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X-ray absorption spectroscopy study at the Si K-edge of tungsten carbide–silicon carbide thin films

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X-ray absorption spectroscopy (XAS) has been used to determine the compositional and structural nature of the phases formed in sputter-deposited W–Si–C films. The Si K-edge was examined to determine the presence and crystallinity of the SiC phase. For a film composition of 22% SiC, the XAS results show that there is at best only a minor amount of crystallization of SiC when deposited at 350 °C, but crystallization becomes more definitive at 600 °C. For a film with 29% SiC deposited at 350 °C, no crystalline SiC was detected.

Keywords: X-ray diffraction; X-ray absorption spectroscopy; Carbides; Physical vapor deposition

Recent studies on the influence of microstructure on the mechanical properties of nanocomposite Me–Si–C and Me–Si–N (where Me is a metallic element) thin films have shown that potentially significant property enhancements can be realized [1–9]. Microstructures that can be obtained in these thin films range from fully amorphous to crystalline, depending on the deposition parameters, particularly the substrate temperature and film composition. The structures of particular interest are those that contain both amorphous and crystalline phases, with each at the nanometer scale. In order to obtain such a structure, it is necessary to achieve some degree of phase separation during deposition, but not so much as to coarsen the structure. Controlling the extent of phase separation can be done by choice of appropriate deposition temperature. However, the addition of silicon to these films also limits phase separation and promotes the formation of amorphous phases. Therefore, it is necessary to understand the nature of phase separation and the kinetics of the process, and how these are affected by both temperature and Si content. Previous studies employing X-ray diffraction and high-resolution transmission electron microscopy (HRTEM) showed how Si induces structural disorder in the W–Si–C thin films [9,10]. However, due to the nanometer-size scales of the structures, it was difficult to obtain chemical information about the phases formed. In this study, we report on the use of X-ray absorption methods to gain information on the compositional nature of the phases formed in these films.

Samples of W–Si–C thin films were deposited using radiofrequency magnetron sputter deposition in a high-vacuum ($\sim 5 \times 10^{-7}$ torr) chamber. Deposition was carried out using commercially available targets of tungsten carbide and silicon carbide. Further details on the method used to deposit these films can be found in Ref. [10]. Substrates used were pieces of (1 0 0) Si wafers and WC–Co cutting tool inserts 1 cm × 1 cm × 3 mm in size. The latter substrates were used to avoid substrate contributions for Si in X-ray absorption spectroscopy (XAS) experiments. Si substrates were used for X-ray diffraction experiments.

Two sets of films were deposited by varying the WC/SiC sputter gun power ratio from 1.3 (set A) to 0.75 (set B). For set A, substrate temperatures of 25, 350 and 600 °C were used, in contrast to the previous work

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[10], in which all samples were deposited at 350 °C. For set B the substrate temperature was kept at 350 °C to focus on compositional effects. In the following, the samples will be labeled according to their set and substrate temperature. All films were deposited using a substrate bias of −50 V, and had a thickness of approximately 5 μm. In addition to these thin film samples, several bulk samples were run in the XAS experiments to use as standards. These included a piece of an Si wafer, a commercially available SiC wafer and a sample of sputter-deposited SiC (room temperature deposition, −50 V bias).

The samples were first analyzed using X-ray photoelectron spectroscopy (XPS) on a Kratos Axis/HS system in order to determine film composition. Analysis was conducted by first ion etching the sample for 15 min (4 kV, 10 mA) to remove surface contaminants, and then acquiring a spectrum using an Mg K_α X-ray source. Compositions were determined from these data using standards supplied with the instrument. X-ray diffraction analysis was carried out on a Rigaku D/MAX-B diffractometer employing Cu K_α radiation. XAS measurements were carried out at the BESSY KMC1 line, using a standard UHV chamber equipped with a solid-state fluorescence detector.

Compositions of the deposited films were carried out using XPS. For set A, the average film composition was 38.7% W, 10.9% Si, 40.3% C and 10.9% O (values in at.%). This gives a W/Si ratio of 3.55 and a relative %Si (Si relative to W + Si) of 22%. Compositions for set B were not measured but, based on linear sputter power/composition ratios, set B is calculated to have 29 relative %Si. This compositional range is comparable to several films investigated in Ref. [10].

