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Effect of substrate temperature variation on nanostructured WC films prepared using HFCVD technique

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Abstract

Nanocrystalline tungsten carbide thin films are deposited on quartz substrates using hot-filament chemical vapor deposition technique. The influence of the substrate temperature on the nanostructured WC films is studied. The scanning electron microscopy indicates that the size of nanoparticles increases from 50 to 150 nm with an increase of substrate temperature from 400 °C to 800 °C. The crystalline structures, chemical bonds, and nanocomposition of WC films are characterized using X-ray diffraction, X-ray photoelectron spectroscopy, Raman scattering, and energy dispersion spectroscopy. The evolution of crystalline structures from α-WC to α-W_2C following variation of substrate temperature is observed.

Keywords: Thin film; Tungsten carbide; CVD; Nanocrystalline structure

1. Introduction

Tungsten carbide (WC) is a very promising material. It can widely be used for hard coatings [1,2], electrochemical sensors [3], and microelectronic interconnect technologies [4] due to its high melting temperature (2870 °C), high hardness, relatively low conductivity, and excellent chemical stability. Many studies have been conducted in synthesis of various compositions of W_xC_{1-x} films based on various techniques, including the reactive sputtering of tungsten with C_xH_y chemistries [5,6], the simultaneous sputtering of tungsten and carbon materials [7,8], the laser ablating W targets in a hydrocarbon environment [9], and the chemical vapor deposition (CVD) [10–12]. In most cases, low temperatures of CVD yielded a poorly crystalline or amorphous WC films [13–15].

In this letter, the nanocrystalline tungsten carbide films are synthesized using hot-filament CVD (HFCVD) techniques at wide temperature range. The effect of deposition temperature on nanostructure and nanocomposite of WC films is studied. All samples have been characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS) and energy dispersion spectroscopy (EDS).

2. Experimental setup

The nanostructured tungsten carbide films are synthesized using HFCVD techniques. The tungsten filament itself acts as a precursor for WC films deposition, the supply of carbon comes from a mixture of 9.9% of methane and 90.1% H_2 gases. Disk type of quartz substrates are used and ultrasonically cleaned in acetone for 10 min first. After placing the substrate, the chamber is pumped down to 2.0×10^{-5} Torr before feeding the gases. The flow rate of mixed gas is 20 SCCM. The gasses pressure inside the deposition chamber is maintained constant to 4 Torr during the deposition.

Substrate temperatures are maintained at 400±10 °C, 600±10 °C and 800±10 °C, respectively. The distance between filament and substrate is 2 cm, and the duration of each deposition is 2 h. The XRD and SEM are used to characterize structure and surface morphology of the films. Quantitative surface analysis

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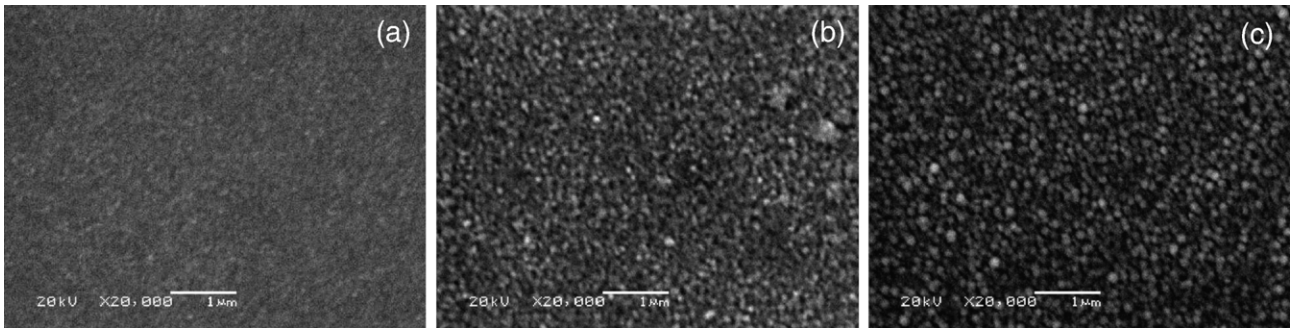

Fig. 1. SEM images of the samples prepared for 2 h at substrate temperatures of a) 400 °C, b) 600 °C, and c) 800 °C.

and chemical states of the grown WC layer at different temperatures are performed using EDS and XPS. The microstructure of the films is analyzed using RS.

3. Results and discussion

Fig. 1 shows SEM images for WC samples grown on quartz surface at 400±10 °C, 600±10 °C and 800±10 °C substrate temperatures. The surface of films is smooth. The size of particles changes from 50 nm to 150 nm with substrate temperatures from 400 °C to 800 °C. The thicknesses of samples are 250 nm for 400 °C, 700 nm for 600 °C, and 1000 nm for the case of 800 °C, respectively. This is an indication that high growth temperature results in a high deposition rate. The reason is that high substrate temperature speeds up the reaction rate of precursor atoms/molecules in the deposition processing. This phenomenon has been confirmed by following results obtained from the Raman scattering of the samples.

