

SOFT X-RAY EMISSION STUDIES OF THIN Si/SiO₂ MULTILAYERS

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INTRODUCTION

The discovery of visible photoluminescence in ultra fine Si particles and Si/SiO₂ multilayers has lead to tremendous interest in their electronic and optical properties [1,2]. 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. In this paper we have measured the change in the electronic structure of amorphous Si layers as a function of thickness in a set of Si/SiO₂ multilayers. The electronic structure of the Si nanostructures is investigated using total fluorescence yield x-ray absorption (XAS) and soft x-ray emission (SXE) spectroscopies. These methods have advantages over conventional electron spectroscopies since they are element specific bulk probes. Therefore we can selectively investigate the electronic structure of the buried Si layers in the Si/SiO₂ multilayer by tuning the excitation energy in the XAS or SXE measurement below the Si L-edge absorption threshold of SiO₂ [3]. Also since both these processes are photon-in photon-out it is possible to overcome charging problems that complicate electron spectroscopy measurement on insulating materials such as SiO₂. The SXE and XAS measurements were performed using synchrotron radiation from the undulator beamline at beamline 8.0 at the Advanced Light Sources. Multilayer film thickness was determined by grazing incidence x-ray diffraction.

EXPERIMENTAL

The Si/SiO₂ multilayers were grown onto Ge 111 substrates in an ion-beam sputtering (IBS) chamber described in details elsewhere.[4] The ion gun was a 3 cm Kauffman source with focusing optics. The Ar ions were incident on the sputter target at 1000 V at an angle of about 45°. The sputtering rate was approximately 0.6 Å/sec for Si and 0.1 Å/sec for SiO₂. The base pressure of the chamber was in the 10⁻⁸ Pa range, and the sputtering gas during deposition was Ar at 2.5 x 10⁻⁴ Pa. The substrates were rinsed in ethanol before loading into the vacuum chamber. The substrates were about 25 cm above the targets, and the nominal layer thickness was monitored by a quartz-crystal oscillator which was placed in close proximity to the substrates. The thickness of the individual SiO₂ layers was kept at 10 Å in all multilayers, and the nominal thickness of the Si layers in the samples was 14, 17, 24, and 64 Å. The bilayer period and the number of bilayer pairs in these samples were varied to obtain a total Si thickness of 640 Å for measurement comparison. A single amorphous Si film was also grown in the study to be used as a bulk standard. X-ray diffraction was performed using Cu K_α radiation generated from a rotating anode system outfitted with a graphite monochromator.

Changes in the conduction band were measured by total fluorescence yield X-ray absorption. With convention electron yield x-ray absorption it is only possible to probe to a depth of 50 Å but with fluorescence yield the electronic structure is sampled to a depth of 0.1 micron, therefore the Si from the entire multilayer is measured. Resolution of the absorption spectra at 100 eV the Si L-edge was approximately 0.07 eV. Changes in the electronic structure

of the VB were monitored by SXE spectroscopy. In the SXE 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 with resolution of approximately 0.2 eV. In all SXE spectra presented the excitation energy was 101 eV. Therefore, the fluorescence spectrum is generated by transitions from the valence band to the silicon 2p core hole. The SXE technique has an advantage over photoemission because it is insensitive to sample charging and is a bulk probe due to the large photon mean free path. By tuning the excitation energy to below the Si L-edge absorption threshold of SiO₂ we selectively investigate the electronic structure of the Si layer and not the SiO₂ layer.

