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Synthesis of BCN thin films by nitrogen ion beam assisted pulsed laser deposition from a B_4C target

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Abstract

Using sintered B_4C as target material, ternary BCN thin films were synthesized on Si(100) substrates by means of reactive pulsed laser deposition assisted by nitrogen ion beam. The composition, bonding configuration and crystalline structure of the synthesized films were characterized by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and transmission electron microscopy. The prepared films contain several bonds including B–C, N–C, B–N with B–C–N atomic hybridization. The ablation of the B_4C target results in the deposition of a film with B:C ratio about 3:1, deficient in boron compared with the target material. Nitrogen provided by the ion beam is incorporated in the film and bonded to boron and carbon. Heating of the substrate enhances the incorporation of nitrogen and influences the bonding configuration and crystalline structure of the film as well.

Keywords: Boron carbon nitride thin film; Reactive pulsed laser deposition; Ion beam assisted deposition; Nitrogen ion beam; Kaufman ion gun

1. Introduction

Materials in the B–C–N system continue to be an attractive research topic because of the interesting properties of this system and have been investigated extensively in recent years. While diamond is known as the hardest material, cubic phase BN (c-BN) is next to diamond in hardness. B_4C is the third hardest material, even harder than diamond and c-BN at high temperatures over 1100 °C. Carbon nitride (CN_x) is currently used as the protective overcoat material. Ternary BCN compounds may combine the advantages of C, BN and B_4C with high hardness, chemical stability at high temperatures and other excellent properties. BCN compounds are interesting in both the cubic (c-BCN) and hexagonal (h-BCN) structures. BCN compounds with cubic structures are expected to be superhard materials combining the properties of diamond and c-BN [1,2], whereas those with hexagonal structures are expected to be semiconducting with various band gap energies depending on the composition and structure [3,4]. Because of these attractive properties and potential applications, the BCN compounds have been investigated theoretically [2,5,6] and experimentally [7–9].

There have been many reports on the preparation of materials in the B–C–N system. Various techniques have been attempted to deposit the ternary BCN thin films, such as chemical vapor deposition [10–14], magnetron sputtering [15–17] and pulsed laser deposition. Using a disk combining together two semi-disks, one of h-BN and one of graphite, as target, Perrone et al. deposited BCN thin films by pulsed laser deposition in nitrogen gas ambient [18]. Wada et al. deposited BCN thin films from a hot-pressed BCN target consisting of graphite and h-BN powders in a 1:1 ratio [19]. The target used by Dinescu et al. for BCN film deposition was also a half graphite and half h-BN disk [20]. We have previously demonstrated that BCN thin films could be synthesized from a B_4C target by means of nitrogen plasma assisted pulsed laser deposition [21]. Here we report on an alternative approach for the synthesis of BCN thin films. Instead of nitrogen plasma, a nitrogen ion beam was used as the reactive nitrogen source to assist reactive deposition of BCN

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thin films from B_4C ablation. In the environment and with the assistance of the nitrogen ion beam, amorphous and nanocrystalline BCN thin films with B–C–N atomic hybridization were synthesized. It is found that the ablation of the B_4C target results in the deposition of a film with B:C ratio about 3:1, and nitrogen from the ion beam is efficiently incorporated in the film and bonded to boron and carbon.

