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Synthesis of nanostructured SiC using the pulsed laser deposition technique

H.X. Zhang [a,b], P.X. Feng [a,b,*], V. Makarov [a,c], B.R. Weiner [a,c], G. Morell [a,b]

[a] Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, PR 00931, USA
[b] Department of Physics, University of Puerto Rico, P.O. Box 23343, San Juan, PR 00931, USA
[c] Department of Chemistry, University of Puerto Rico, P.O. Box 23346, San Juan, PR 00931, USA

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ABSTRACT

We report the new results on the direct synthesis of nanostructured silicon carbide (SiC) materials using the pulsed laser deposition technique. Scanning electron microscopy images revealed that SiC nanoholes, nanosprouts, nanowires, and nanoneedles were obtained. The crystallographic structure, chemical composition, and bond structure of the nanoscale SiC materials were investigated using X-ray diffraction, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and Raman scattering spectroscopy. The transverse optical mode and longitudinal optical mode in Raman spectra were found to become sharper as the substrate temperature was increased, while the material structure evolved from amorphous to crystalline.

1. Introduction

Silicon carbide is a well-known wide band gap semiconductor with excellent properties for devices operating under extreme conditions such as high temperature, high power, and high frequency, which make it a promising material for the electronic devices [1]. Nanostructured silicon carbide (SiC) has been shown to exhibit superior properties (greater elasticity and strength) vs. bulk SiC and has potential applications in light-emitting diodes and UV photodetectors due to higher light-emission efficiency [2]. There is significant interest in the synthesis of nanostructured SiC including nanospheres, nanowires, nanorods and so on as novel functional materials for nanoscale engineering [3].

Recently, Lin et al. [4] reported the chemical vapor deposition (CVD) synthesis of silicon carbide nanocones on the surface of silicon oxycarbide. Zhang et al. [5] synthesized SiC nanorods via catalyst-assisted crystallization of amorphous silicon carbonitride. Ho et al. [6] used a vapor–liquid–solid (VLS) process to grow nanoflower-like structures with the help of gallium nitride powder. Dai et al. [7] reported the synthesis of SiC nanowires by using a carbon template method. However, these products were available just based on complicate fabrication process, cost of expensive carbon nanotube or the use of the explosive precursor and so on. In addition, the synthesized materials were low yield and time consuming.

In this paper, we report a simple approach to synthesize nanostructured SiC films, including nanoholes, nanosprouts, nanowires, and nanoneedles by the pulsed laser deposition (PLD) technique. Experimental data indicate that the present new approach can be used to control the growth of various types of nanostructured SiC films.

2. Experimental details

An ArF Lambda Physik 1000 excimer laser (193 nm, ~20–30 ns, and 10 Hz repetition rate, and 200 mJ pulse energy) was used to irradiate the commercial silicon carbide target (the concentration is Si 50% and C 50%) at 2.0×10^{-5} Torr in the chamber. The laser beam, focused with a 30-cm focal length fused silica lens, was incident at 45° relative to the target surface. The diameter of the focused spot of the laser beam on the SiC target (purity up to 99.99%) was about 3 mm. The power density of the laser on the target was 1.1×10^8 W/cm^2 per pulse. The SiC target was rotated at circa 200 rpm. Both silicon (Si) and molybdenum (Mo) wafers were used as deposition substrates, and were placed 4 cm away from the target as shown in Fig. 1. A heater and thermocouple were used to obtain and monitor the desired substrate temperature. Prior to laser irradiation, the Si (1 0 0) and Mo wafers were polished by diamond powder and rinsed in acetone and methanol in sequence. The duration for each deposition was 30 min.

3. Result and discussion

Fig. 2 shows typical SEM images of nanostructured surfaces of SiC films prepared on silicon substrates using PLD techniques at

* Corresponding author at: Department of Physics, University of Puerto Rico, P.O. Box 23343, San Juan, PR 00931, USA.
E-mail address: peterxianping@vmail.uprrp.edu (P.X. Feng).

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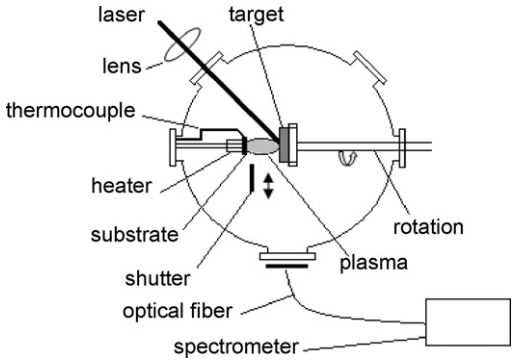

Fig. 1. Experimental setup for synthesis of nanostructured SiC using the PLD techniques.

substrate temperatures of (a) 500 °C, (b) 1000 °C, and (c) 1200 °C, respectively. Different morphologies were observed in the SiC nanostructures for different substrate temperatures, but otherwise identical growth conditions. At 500 °C, quasi square-shape nanoholes with sizes of 150–50 nm are uniformly distributed on the surface of sample (Fig. 2a). Raising the substrate temperature to 1000 °C leads to slightly ambiguous nanorod structures as shown in Fig. 2b. Following growth at 1200 °C, the sprout-like nanostructures (Fig. 2c) with diameter of circa 250 nm and length of circa 4 μm are clearly visible. The aligned rod arrays are perpendicular to the substrate. Such consistent alignment is attractive, as it allows the aligned SiC nanorods to be tuned to meet specific requirements. Apparently, the thickness of SiC film grows with the increase of substrate temperature.