RESULTS

Figure 1 shows the low angle x-ray diffraction scans of the samples. The grazing incidence data gives information about the quality of the film, the multilayer uniformity and interfaces. All the scans from the multilayers show strong high order Bragg's peaks indicating a reasonably strong compositional modulation along the growth direction. The bilayer thicknesses of the multilayers were determined using the equation:

$$n^2\lambda^2 = 4 \Lambda^2 \sin^2\Theta + 2\delta,$$

where λ is the x-ray wavelength (0.154 nm), $\Lambda = t_{\text{Si}} + t_{\text{Ge}}$ is the bilayer thickness, δ is the index of refraction at the x-ray wavelength, and Θ the angles of the Bragg's peaks in the measurements. To eliminate the unknown δ from the equation, we make use of the equation above from 2 peaks:

$$(n^2 - (n-1)^2) \lambda^2 = 4 \Lambda^2 (\sin^2\Theta_n - \sin^2\Theta_{n-1}),$$

and solve for Λ . From the deposition rate parameters, the nominal thicknesses of the Si layers deposited were estimated to be 14 and 24 Å. The actual thicknesses of the pure Si layers in the samples are less than these values due to some intermixing of the oxides and the Si during deposition to form a non-stoichiometric oxide layer at the interfaces.

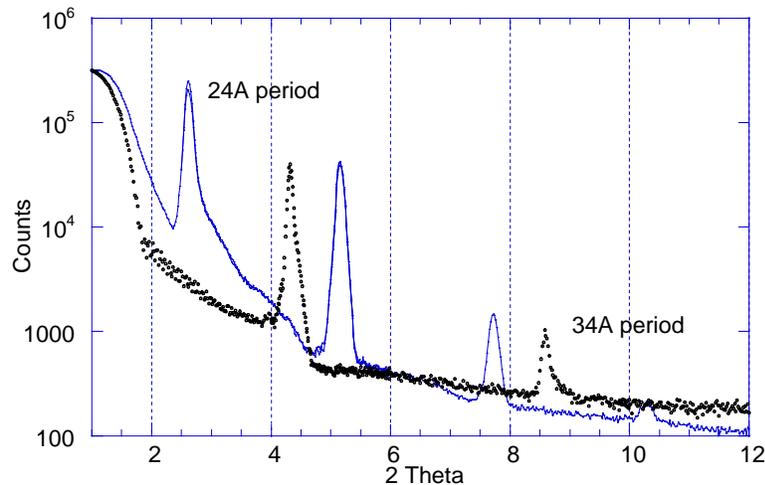


Fig.1. Low angle x-ray diffraction profiles of the two Si/SiO₂ samples.

In Fig.2 we show L_{2,3} edge x-ray absorption for bulk a-Si and the three Si/SiO₂ multilayer samples with different Si layer thickness measured in total fluorescence yield mode. The L-edge of the multilayer is shifted to higher energy relative to the bulk amorphous silicon in agreement with quantum confinement effect which raises the energy of the bottom of the conduction band as the Si layer thickness is decreased. Due to the spin orbit interaction the silicon 2p core level is split into two states separated by 0.61 eV[5]. Thus the L_{2,3} edge XAS spectrum is a

superposition of the absorption structure related to transitions from the Si $2p_{3/2}$ and Si $2p_{1/2}$ core levels. This spin orbit splitting is clearly seen in the bulk a-Si absorption edge but becomes less pronounced with increasing blue shift in the L-edge of the multilayers. We also note that the onset of the absorption edge of the Si in the multilayers is not as sharp as that in the bulk a-Si. We attribute these features to the variation of layer thickness at the Si-SiO₂ interface. As the Si layer thickness decreases the effects on the quantum confinement energy of a given fluctuation in the layer thickness increases. In other words a one monolayer fluctuation at the interface in a thin silicon layer broadens the absorption edge much more than a one monolayer fluctuation in a thicker layer. These broadening effects were not observed in recent electron yield measurement on Si/SiO₂ multilayers, perhaps due to the fact that the electron yield measurement is only sensitive to the top Si layer and don't see the other layers [2].