XRD results are shown in Figure 1. For sample A-25, two broad peaks are observed, one at $2\theta = 38°$ and the second at $2\theta = 72°$. The peak with maximum intensity has a q ($=4\pi\sin\theta/\lambda$) value of 26.5 nm^{-1}, and the location of the second smaller peak at 1.8 times this value indicates the structure is primarily amorphous. For sample A-350, subtle changes in the spectrum are observed. The nature of these changes becomes clearer when the 600 °C sample spectrum is examined. For this spectrum Bragg peaks begin to emerge and analysis of the peak positions indicates the formation of an FCC structure, suggesting formation of a W-rich phase similar to cubic WC_{1-x} (PDF #20-1316), which was also observed in Ref. [10]. In general, crystallization is promoted by both increased temperature and reduced Si content. This is supported by the spectrum for sample B-350, which is similar to the room temperature sample spectrum of lower Si content (A-25). The sample of sputter-deposited SiC was also examined, and found to be amorphous.

Because of the broad nature of the peaks, other phases may be present but difficult to distinguish, such as β-SiC (cubic, PDF #29-1129). In addition, because of the lower atomic number and weak scattering power of SiC, tungsten carbide phase will dominate the XRD patterns. Therefore, based on XRD, limited information can be obtained on the crystallization of SiC phases. TEM examinations of similar samples [9,10] showed that at high Si concentrations the structure at 350 °C deposition temperature was highly disordered, but consisted of two phases, as indicated by areas of lighter and darker contrast in the image. It was suggested that these areas represent SiC- and WC-rich regions. The purpose of the XAS experiments was to further examine this hypothesis by investigating the Si K-edge spectrum.

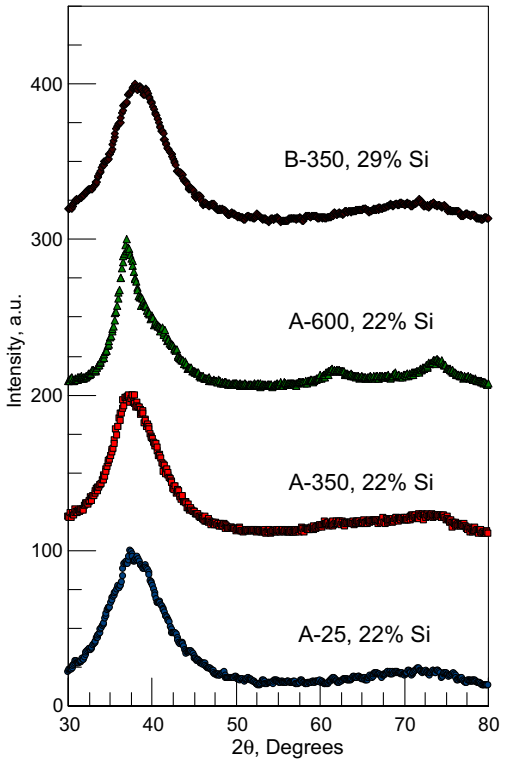

Figure 1. XRD patterns for W–Si–C samples, showing the effects of temperature (A-25, A-350 and A-600) and Si content (A-350 vs. B-350). Definitive Bragg peaks are observed in sample A-600, and the peak positions indicate an FCC phase.

Figure 2 shows Si K XANES spectra, recorded in fluorescence yield mode, of samples grown by magnetron sputtering at different substrate temperatures. The top spectra correspond to crystalline Si, crystalline SiC and sputtered SiC, and are included as reference samples. The spectrum of Si is almost featureless, with an absorption threshold at 1838.3 eV (marked with a solid line) and a small peak just above the threshold, at 1840.8 eV. The height of this peak is very sensitive to the incidence angle of the synchrotron linear polarized light on the sample [11]. The line shape of this spectrum agrees well with results from previous works [12].

The absorption threshold of both SiC samples is shifted 2.0 eV with respect to pure Si, being located at 1840.3 eV. Nevertheless, there are clear differences in the lineshape of both spectra. The first peak after threshold is located at lower energy for the sputtered sample (feature A, at 1844 eV), as compared with the SiC wafer (feature B, at 1845.7 eV). On the other hand, feature C is present in both spectra and at the same energy position, 1858 eV, although with a higher intensity in the case of the crystalline sample. An additional feature, at 1894 eV photon energy, is only present in the spectrum of crystalline SiC. These observations allow us to assign feature C to SiC, independently whether it is crystalline or not.