2. Experimental details

BCN films were prepared by pulsed laser ablation of a sintered B_4C target with nitrogen ion beam assistance. Fig. 1 shows schematically the experimental arrangement for film deposition. Target ablation and film deposition were performed in a spherical stainless steel deposition chamber with a diameter of 450 cm. A Kaufman ion gun used to generate nitrogen ion beam was directly attached to the deposition chamber. After the system was evacuated to a bass pressure lower than 1×10^{-4} Pa, pure (>99.9999%) nitrogen gas was fed into the Kaufman ion gun at a pressure of 2×10^{-2} Pa as the working gas. The working gas was excited and a nitrogen ion beam was generated by the ion gun. The ion beam was then introduced into the deposition chamber both as an environment in which target ablation was performed and as an assistance source for film deposition. The energy of the nitrogen ion beam was kept at 100 eV after preliminary trials. The diameter of the ion beam was about 70 mm. The ion beam was incident on the substrate at an angle of 45°. Laser pulses (wavelength = 532 nm; pulse duration = 5 ns) from a frequency-doubled Nd:YAG laser (Continuum, Surelite II-10) were used to ablate the B_4C target at an incident angle of 45° after being focused by an f-400 mm spherical lens. The laser worked at a repetition rate of 10 Hz. The laser fluence on the target surface was set at about 5 J/cm^2, hence with a power density of about 1×10^9 W/cm^2, as compared with Ref. [21] where a Quantel YG580 Nd:YAG laser was used with a longer pulse duration of 15 ns and a less power density of about 3.3×10^8 W/cm^2. The target was kept rotating when being ablated by the laser pulses to prevent crater formation. Besides B_4C, the target material employed also contained about 5% oxygen. Polished (100)-oriented Si (electrical resistivity ~ 5 Ω cm) wafers were used as the substrates after being chemically cleaned. The distance between the target and the substrate was 50 mm. Target ablation was performed in the environment of the nitrogen ion beam. The ablation plume expanded through the nitrogen ion beam and deposited on the substrate. The substrate was held at ambient temperature (RT) that was slightly heated due to the bombardment by the nitrogen ion beam or at elevated temperatures up to 600 °C. For comparison, we also prepared some films in vacuum (lower than 1×10^{-4} Pa) or in low-pressure (2×10^{-2} Pa) nitrogen gas which was not discharge excited, i.e. without ion beam assistance, at room temperature (RT). All the films were prepared for 60 min.

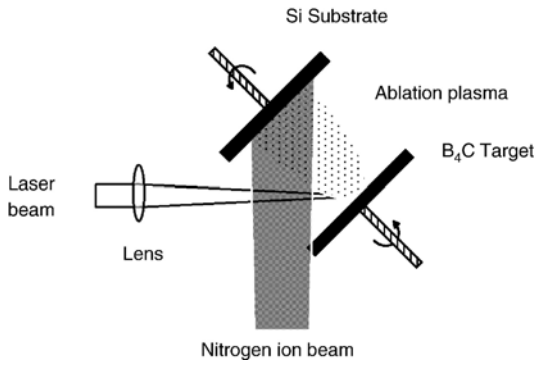

Fig. 1. Schematic diagram of the experimental arrangement for nitrogen ion beam assisted pulsed laser deposition of BCN thin films.

The prepared films were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). A VG Scientific MicroLab 310-F spectrometer was employed by using mono-chromatized Al Kα radiation (1486.6 eV) to excite photoelectrons from the samples for composition determination and chemical bond characterization. With a Nicolet Magna-IR 550-II instrument, FTIR measurement was carried out to determine the infrared vibration properties of the prepared films. The crystalline structure of the BCN films deposited with nitrogen ion beam assistance was characterized by transmission electron microscopy (TEM). For preparing TEM samples, the films were scratched off from the substrates, floated in water, and then collected on carbon grid for TEM observation. TEM was performed with an electron energy of 200 keV using a JEOL 100CX transmission electron microscope.

We also recorded the optical emission spectra of the luminous plume generated by ablating the B_4C target during film preparation to analyze the composition of the plume. The plume was imaged onto the entrance slit of a 500-mm focal length spectrometer (Acton Research, Spectra Pro 500i). The resolved emissions were detected and recorded by a gated intensified charge coupled device (ICCD) (Andor Technology, iStar DH720) which was attached on the exit port of the spectrometer.

3. Results and discussion

The surface of all films shows smooth appearance and good adhesion to the Si substrates prepared whether with ion beam assistance, or without ion beam assistance in vacuum or in low-pressure nitrogen ambient. From α-step measurement, the film thickness was determined and the deposition rate was derived. For the films prepared with ion beam assistance at RT and 600 °C, the thickness is 550 nm and 540 nm, respectively, both with a deposition rate of about 9 nm/min. Without ion beam assistance, we got films with a thickness of about 900 nm for 60-minute deposition whether in vacuum or in 2×10^{-2} Pa N_2. The deposition rate was thus derived to be about 15 nm/min. The lower deposition rate of ion beam assisted deposition is mostly due to the re-sputtering of the growing film by the ion beam.

The composition of the prepared films was determined from XPS measurement after sputter cleaning of the surface. Table 1 summarizes the composition of the prepared films. The B:C atomic ratio was determined to be approximately 3:1 for all the