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SUB-eV CORE LEVEL SHIFTS IN Si GRAIN BOUNDARIES AND NANOTWINS

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ABSTRACT

Using transmission electron microscopes (TEM) with high energy resolved sources like cold field emitter electron guns or conventional field emitters with a pre-specimen monochromator resolutions in the electron energy loss spectrum (EELS) of less than 0.2eV can easily be reached. With such set-ups small core level shifts can be observed at grain boundaries. The core level shifts can be traced back to a change in bond length which introduces a shift in the density of unoccupied states of the boundary forming atoms. We compare experimental data with full potential linear augmented plane waves (FPLAPW) calculations done with the WIEN2k code.

EXPERIMENTAL

Experiments were carried out at two different specimens to be sure that no specimen specific effect was measured. One specimen was an epitaxially grown thin film on a Si (100) substrate with many defects, the other one was a polycrystalline (pc) silicon thin film grown by metal induced crystallisation (MIC).
Cross sectional specimens of the pc-Si films were grinned and ion milled for EELS investigations. The last step of ion milling was an extremely soft treatment to prevent the specimen surface to be covered with an amorphous layer due to beam damage. After ion milling the specimens were transferred to the TEM in a vacuum box to avoid oxidation. EELS measurements were done in the pre-specimen monochromator equipped “TECNAI F200 mono” of TU Delft that is also furnished with a ultra stable high-tension tank and an high resolution spectrometer. The spectrometer dispersion was set to 0.02 eV per channel for band gap measurements and 0.2 eV for core level measurements. All EELS measurements were done in nanoprobe mode of the microscope, which allows spot sizes down to 3Å. For our experiments we chose a spot size of 8Å to have more intensity in the EEL signal.

RESULTS

Measurements *A* and *B* were acquired at a grain boundary in the MIC pc-Si thin film. In figure 1 the grain boundary and positions of measurements are shown in an high resolution TEM (HRTEM) image. In figure 2 the Si-L_3 edges are shown. The energy shift at the energy onset (figure 3) between *A* – in the bulk – and *B* – at the interface – is +0.2 eV. The same phenomenon can be found in the epitaxially grown thin film where one EELS spectrum was collected in an undistorted area (*c-Si*), another one in a polycrystalline defect (*pc-Si*), and a third one was acquired in an area full of microtwins (*micro twinning*) with an extension of only 3-5 atomic layers. A change of the bond length can be identified as the reason[(1)]. Another possible effect that might

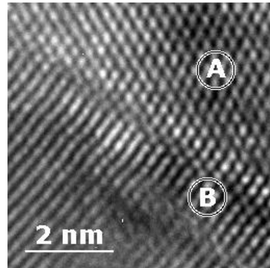

Figure 1: HRTEM image of Si-Si grain boudary. *A* and *B* are the positions of the electron beam for the measurement corresponding to fig. 3.

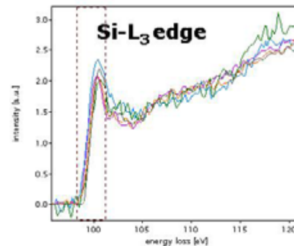

Figure 2: Si-L_3 edge at 99 eV energy loss. The region of interest is shown more detailed in fig. 3. It is clearly visible that the edge onsets are at different energies.

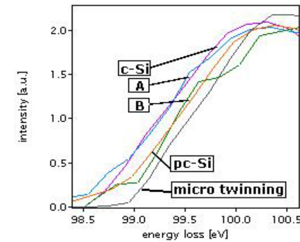

Figure 3: edge onset of the Si-L_3 edges. An energy shift of 0.2 eV between *A* and *B* as well as *c-Si* and *pc-Si* can be observed. The *micro twinning* region shows 0.3 eV shift.

be responsible for the shifts – a band gap chang –was investigated, too. Direct measurements of the Si band gap in EELS were not successful because changes in the range of 0.1 eV can hardly be observed but are predicted by simulations (figure 4). FPLAPW calculations were used to simulate the energy shift of the edge onset of the Si $L_{2,3}$, L_1, and K edge (figure 5). Due to the fact that the edge onset energy depends on the band gap and the total energy of the electrons the band gap energy was calculated which is varying with bond length by about ±0.1 eV for a change of ±2% in the lattice parameter. The total energy shift of 0.2 eV for the L_3 edge in the experiment belongs to a dilation of the lattice parameter by 1.86%.

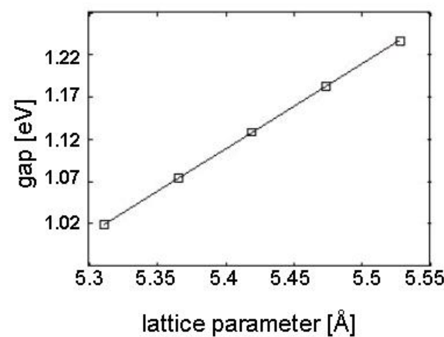

Figure 4: Gap width (in eV) with varying lattice parameter. The lattice parameter of c-Si is 5.429Å.

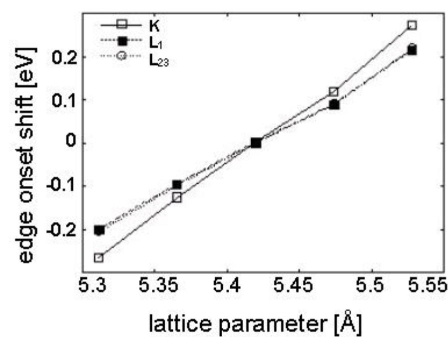

Figure 5: Energy shift of the ionisation edge vs. lattice parameter for the Si $L_{2,3}$, L_1, and K edges.

REFERENCES

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