

Electron-assisted deposition of cubic boron nitride by r.f. magnetron sputtering

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Abstract

Cubic boron nitride (cBN) has been deposited on silicon (100) substrates by means of radio frequency (r.f.) magnetron sputtering in nitrogen using a hexagonal boron nitride target with the assistance of a simultaneous electron bombardment of the growing surface. Unlike most thin-film deposition processes for cBN, intentional bombardment of the growing surface by ion beams within specific ranges in energy and flux is not required for this process to achieve high-purity cBN films. Fourier transform infra-red (FTIR) spectra of cBN films show a strong absorption band around 1070 cm^{-1} . With electrons bombarding the growing surface at a current density of 140 mA cm^{-2} or higher, pure (according to FTIR spectra) cBN films are deposited on silicon substrates at temperatures above 750°C . The effects of electron current density and nitrogen gas pressure on the synthesis of cBN films will be discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cubic boron nitride; Electron; Ion; r.f. magnetron sputtering

1. Introduction

Boron nitride is isoelectronic with carbon. The hexagonal boron nitride (hBN) is sp^2 -bonded and structurally analogous to graphite. Cubic boron nitride (cBN) is sp^3 -bonded and is physically and structurally similar to diamond [1]. Cubic BN is of great interest because of its excellent properties, such as high hardness, thermal conductivity, and wear resistance. Its high thermal stability in the presence of oxygen and chemical inertness with ferrous materials are also desirable for applications requiring exposure of the coatings to high temperature and highly oxidizing environments as well as for the cutting of ferrous alloys. Ion plating [2], ion-assisted pulsed laser deposition (PLD) [3], r.f. sputtering [4], plasma-enhanced chemical vapor deposition (PECVD) [5] and electron-enhanced CVD [6] have been reported to deposit BN films containing varied fractions of cBN phase. These deposition techniques rely on either ion bombardment with the substrate being negatively biased or electron assistance with the substrate being positively biased. Although boron nitride films containing some

fraction of cubic phase boron nitride have been achieved by these techniques, very few techniques have been reported to produce pure or near 100% cubic phase boron nitride films. Most of the techniques that produce high-purity cubic phase boron nitride films require the use of energetic ion bombardment. Ion flux and energy were reported to be the key parameters for the success of ion-assisted cBN deposition. The existence of a range of ion energy and flux in which crystalline cBN grows has been reported by Messier et al. [7]. As a result of energetic ion bombardment, cubic boron nitride films do not have grain sizes as large as scientists and technologists desire. All the cubic boron nitride films deposited with the assistance of ion bombardment are nanocrystalline. We have, therefore, focused our efforts on thin-film deposition techniques without energetic ion bombardment of the growing surface.

2. Experimental

In this work, electrons instead of ions bombard the growing substrate surface during the cBN deposition. Fig. 1 shows the schematic diagram of the electron-assisted r.f. magnetron sputtering apparatus. Silicon (100) substrates were etched in HF solution to remove

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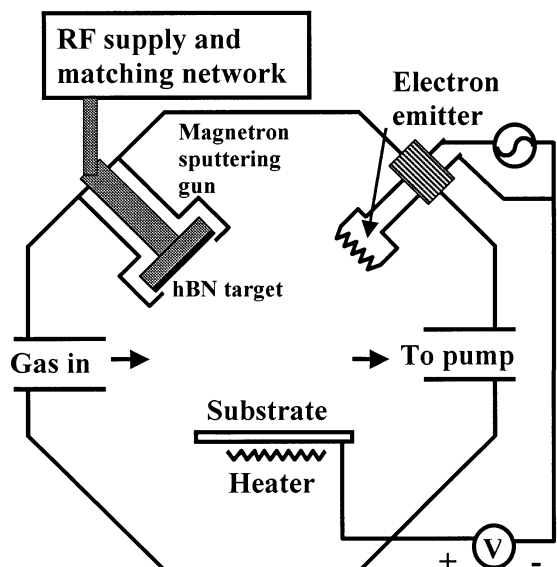


Fig. 1. Schematic diagram of an electron-assisted r.f. magnetron sputtering apparatus.

the native oxide before the deposition. The distance between the substrate and the hBN target was about 5 cm. A remote hot tungsten filament located outside the r.f. magnetron discharge zone was biased to a negative potential relative to the substrate by a d.c. power supply. By controlling the power to the filament and the positive biasing voltage at the substrate with respect to the hot filament, the electron current was adjusted. A ceramic ring was placed on the top of the silicon substrate as shown in Fig. 2 so that the electron current would flow through the silicon substrate, the conductive graphite substrate holder, and the conductive rod and then return to the power supply. The electron current density was calculated by dividing the total electron current by the area of the opening of the

