTorr and deposited on a Ge substrate. AFM measurements after spectroscopic characterization show that the average diameter of the clusters is 1.6 nm in the 40 mTorr sample and 2.0 nm in the 80 mTorr sample. In Fig.1 we show the x-ray absorption spectra of the L_{2,3} edge absorption for bulk silicon and the two silicon nanocluster samples. The L_{2,3}-edge of the cluster samples is shifted to higher energy relative to the bulk silicon by 0.14 eV for the 2.0 nm clusters and 0.22 eV for the 1.6 nm clusters, in agreement with quantum confinement which raises the energy of the bottom of the conduction band as the nanocluster particle size is decreased. In addition the well defined double threshold behavior associated with the 0.6 eV splitting of the Si 2p core level is less pronounced in the L-edge of the nanoclusters. We also note that the onset of the absorption edge in the clusters is not as sharp as that in the bulk silicon. We attribute these features to a distribution of quantum shifts caused by the variation of particle size within the sample.

Changes in the electronic structure of the VB were monitored by SXF spectroscopy on the same samples that there previously investigated by x-ray absorption. In the SXF process a valence electron fills the core vacancy previously generated by the absorption of a photon. The generated fluorescence photon was analyzed in a spherical grating Rowland spectrometer. In all spectra presented the excitation energy was chosen to be below the Si L₂ absorption edge as determined from the absorption spectra. Therefore, the fluorescence spectrum is generated by transitions from the valence band to the silicon 2p_{3/2} core hole. The SXF technique has an advantage over photoemission because it is insensitive to sample

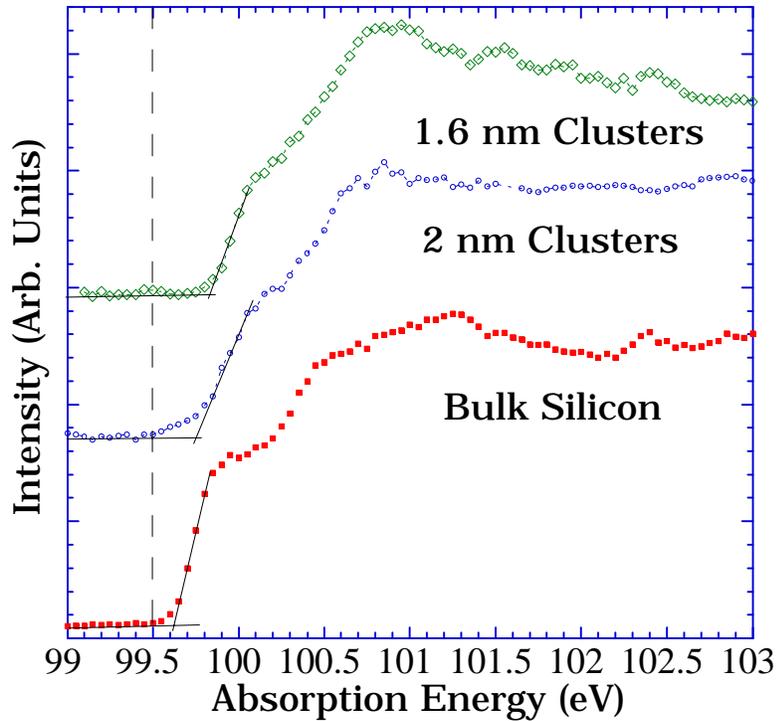


Fig. 1. Fluorescence yield x-ray absorption spectra at the silicon $L_{2,3}$ edges in bulk silicon, of silicon nanoclusters with an average size of 2.0 nm and 1.6 nm. The solid line indicates the extrapolation of the L_3 edge to baseline in order to determine the CB edge position.

charging and is a bulk probe due to the large photon mean free path (~ 0.1 micron). By tuning the excitation energy below the Si L -edge absorption threshold of SiO_x we selectively investigate the electronic structure of the Si nanocluster not any surface oxide or substrate feature.

In Fig. 2 we show the SXF spectra for bulk silicon and the same two cluster samples as shown in Fig. 1. The SXF spectra were excited at 100 eV for the bulk silicon and the 1.6 nm clusters and 100.2 eV for the 2nm clusters. The bulk silicon SXF spectrum exhibits the three characteristic peaks, one at 89 eV associated with low-lying 3s states, another due to a density of states (DOS) maximum at 91.5 eV with strong s-p hybridization and a high DOS at 96 eV which is dominated by p-type states [5]. The intense peak at approximately 100 eV is due to reflected light from the undulator beamline into the spectrometer. The corresponding peak in the bulk Si spectrum is very weak as the reflectivity of the polished Si wafer is low in the non-specular position. Using these reflection peaks we reference the emission energy to the excitation energy and the x-ray absorption spectra.

