Syntheses of superhard hexagonal tungsten carbide films by N alloying

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We synthesized N-alloyed tungsten carbide thin films on Si(100) substrates at 500 °C using direct-current reactive magnetron sputtering in a mixture of CH₄/N₂/Ar discharge and explored the effects of N alloying on the preferred orientation, phase transition, and mechanical properties of the films by using x-ray diffraction, x-ray photoelectron spectroscopy, and nanoindentation measurements. We found that N alloying significantly influenced the compressive stress, which led to a pronounced change in the preferred orientation, phase structure, and hardness for the tungsten carbide film. A phase transition from β-WC to α-WC occurred when N alloying was in the range of 2.9 and 4.7 at. %, meaning that α-WC can be obtained at relatively low temperature (500 °C). To reveal the relationship between the stress and phase transition, as well as preferred orientation, the density-functional theory based on first principles was used to calculate the elastic constants and shear modulus for tungsten carbide with a structure of β-WC or α-WC. The calculated results showed that the preferred orientation depended on the competition between strain energy and surface energy, as well as the grains competitive growth, and the phase transition could be attributed to a decrease in the strain energy. The hardness of α-WC was harder than β-WC because the shear modulus for α-WC was larger than that of β-WC, whereas the bulk modulus for α-WC was almost equal to that of β-WC. In addition, the effects of substrate bias (Vb) on the intrinsic stress, preferred orientation, and phase transition for the WC₀.₂₅N₀.₇₅ films by virtue of X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and selective area electron diffraction (SAED) were also explored.