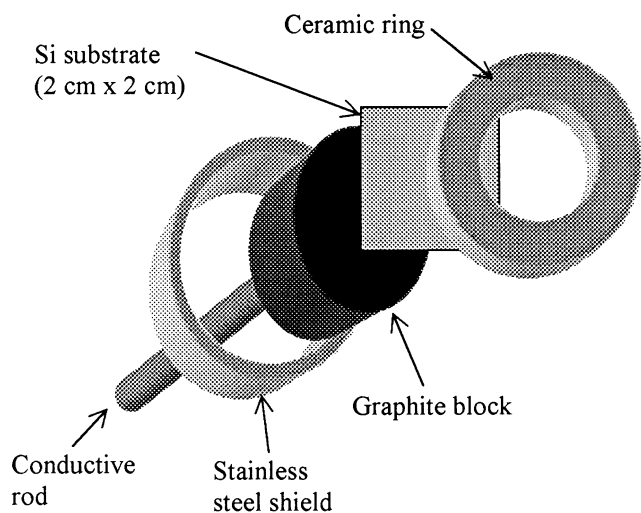


Fig. 2. Schematic diagram of the substrate holder.

Table 1

Experimental parameters for the deposition of BN films

r.f. power	150–220 W
Substrate temperature	700–900°C
N ₂ flow rate	3–20 sccm
Pressure	5–55 mTorr
Electron current density	0–400 mA cm ⁻²
Substrate bias voltage w.r.t. the hot filament	0 to +300 V

ceramic ring. Table 1 lists the major experimental parameters. The film thickness was measured by means of Alpha-Step-200. The typical film thickness was 90–350 nm, corresponding to a growth rate of 5–15 nm min⁻¹.

3. Results

Boron nitride (BN) films were characterized using the microscopic FTIR spectroscopy. Fig. 3 shows the infra-red absorption spectra for BN films sputter deposited on silicon in nitrogen plasma with simultaneous electron bombardment at different electron current densities. Fig. 3a shows the spectrum for a BN film deposited with 140 mA cm⁻² electron current density. A strong IR absorption band near 1070 cm⁻¹ corresponding to the cBN reststrahlen band can be clearly seen on the spectrum [8]. Fig. 3c shows a hBN film deposited with an electron current density of

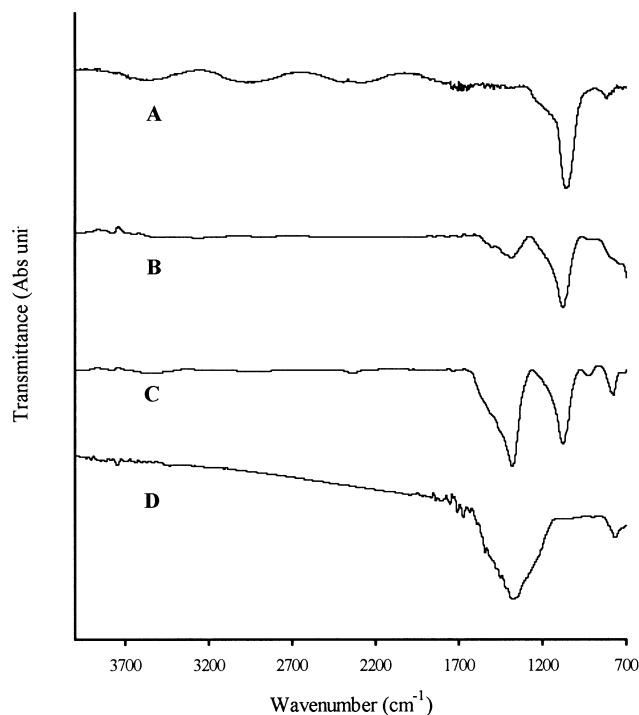


Fig. 3. FTIR spectra of BN films deposited in N₂ with (a) 140 mA cm⁻², (b) 75 mA cm⁻², and (c) 25 mA cm⁻² electron current density, and (d) no electron bombardment.

25 mA cm⁻². Two hBN absorption peaks corresponding to the in-plane B–N–B stretching near 1380 cm⁻¹ and the out-of-plane B–N–B bending near 780 cm⁻¹, respectively, were detected [4]. Fig. 3b shows the spectrum of a film deposited with electron bombardment at 75 mA cm⁻² electron current density. This film contains mixed phases of cBN and hBN. Films deposited without being bombarded by electrons do not include an absorption band corresponding to cBN in their FTIR spectra (Fig. 3d).

Fig. 4 shows the dependence of the fraction of the cBN phase in the deposited BN films on the current density of the electron bombardment. The fraction of cBN phase increases with the electron current density. When the electron current density exceeds 140 mA cm⁻², nearly 100% cBN is obtained. Unlike ion-assisted cBN deposition processes, a rather wide process parameter window exists for the electron-assisted deposition of cBN films.

Fig. 5 shows the relationship between the N₂ pressure and the content of the cBN phase in the BN films. At a pressure below 5 mTorr, the sputtering rate drops quickly. The thickness of cBN films thus decreases with the pressure. At a N₂ pressure above 30 mTorr, the cBN content begins to decrease with increasing pressure. The optimal pressure window for sputter deposition of cBN is between 7 and 20 mTorr under our experimental conditions.

