

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

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The influence of microstructure on the mechanical properties of nanocomposite ceramic films is currently a subject of active research and investigation¹⁻³. Microstructural features in thin films that can influence mechanical properties include grain size and morphology, defect content, film porosity and phase content. The presence of multiple phases within the film can enhance film strength and toughness, as well as provide multifunctional capabilities. Therefore, a detailed understanding of microstructural evolution in thin films is essential to understanding and controlling their mechanical and physical properties.

In our present work, we are investigating the effects of Si additions on microstructure and phase formation in WC thin films⁴⁻⁶. The films are deposited by co-deposition from WC and SiC targets in a magnetron sputter deposition system, a method that easily allows us to maintain the WC-SiC stoichiometry. By using the co-deposition method, we also can explore the complete compositional range between WC and SiC, or more closely examine a specific compositional range of interest. Previous X-ray diffraction and TEM studies revealed that an increase of SiC content in WC produced a grain refining and amorphizing effect. In the range of 11 to 26% SiC, a hierarchical dense structure composed of sharp boundaries and refined grains was observed. At this point, a chemical analysis of the observed phases to determine their composition seems crucial to carry out our investigations.

The driving force for microstructure development in these films is the bonding differences between SiC and WC. SiC is covalently bonded and exhibits tetrahedral bonding arrangements between Si and C atoms. For the metallic carbide, the most common structure in the deposited films (the B1 structure) results in C atoms occupying octahedral sites with six nearest neighbors. This difference in bonding drives phase segregation, and in equilibrium complete phase separation between the metallic carbide and SiC is expected. However, the deposition conditions typical of our experiments represent significant kinetic constraints that result in highly disordered phases and incomplete phase separation.

The small size of the phases, in the nanometer scale, makes it difficult to obtain their chemical composition by conventional spectroscopic techniques. On the other hand, X-ray absorption spectroscopy is very sensitive to the local chemical environment around a specific atomic element. Consequently, we have performed X-ray absorption spectroscopy experiments at the Si-K edge of WC-Si thin films grown under different conditions. Samples were grown by magnetron sputtering codeposition using a power of 200 W on the WC target and 150 W on the SiC target. at a magnetron power. Substrate temperature was varied between RT and 600°C. An additional sample was grown with a different power ratio (150 W on the WC target an 200 W on the SiC target) with the substrate at 350°C for comparison. A Si wafer, a SiC wafer, and a SiC sample grown by sputtering, were also measured as references. XAS measurements were carried out at the BESSY KMC1 line, using a standard chamber equipped with fluorescence and total electron yield detection.

Figure 1 shows X-ray absorption spectra, recorded in Fluorescence Yield (FY) mode of samples grown by magnetron sputtering at 200 W power on the WC target and 150 W on the SiC target, and with different substrate temperature. The top spectra correspond to crystalline Si, crystalline SiC, and sputtered SiC, and are included as reference samples. The sputtered

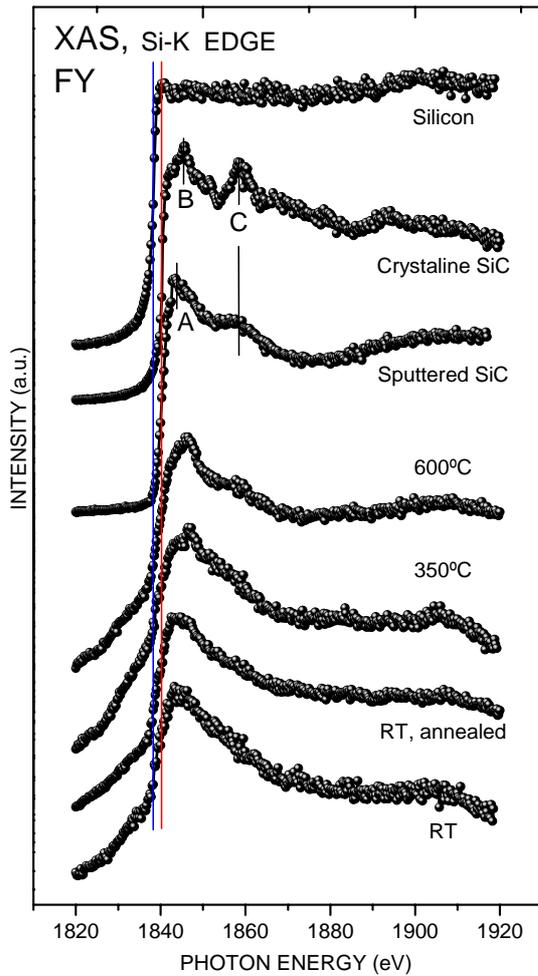


Figure 1: Si-K edge X-ray absorption spectra of WC-Si samples grown with different substrate temperature. Crystalline Si and SiC, and amorphous SiC are also shown for comparison

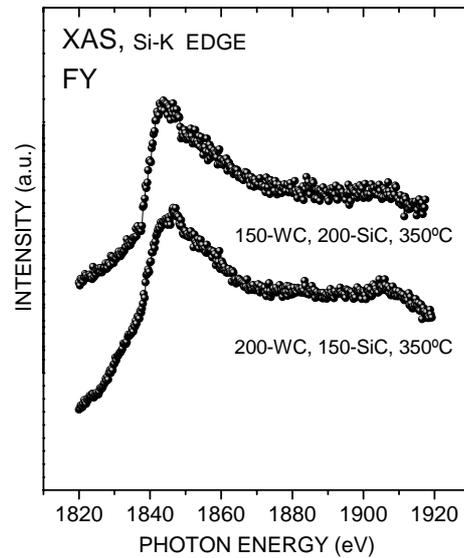


Figure 2: Si-K edge X-ray absorption spectra of two WC-Si samples grown with a substrate temperature of 350°C but with different composition

SiC sample was obtained by magnetron sputtering with 200 W on the SiC gun. XAS 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.⁷ The lineshape of this spectrum agrees well with previous results from other works.⁸

The absorption threshold of both SiC samples is shifted 2 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 an energy of 1894 eV, 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. Feature A could be assign to non-crystalline SiC, whereas features B and that at 1894 eV are typical of crystalline SiC.

For the WC-Si samples it is not easy to determine the absorption threshold, because, due to the poor 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 be a proof that both species are present. Feature C is absent in sample grown at RT, but it starts to be visible for the annealed sample and that

grown at 350°C. In the latter case, feature B, typical of crystalline SiC, starts to develop, suggesting that, at this temperature, SiC grows in crystalline form. Finally, the sample grown at 600°C shows a clear feature C and, again, a peak at the position of feature B, which suggests that, in this case, the amount of SiC is the highest, and it is in crystalline form.

Figure 2 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 grown at higher SiC power, suggesting the higher the Si content, the lower the degree of crystallization.

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