The overall appearance of the nanocluster spectra is different than that of the bulk silicon. In the nanocluster spectra the valence band is shifted to lower emission energy by 0.30 eV and 0.51 eV for the 2.0 nm and 1.6 nm clusters respectively. The VB edge is much sharper in the cluster samples than in the bulk Si opposite to what is observed in the x-ray absorption edge. Also the shape of the spectra is flattened from a peak like feature in the bulk Si to a plateau in the silicon nanoclusters. This effect has been observed in the SXF spectra of porous silicon and has been attributed to changes in the DOS at the VB edge due to confinement effects in the Si crystallites which alter the bulk electronic band structure [5].

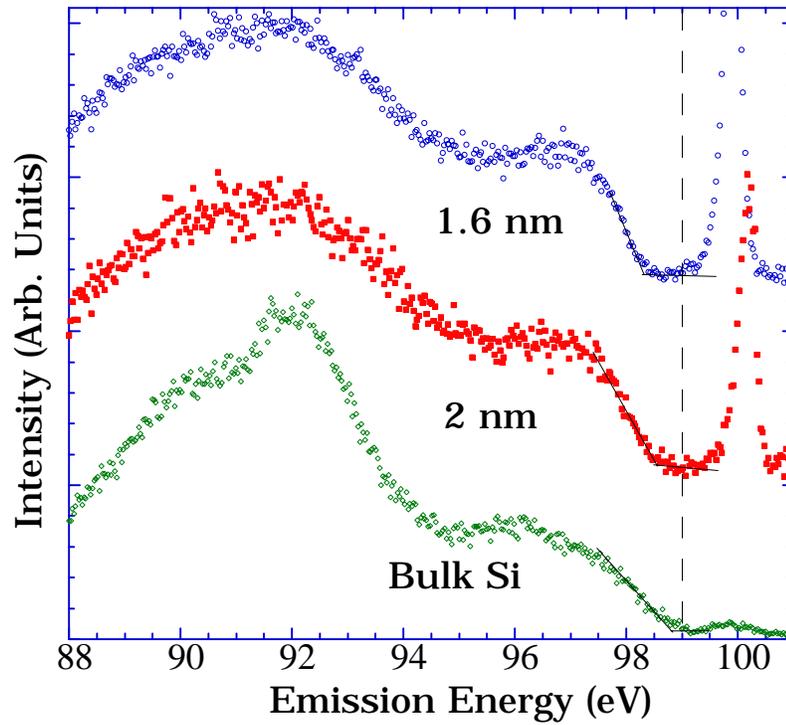


Fig. 2. The L_3 emission spectrum of bulk silicon and the 2.0 and 1.6 nm diameter cluster samples. The excitation energy is 100 eV for the bulk silicon and for the 1.6 nm clusters and 100.2 eV for the 2nm clusters. This corresponds to the L_3 edge measured in the absorption spectra so the L_2 edge is suppressed. The solid lines indicate the extrapolation of the high energy cut-off to the baseline in order to determine the VB edge position.

The pronounced peak at 91.5 eV is not observed in the SXF spectra for the silicon nanoclusters. In fact the spectra looks more like what is observed for amorphous silicon [6]. Yet x-ray diffraction and TEM studies of these clusters have shown they are crystalline in nature [4]. It is interesting to note that the peak at 91.5 is observed in the SXF spectra of hydrogenated porous silicon [5].

It can be seen that the smaller silicon nanoclusters exhibit a larger VB shift as well as a larger conduction band shift. The VB shifts are larger than the shifts in the CB in accordance with theory and are similar to recent photoemission data on silicon clusters although the ratio of the conduction band shift to valence band shift is slightly larger than that found in the photoemission study [7].

In conclusion, we were able to investigate the unoccupied and occupied electronic states in silicon nanoclusters combining total fluorescence yield x-ray absorption and selectively excited SXF spectroscopy. We observe shifts in the both the CB and VB edges indicating quantum size effects in the band structure of the nanoclusters. The onset of the absorption edge progressively broadens with increased confinement due to a distribution in cluster size. A steeper VB edge is observed in the nanoclusters as compared to bulk Si due to a change in the DOS at the VB edge.

ACKNOWLEDGMENTS

This work was supported by the Division of Material Science, Office of Basic Energy Sciences, and performed under the auspices of the Department of Energy by LLNL under Contract No. W-7405-ENG-48, this work was done at the ALS, which is supported by the Department of Energy under Contract No. DE-AC02-76CH0016.

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