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Stress reduction in nanocomposite coatings consisting of hexagonal and cubic boron nitride

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Abstract

Cubic boron nitride (c-BN) can be produced by PVD and CVD techniques by intensive ion bombardment leading to highly stressed films. To overcome the problem of highly stressed films, nanocomposite coatings consisting of hexagonal and cubic boron nitride (h-/c-BN) phases have been successfully deposited by reactive rf magnetron sputtering from an h-BN target at a substrate temperature of 350 °C and a dc substrate bias of −700 V close to the resputtering limit. The morphology of the films was characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction/reflectivity (XRD/XRR) and high-resolution transmission electron microscopy (HRTEM). At low ion energy levels corresponding to low substrate bias values of up to ≈200 V pure h-BN was deposited. Higher ion energies led to a strong increase of the c-BN content as well as the residual stress in the films reaching their maximum at ≈−300 V substrate bias before decreasing again. Both the c-BN content and the residual stress showed qualitatively the same behaviour with a steeper drop of the residual stress between the maximum and the resputter limit. HRTEM investigation of the films with the maximum densification deposited at a substrate bias of ≈−300 V showed an h-BN interlayer growing on the Si substrate with the basal planes perpendicular to the substrate surface on which then almost pure c-BN was identified. The density of these coatings was 3.5 g/cm^3 and the residual stress was determined to ≈−29 GPa. Depositing boron nitride at a substrate bias of −700 V, these films comprised a hexagonal interlayer and c-BN in an h-BN matrix on top showing a lower density of 3.2 g/cm^3 and a significantly reduced residual stress of −9 GPa. A further reduction of the residual stress can be achieved by a following heat treatment at 900 °C for 2 h resulting in a value of ≈−3 GPa.

Keywords: Cubic boron nitride; Stress reduction; FTIR; TEM; Nanocomposite

1. Introduction

Boron nitride exists in its equilibrium state either as the sp^2-bonded hexagonal (h-BN) or sp^3-bonded cubic (c-BN) modification, depending on temperature and pressure conditions. Intensive studies have been addressed recently to the thin film synthesis of cubic boron nitride by physical vapor deposition (PVD) and plasma-assisted chemical vapor deposition (PA-CVD) techniques [1–6], inspired by the well-known outstanding properties of the bulk material, such as high hardness, chemical inertness against ferrous metals and oxygen at high temperatures [7] and excellent thermal conductivity, high electrical resistivity and optical transparency in the visible and infrared range. These remarkable properties make c-BN a promising candidate for a wide range of applications, as protective coatings for cutting tools [8], functional material for high-temperature, high-power optical and electronic devices [9]. As a band-gap semiconductor, c-BN can be either, in contrast to diamond, p-type doped or n-type doped [10–12]. Cubic boron nitride have been successfully grown by ion-assisted PVD and PA-CVD methods, in which an adequate ion impact is considered to be indispensable for the formation [13]. This, however, results in lattice defects, binding deformation, and hence, large levels of bi-axial stress induced by strong impact energies resulting in delamination of films with a thickness above a certain value, thwarting the expected applications of this material. Therefore, it is of great importance to minimize the deposition energy such that the generation of excessive defects can be largely avoided, while, on the other hand, the cubic phase fraction should be kept as high as possible. Also several other possibilities to deposit c-BN films

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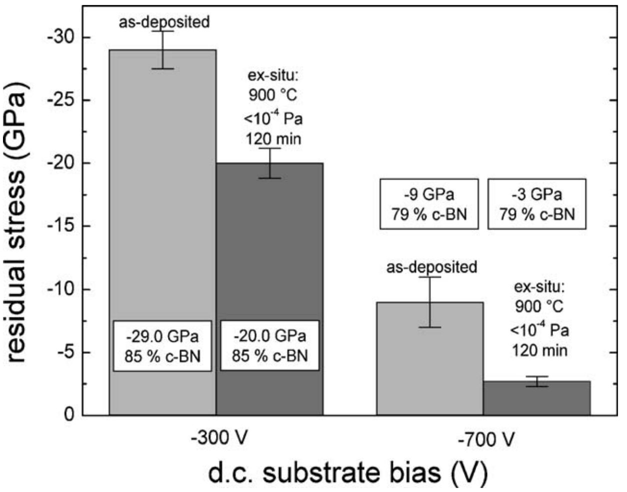

Fig. 1. Comparison of the c-BN fraction and film stress of the as-deposited and post-annealed films deposited at $U_b = -300$ V and $U_b = -700$ V.

with increase the adhesion, such as post-deposition ion implantation, buffer layers, etc. [14–17], have been performed, but with limited success. More efforts with regard to this topic are obviously necessary. In this work, deposition of boron nitride at high ion energies close to the resputter limit as a promising concept for stress reduction is discussed.

