XANES and XEOL investigations of SiC microcrystals and SiC nanowires

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Abstract. X-ray absorption near-edge structures (XANES) at Si and C K-edge as well as X-ray excited optical luminescence (XEOL) have been used to investigate the electronic structures and optical properties of SiC microcrystals (SiCmcs) and SiC nanowires (SiCnws). SiCnws synthesized via thermal evaporation, have a SiC (β-phase)-core-SiO₂-shell morphology. We found that the XANES for SiCmcs, a 6H-SiC (α-phase) structure, shows reasonable agreement with density functional theory (DFT) calculations. As for SiCnws, we observed both SiO₂ and SiC features at the Si K-edge. It is interesting to note that upon X-ray excitation, SiCmcs emit bright light at the wavelength of 600 nm (2.07 eV), although bulk α-SiC has an indirect bandgap of 3.02 eV. SiCnws, on the other hand, exhibit luminescence at 460 nm with a shoulder at 600 nm. The analysis of these data and its implications are presented.

1. Introduction

Silicon carbide (SiC) is an indirect band gap semiconducting material, which has a large potential for applications due to its high stability, chemical inertness, and excellent thermal conductivity [1]. SiC exists in a variety of polytypes depending on the stacking modes of Si-C tetrahedral structures. 6H-SiC, one of the α-phase polytypes, has a hexagonal lattice with six layers of Si-C tetrahedra and is the most stable polytype in nature. 3C-SiC (β-SiC), on the other hand, is the only cubic structure among all SiC polytypes. The band gap of SiC increases with increasing hexagonal characters in polytypes (i.e., 2.2 eV in cubic 3C-SiC and 3.02 eV in 6H-SiC [2]). Recently, micro- and nano-sized SiC materials are given great attention in the fabrication of electronic devices in a micro or even nano scale, thus it becomes crucial to understand the properties of micro- and nano-SiC for their further applications.

In this paper, we reported a comparative study of α-SiC microcrystals (SiCmcs) and β-SiC nanowires (SiCnws) on their electronic structures and optical properties. The electronic structures were examined using X-ray absorption near-edge structures (XANES). By scanning the energy from below up to 50 eV above the edge, K-edge XANES monitors the electronic transitions from 1s core level to unoccupied states of p character of the absorbing atom. In the work, Si and C K-edge XANES of SiCmcs and SiCnws will be reported together with theoretical calculations.

Optical properties were studied using X-ray excited optical luminescence (XEOL). XEOL monitors the light emission from the sample due to either excitonic electron-hole recombination or defects by tuning the excitation photon energy across the absorption edge of the absorbing atom.
2. Experiment and calculation

SiCmcs (α-phase, 200-450 mesh particle size, Aldrich) were used directly as purchased. SiCnws were synthesized via a thermal evaporation method [3]. In brief, by rapidly heating SiO powders in an activated carbon fiber (ACF) coated graphite crucible, a thick layer of SiC nanowires were deposited on the ACF surface following an oxide-assisted cluster growth mechanism.

Morphologies of SiCmcs and SiCnws were characterized using scanning electronic microscopy (SEM, LEO1530) and transmission electron microscopy (TEM, JEM-2010). The XANES measurements were carried out at the spherical grating monochromator (SGM) beamline at the Canadian Light Source (CLS), the University of Saskatchewan. XANES were recorded in total electron yield (TEY) and fluorescence yield (FLY), providing surface and “bulk” sensitivity, respectively. XEOL spectra were collected using an optical spectrometer (QE65000, Ocean Optics). All spectra were normalized to the incident photon flux.

Density functional theory (DFT) together with Generalize Gradient Approximation (GGA) was used for the theoretical calculation of the electronic structure of β-SiC [4]. The full potential augmented plane wave method was utilized in the numerical calculation employing the WIEN2k code [5]. Since SiC has the same local structure despite of their phases, cubic SiC is chosen to model both SiC materials given its high symmetric unit-cell structure. F-43m symmetry group in which Si occupies 4a site of (0,0,0) and C occupies 4c site of (1/4,1/4,1/4), is used for calculation. XANES were calculated using the electrical dipole transition, convoluted by instrumental Gaussian and core-hole lifetime Lorentzian broadenings [6].

3. Results and discussion

Figure 1 shows the morphologies of SiCmcs and SiCnws. From figure 1(a), we see that SiCmcs exhibit irregular shapes with particle size around 50 μm. SiCnws, shown in figure 1(b), have uniform diameters with the length of a few microns. The observed impurities are residue carbon during synthesis. The as-grown SiCnws have a core-shell structure which can be clearly seen from the TEM image (figure 1(c)). The SiC core is covered by a layer of amorphous SiO₂, which is due to the side-reaction of SiO [1].