The obvious variations of nanostructures probably are related to the large strain from the misfit in lattices between the SiC films and the substrate, which unavoidably lead to structural transitions [8]. The misfit in lattices between films and substrates can be enhanced with the increase of substrate temperature. Basically, the overlayer will grow with a stacking fault after a first coherent layer. When the film was much thicker than critical thickness, the initial smooth surface of the film will become the fractal-like structure, then enhanced, and eventually the thin film will transformed into nanostructured SiC films shown in Fig. 2.

Energy dispersive X-ray spectroscopy (EDX) was employed to quantitatively analyze the chemical composition of the SiC samples. The samples mainly consist of silicon and carbon. A small amount of oxygen was also detected, which possibly derived from the residual air in the chamber and oxygen adsorption during the transport of the samples from the growth chamber to the spectrometer. EDX data show that the carbon atom concentration (at.%) is approximately 24.18% 17.95%, and 15.20% for the samples prepared at 500 °C, 1000 °C, and 1200 °C, respectively, while the silicon atom concentration varies from 75.65%, 81.12% to 83.51%. It is expected that the partial of the silicon signal in EDX data is a contribution from the silicon substrate.

The crystallographic structures of the samples were examined using X-ray diffraction (XRD). Fig. 3 shows typical XRD patterns of samples prepared at 1000 °C and 1200 °C. The (1 1 1), (2 0 0), (2 2 0), and (3 1 1) diffraction peaks were identified. The shoulder associated with stacking faults, which serves as a common feature of SiC material, were also observed, demonstrating the crystalline nature of the sample prepared at the temperature 1200 °C [6,9]. No diffraction peak was detected from the XRD spectrum of the sample prepared at 500 °C except the substrate peak, indicating that the low temperature of deposition yields amorphous SiC film, whereas higher temperatures deposition gives rise to polycrystalline structures of SiC sample. Therefore, we conclude that both crystalline structures and surface structures are mainly dependent upon substrate temperature during deposition.

X-ray photoelectron spectroscopy (XPS) technique was also used to characterize the samples and the spectra of core-level C 1s and core-level Si 2p peaks are shown in Fig. 4. Based on the literature [10,11], the C 1s core was deconvoluted into two components situated at 283.1 eV and 284.3 eV that were associated to the SiC bond and the adventitious carbon (i.e. the graphite-like cluster in the films), respectively.

From XPS data, the intensity ratio of SiC/C–C(sp^2) varies from 0.7 to 0.96 following an increase of the substrate temperatures. The presence of oxygen in the structures was disregarded because of the low intensity of the O 1s peak. Two subpeaks situated at 99.2 eV and 101 eV in Si 2p XPS spectrum were also identified based on previous publications [11]. The ratio of SiC/Si increases from 0.4 to 1.02, which is in good agreement with the data of SiC/C–C(sp^2) ratio.

Raman scattering spectra of the nanostructured SiC films were also obtained at room temperature by using a triple monochromator (ISA J-Y Model T64000) with an excitation wavelength of 514 nm (Ar^+ ion laser). The microscope was used for focusing the laser beam onto the surface of samples. Two Raman peaks at 796 cm^{-1} and 972 cm^{-1} were assigned to the transverse optical (TO) mode and longitudinal optical (LO) mode phonons of cubic SiC, respectively, confirming the presence of crystalline structures of β-SiC [12]. The LO feature becomes sharper as the substrate temperature was increased. The variations of LO mode, and the signal of the TO mode from a broad low intensity peak in Fig. 5a to a tiny peak in Fig. 5b and then to a sharply crystalline peak in Fig. 5c are most likely related to the evolutions of structures of samples from the amorphous to polycrystalline structure following an increase of substrate temperature. The clear LO signal in amorphous SiC shown in Fig. 5a is probably concerned with the silicon substrate. Raman data are in good agreement with the results obtained from the XRD spectrum. It should be mentioned that the asymmetric broadening of the peak at 796 cm^{-1} in Fig. 5c possibly indicates the stacking faults of SiC nanocrystallites [12].

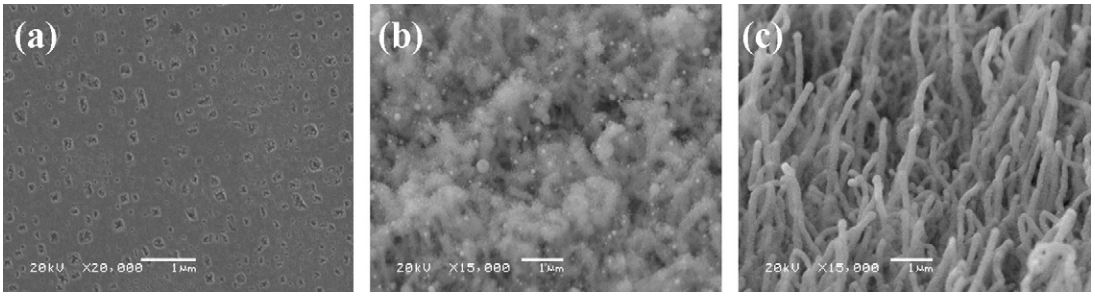

Fig. 2. SEM images of nanostructured SiC films prepared on Si substrates using PLD at substrate temperatures of (a) 500 °C, (b) 1000 °C, and (c) 1200 °C, respectively.