2. Experimental details

2.1. Film deposition

In the present work, boron nitride films were deposited by unbalanced radio-frequency (rf) magnetron sputtering (13.56 MHz) with a hot-pressed hexagonal boron nitride target of 99.999% in purity, 76 mm in diameter and 6 mm in thickness. The distance between the target and the substrates was 120 mm and the base pressure before deposition was lower than 5×10^{-4} Pa. The substrates were biased using a direct current (dc) power supply. The rf power applied to the target was $P = 500$ W for the sample biased to $U_b = -300$ V and $P = 425$ W for the sample biased to $U_b = -700$ V. Due to progressive target erosion, the target power had to be changed in order to keep the ion flux ratio, with respect to the film-forming particles, constant. Double-sided polished, (100)-oriented single-crystalline silicon (B-doped, 1–30 Ω cm, 350 μm thick) was used as substrate material. Prior to deposition, the substrates were ultrasonically cleaned in isopropanol and then in acetone, for 15 min each and further sputtered-clean in an argon discharge and a dc substrate bias of $U_b = -500$ V at a pressure of 0.2 Pa (60 cm) for 30 min. The film deposition was carried out in a mixed working gas consisting of 90% argon and 10% nitrogen and a total pressure of 0.3 Pa at a substrate temperature of 350 °C. The deposited films were post-annealed at 900 °C for 120 min at a pressure $< 10^{-4}$ Pa.

2.2. Film characterization

The phase composition of the films was quantified by Fourier-transform infrared spectroscopy (FTIR) in transmission mode. For h-BN, the infrared spectra mainly show two absorption bands at 817 and 1375 cm^{-1}, respectively. The first one is due to out-of-plane B–N–B bending, and the latter results from the in-plane B–N stretching of the hexagonal lattice [18]. The cubic structure can be identified by its characteristic transverse optical (TO) mode near to 1056 cm^{-1} [18]. The peak position of the TO absorption mode can, however, be affected by the stress level of the deposited films. With increasing stress, the position is shifted to higher wave numbers for constant ratio $B/N = 1$ [14] and typically lies between 1070 and 1100 cm^{-1}, depending on the growth parameter. The volume fraction of the cubic phase can be determined from the intensity ratio of the c-BN TO and the sum of c-BN TO and the h-BN in-plane stretching absorption bands [9].

X-ray reflectivity was used to determine the density of the films by fitting the measured reflectivity curve. A Tecnai G^2 TF 20 UT equipped with a field emission gun (FEG) operated at 200 kV for a point resolution of 1.9 Å was used for nanostructural investigations. The film thickness was evaluated by a surface profilometer (KLA Tencor P-10). The surface profilometer was also used to measure the radius of curvature of the silicon substrates before and after the deposition determining the film stress using the well-known Stoney equation [19]. In addition, the position of the c-BN Reststrahlen band was also used as an auxiliary measurement for the film stress.

3. Results and discussions

The new coating concept for the production of low-stress boron nitride films with a sufficient amount of the cubic phase, presented in this work, is based on the fact of stress reduction, resulting from surface relaxation and diffusion, when the ion energies exceeds the value necessary for a maximum densification [15]. The maximum densification for c-BN is reached at a substrate bias of −300 V containing 85% of the cubic phase exhibiting an extremely high compressive stress of −29 GPa, as published in an earlier work [20]. To achieve a reasonable stress relaxation, the boron nitride films were deposited near the

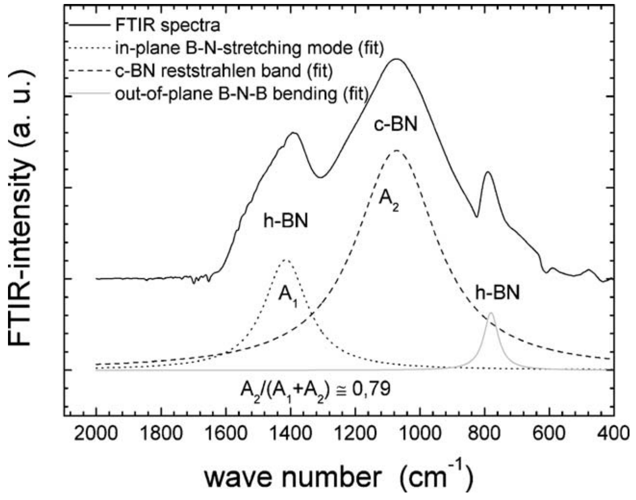

Fig. 2. FTIR spectra and the simulated Lorentz profiles of the as-deposited boron nitride film; $P = 425$ W, $U_b = -700$ V.