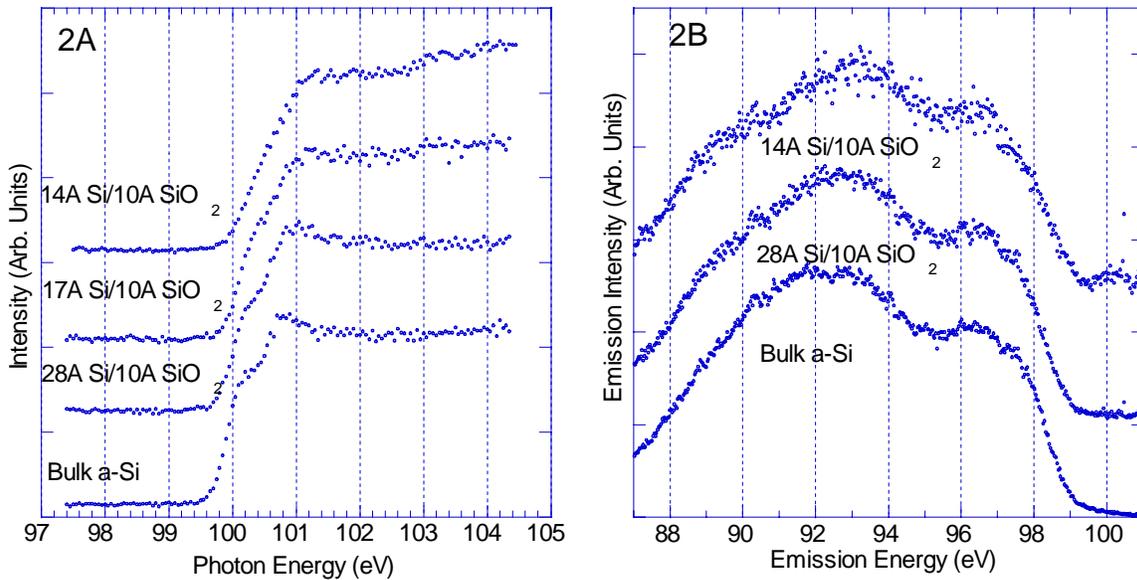


Fig. 2A. Fluorescence yield x-ray absorption spectra at the silicon $L_{2,3}$ edges in bulk a-Si, and Si/SiO₂ multilayers with Si thickness of 14, 17 and 24 Å. Fig. 2B. The L emission spectrum of bulk a-Si and two Si/SiO₂ multilayers with Si thickness of 14 and 24 Å. The excitation energy is 101 eV for all spectra which is below the L-edge for SiO₂.

In Fig. 3 we show the SXE spectra for bulk a-Si and two of the multilayer samples shown in Fig. 2. The bulk a-Si SXE spectrum exhibits the two characteristic peaks: one at 92 eV associated with 3s states in the valence band, and a high DOS at 96 eV which is dominated by p-type states [6]. The splitting in the 3s states observed in the SXE spectra of crystalline Si is not observed in the a-Si spectra. No shift in the multilayer valence band spectra is observed when compared to that of bulk a-Si and the overall appearance of the multilayer spectra is identical than that of the bulk a-Si. This result is different than recent photoemission studies of Si/SiO₂ multilayers where small shifts on the order of 0.15 eV were observed in the valence band edge [2]. It is also different to results observed for thin films of silicon nanocrystals and porous silicon where the shift in the valence band is reported to be a factor of two larger than the shift in the conduction band [7,8]. At the present time it is not understood why no shift is measured in the valence band when shifts are clearly observed in the conduction band. It is interesting to note that a plot of the shift in the CB edge as a function of layer thickness in the Si/SiO₂ multilayers is the same as the shift in the CB edge as a function of particles size in silicon nanoclusters [7]. The

multilayer should have a smaller shift because the confinement is only in one dimension compared to three dimensions in the nanoclusters.

In conclusion, we were able to investigate the unoccupied and occupied electronic states of a-Si layers in a Si/SiO₂ multilayer combining total fluorescence yield x-ray absorption and selectively excited SXE spectroscopy. We observe shifts in the CB edge as a function of layer thickness but not in the VB. The onset of the absorption edge progressively broadens with increased blue shift due to interface roughness in the multilayers.

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