Although the momentum transfer to the growing surface by the light electrons is far less significant than that by ion bombardment, the energy transfer by the electron bombardment to the substrate is rapid and very efficient. At a current density of 45 mA cm⁻², electron bombardment heats the substrate to above 850°C quickly during the deposition according to a dual color

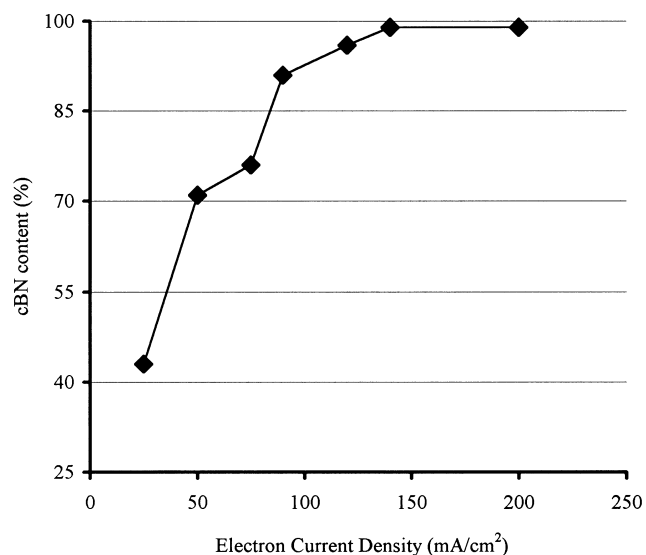


Fig. 4. Dependence of the cBN fraction in the deposited BN films on the electron current density.

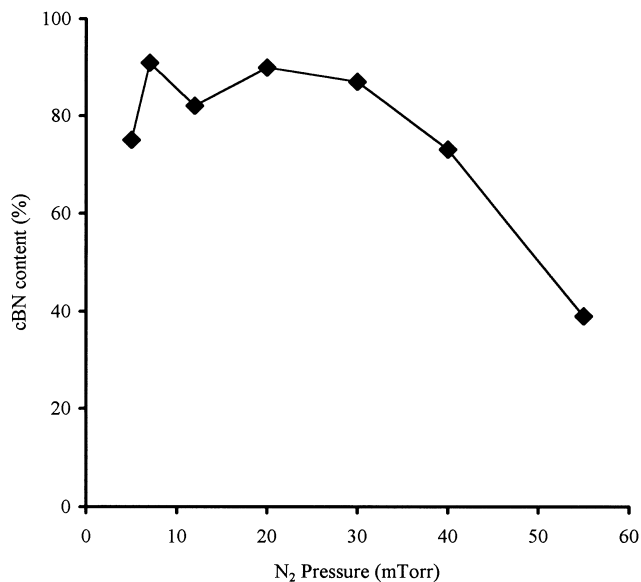


Fig. 5. Dependence of the cBN fraction in the deposited BN films on N₂ gas pressure.

optical pyrometer. For experiments carried out with lower electron current densities, an additional heating lamp was used to maintain the substrate temperature between 800 and 900°C. To explore the effects of substrate temperature on the deposition of cBN, several films were deposited without additional lamp heating. In those cases, the substrate temperature ramps up from room temperature to about 700°C quickly and then continues to increase slowly to above 800°C during the experiments. BN films deposited at lower substrate temperatures contain less cubic phase BN.

4. Discussion

There are two popular models for the roles played by energetic particles (for example, ions and electrons) bombarding the substrate during the BN film growth. The thermal spike model, introduced by Seitz and Koehler [9], treats a bombarding particle as an energy carrier. As the particle collides with the growing surface, it creates an atomic-scale, high-energy region, where the conditions are similar to that for high-pressure, high-temperature synthesis of cBN. The second model emphasizes the momentum transfer during the collision between the incoming particles and the growing surface [10]. The model predicts that the bombarding particles hammer the growing surface through the momentum transfer followed by a series of atomic displacement. For the role of ion bombardment in the cBN formation, Messier et al. [7] have reported that the momentum transfer model is consistent with their results. However, in case of electron bombardment, the momentum sharing between the electrons and the surface atoms is

inefficient due to the large mismatch between the mass of an electron and the mass of a surface atom. Although it is considered less likely for electron bombardment to create so-called ‘thermal spikes’ like ion bombardment does, the amount of energy transferred by the large flux of electrons to the growing surface of the cBN films contributes significantly in some way to the formation of the cubic phase. The electron flux bombarding the growing surface of the BN films not only deposits energy into the growing cBN film but also greatly enhances the concentration of radicals that are critical to the cBN growth near the growing surface by electron impact dissociation and excitation of gas particles.

5. Conclusion

In summary, boron nitride films with corresponding FTIR spectra indicating a high purity or nearly 100% cubic phase content have been deposited by r.f. magnetron sputtering in nitrogen with simultaneous electron bombardment. With electron bombardment at a current density of more than 140 mA cm^{-2} , high-purity cBN

films were obtained on silicon at the substrate temperature above 750°C . Further studies on the effects of gas mixtures, gas pressure, electron energy, substrate materials, and deposition rate on the content of cBN in sputter deposited BN films are being conducted.

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