3.1. XANES of SiCmcs and SiCnws: Si K-edge and C K-edge

Figure 2(a) shows Si K-edge XANES of SiCmcs. With a shoulder A at 1841 eV, three peaks in both TEY and FLY, labeled as B, C, and D, are the typical features of SiC crystal. The shoulder is considered as Si 1s→3p dipole transition, while peaks at higher energies are resonances caused by multiple scattering of outgoing photoelectrons from neighboring atom, probing unoccupied density of states (DOS) of p character [7]. The attenuated peaks in FLY are caused by self-absorption. Despite some differences in the relative intensity, the DFT calculation reproduces the peaks at the near-edge region. At higher energy (>1870 eV), the features broaden due to the increased lifetime of electronic transitions [6].
In SiCnws, the observed XANES exhibit features different from the calculated spectrum (figure 2(b)). Both TEY and FLY have similar features with a sharp peak at \(\sim1847\) eV followed by a broadened peak between 1854 eV and 1865 eV. A 1841 eV shoulder characteristic of SiC is also visible. As observed from TEM, the as-grown SiCnws have a SiC-core-SiO\(_2\)-shell structure. Thus, the XANES of SiCnws contains both features of SiC and SiO\(_2\). Compared with the TEY of thermally oxidized SiO\(_2\), peak E and peak F correspond to the white line and the shape resonance of SiO\(_2\), respectively. Higher intensity of peak E in TEY than FLY also suggests the SiO\(_2\) is mostly on the surface, which confirms the core-shell structure. The difference curve of normalized SiCnw-FLY and SiO\(_2\) is compared with the TEY of SiCmcs, and it can be seen that all characteristic SiC features emerge after the removal of SiO\(_2\) contribution.

The C K-edge XANES of SiCmcs are shown in figure 3(a). Both TEY and FLY have prominent features at \(\sim290\) eV. The dip of the TEY at \(\sim285\) eV is due to an experimental artifact (charging), as this is not observed in FLY. DFT calculation shows reasonably agreement at near-edge region, as the major features at 285 eV–295 eV can be clearly identified. However, the C K-edge XANES of SiCnws display a sharp peak around 285 eV which is not observed in SiCmcs. This 285 eV peak, is from impurity (i.e. carbon residue) and is attributed to the carbon 1s\(\rightarrow\)\(\pi^*\) transition, arising from unsaturated carbon with \(sp^2\) hybridization [8]. The difference curve between FLY (bulk) and TEY (surface) after scaling (normalize to the 285 eV peak) displays features very similar to those of SiCmcs.

3.2. XEOL of SiCmcs and SiCnws
The XEOL spectra of SiCmcs and SiCnws with excitation energy tuned across Si K-edge are shown in figure 4. It is interesting to note that upon excitation, both SiCmcs and SiCnws emit bright luminescence but at different wavelengths. SiCmcs emit light at the wavelength \(\sim600\) nm (2.07 eV).
The intensity of luminescence decreases when approaching the edge jump and increases above the edge jump, showing an inverted trend compared with normal XANES. This may be due to the saturation effect, as the size of SiCmcs (~50 μm) is larger than the one-absorption length at Si K-edge (less than 10μm). The luminescence most likely arises from surface (defect) states as the energy is much smaller than the band gap of α-SiC (3.02 eV).

Figure 4 XEOL spectra of a) SiCmcs and b) SiCnws.

However, in SiCnws, the luminescence is centred at wavelength of ~460 nm (2.70 eV). This is due to light emission from oxygen vacancy of SiO2, as it reaches its highest intensity at SiO2 white line (~1847 eV) [9]. It can also be seen that luminescence shows an asymmetry with a long tail toward the longer wavelength. Thus the embedded SiC core also contributes to the light emission, though the intensity is not strong enough to be distinguished as a peak but with curve fitting it yields a peak at 600 nm (not shown).

4. Conclusion

Electronic structures and optical properties of two SiC based materials were examined using XANES and XEOL. SiCmcs show well-defined spectral features at both Si and C K-edges. The DFT calculation reasonably reproduces these near-edge features. SiCmcs emits bright light at the wavelength of ~600 nm upon X-ray excitation. As for the SiCnws core-shell structure, both SiO2 (shell) and SiC (core) contribute at the Si K-edge, where the SiO2 feature is dominant. It is also found that both SiO2 and SiC contribute to the luminescence at ~ 460 nm and ~ 600 nm, respectively, mainly of a trapped exciton/defect origin.

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