Fig. 2 shows the XRD patterns of WC films. Two XRD peaks marked with SiO_2 are from the substrate. All other XRD peaks are related to WC film. The XRD patterns indicate the crystalline structure of WC film exhibits hexagonal α-WC and hcp α-W_2C structures [16,17]. As increasing the substrate temperature from 400 to 800 °C, the peak of hcp α-W_2C becomes more obvious and narrower, whereas the signal of hexagonal α-WC nearly vanishes. The phase variation from α-WC to α-W_2C is probably due to an apparent decreasing of the carbon-sticking coefficient with the increase of substrate temperatures. Consequently, the ratio of W/C content inside the samples increases at high deposition temperature.

The Raman spectrum done for each sample is shown in Fig. 3. The signal marked with 'S' is from the substrate. This signal becomes weaker due to the attenuation of thicker WC film prepared in the case of higher substrate temperature deposition. Clearly, the high substrate temperature deposition yields a high growth rate. This is in agreement with the results obtained from thickness measurements.

The bands situated at around 700 and 800 cm^{-1} can be associated to W–C stretching models, marked with 'W_1' and 'W_2'. With an increase of the substrate temperature from 400 to 800 °C, the peak 'W_1' shifts from 685.1 to 692.8 cm^{-1}, and the peak 'W_2' shifts from 800.0 to 806.9 cm^{-1}, respectively. Small shifts of the bands may be related to phase change between stable hexagonal crystalline α-WC and metastable hcp crystalline α-W_2C, and content change of carbon inside the samples. It is different from the Raman bands for monoclinic WO_3 [18], where no shifts of the peaks associated to W–O are found because of the high stability of monoclinic WO_3. The widths of the bands W_1 and W_2 (Fig. 3) are slightly large, round 50 cm^{-1}. This may be due to the existence of certain lattice distortion [19] in the crystal structure of the samples.

A tiny peak marked with 'C' at around 1550 cm^{-1} is also observed and associated to the carbon phase. According to the literatures [20,21], this is a typical G-band (Fig. 3.2) of the carbon phase. The shifts of Raman G-bands from 1582.7 to 1532.9 cm^{-1} are clearly visible with increasing of the substrate temperature from 400 to 800 °C, which suggests the variation of the chemical environment for different deposition temperatures. The broad profile of G-band with its weak intensity probably indicates the existence of a little amorphous carbon inside the samples. Therefore, we can conclude that the obtained films contain both crystalline WC and amorphous carbon phases. However, the crystalline WC dominates the sample's structure and content.

EDS shows the atomic content ratio of W/C increases from 0.93 to 1.18, and finally goes up to 1.39, as the substrate temperature increases from 400 to 600 °C, and then to 800 °C. This phenomenon is in agreement with the phase evolution identified by XRD pattern above. In HFCVD processing with mixture of CH_4/H_2 gases, carbon incorporation within the WC films is attributed to CH_3 radicals generated in the plasma [6]. As increasing the substrate temperature, the tungsten composition increases and the carbon composition decreases, which perhaps is due to the small CH_3-C sticking-coefficient at a high substrate temperature.

Comparing the ratio of W/C compositions atomic content obtained from EDS with the crystal structure phase data from the XRD, unreactive carbon composition exists inside WC films can be estimated. At low substrate temperature of 400 °C, the XRD pattern shows the sample has a mixture state of α-WC and α-W_2C, so the unreactive carbon concentration in the sample is around 3.8% that is

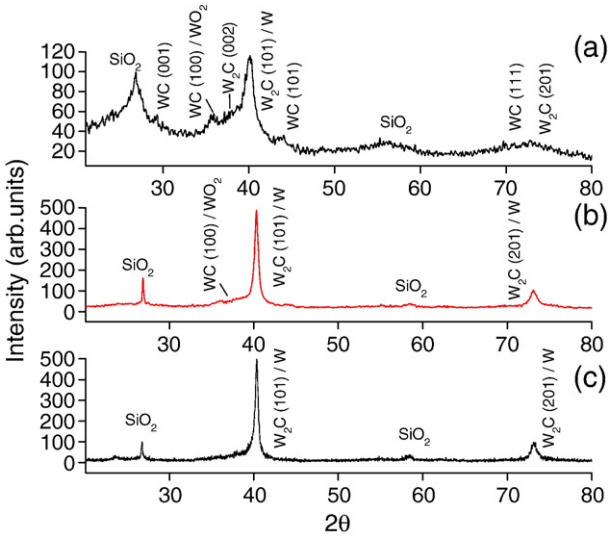

Fig. 2. XRD of the samples prepared for 2 h at substrate temperatures of a) 400 °C, b) 600 °C, and c) 800 °C.