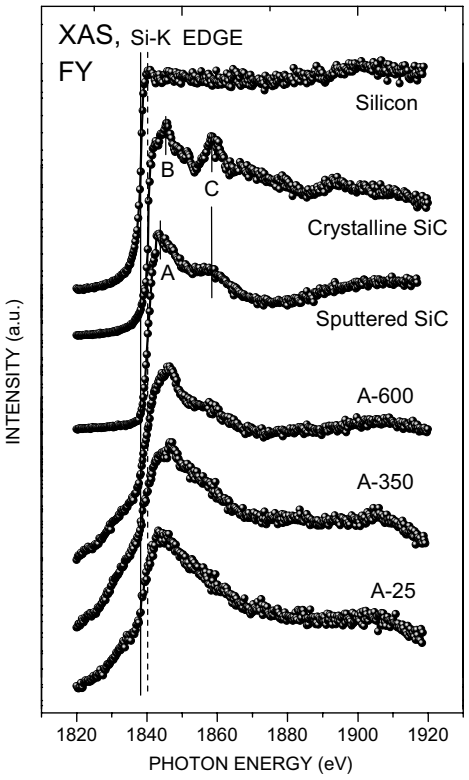

Figure 2. Si K-edge XANES spectra of WC–Si samples grown with different substrate temperatures. Crystalline Si and SiC and amorphous SiC are also shown for comparison.

Feature A could be assigned to non-crystalline SiC, whereas features B and that at 1894 eV are typical of crystalline SiC.

For the W–Si–C samples the absorption threshold is difficult to define because, due to the low signal to background intensity, the pre-edge region is not well defined, as it is not the threshold itself. However, for all samples the threshold seems to be at an intermediate value between those of Si and SiC, which could indicate both species are present. Feature C is absent in the sample grown at room temperature, but a maximum near that of feature A indicates an amorphous structure. For samples A-350 and A-600, the maximum shifts to a location near feature B, suggesting the presence of crystalline SiC, which can be related to the segregation of the film into SiC-rich and WC-rich regions, consistent with microscopy observations [10]. Feature C starts becoming visible for sample A-600, grown at 600 °C. The presence of both features B and C, also found in the spectrum of crystalline SiC, suggests that at this temperature SiC is present in a more crystalline form.

Figure 3 shows XAS spectra of two samples grown at 350 °C with different power ratios. The intensity of feature A, assigned to non-crystalline SiC, seems more intense for the sample with the higher SiC content, suggesting that the higher the Si content, the lower the degree of crystallization. This is consistent with the XRD data shown in Figure 1.

In our previous work on WC/SiC films [10], the results of the microscopy investigation revealed the development of a two-phase morphology for samples deposited at 350 °C and near the composition of the

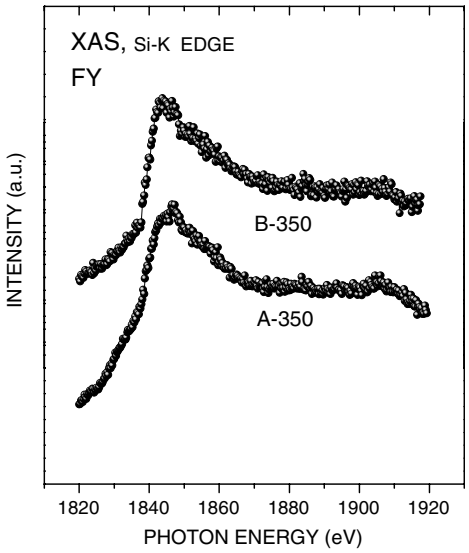

Figure 3. Si K-edge XANES spectra of two WC–SiC samples grown with a substrate temperature of 350 °C but with different compositions.

films examined here. While no chemical information was obtained in Ref. [10], it was proposed that this two-phase morphology represented SiC-rich and WC-rich regions. In the present study, we confirm the presence of SiC-rich regions by comparison to bulk and sputter-deposited SiC. In addition, we have examined samples deposited at 25 and 600 °C. The XRD patterns for the 22% Si film deposited at 600 °C shows evidence for crystallization, but it is not clear for which phase. The XAS results show that there is at best only a minor amount of crystallization of SiC at 350 °C, but crystallization becomes more definitive at 600 °C. However, the degree of crystallization is still well below that observed in the SiC wafer. Examination of the effects of composition (22 vs. 29% SiC) showed that the additional Si reduced the ability of SiC to form crystalline structures. The understanding of these combined compositional and temperature effects will help guide the development of superhard coatings materials based on amorphous/crystalline structures.

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