

How to exploit ion-induced stress relaxation to grow thick c-BN films*

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Abstract: A recently developed procedure is reviewed allowing thick (>1 μm), high-quality c-BN films (>80 % c-BN) to be grown. It is based on the observation that compressive stress inevitably present in such films can be released by medium-energy (some hundred keV) ion irradiation without destroying the cubic phase.

INTRODUCTION

When talking about cubic boron nitride (c-BN), the property most widely known is its hardness, which is second after diamond. Additional to hardness, there are still other features suggesting such a comparison to diamond. One certainly is the structural similarity and analogy of the carbon modifications diamond and graphite to the cubic and hexagonal (h-) phases of BN, the latter being also addressed as “white graphite”. Also, with respect to heat conductivity, c-BN is only slightly inferior to diamond [13 vs. 20 W/(cmK)]. Furthermore, if it comes to dopability or chemical resistance against oxidation or carbide formation with Fe, Ni, or Co, c-BN is even superior to diamond, offering p- and n-doping and chemical stability up to 1600 K. As a consequence, c-BN offers a high potential for various applications, especially if corresponding sufficiently thick films would be available. That’s where the problems begin. Despite its promising aspects, the technological know-how to prepare c-BN films is well behind that of growing diamond films by, for example, different variants of plasma CVD techniques. This has to do with the fact that independent of preparational details a necessary condition to obtain c-BN films is low-energy ion bombardment during their growth. Such a bombardment allows for a densification of a film during its deposition, which probably is the most important effect to obtain the dense cubic phase [1,2]. Thus, from a more fundamental point of view, either direct ion beam deposition [3] or dual beam techniques [4] appear especially appropriate allowing good control of the fluxes and energies of both the deposited and bombarding species. Other techniques applied so far to prepare c-BN films include bias sputtering [5,6] and beam-assisted evaporation [7,8], as well as plasma-enhanced deposition [9]. A recent review on various preparation methods is given in [10].

There are some more features characteristic of c-BN films. The standard samples are nanocrystalline (typical grain size 5 nm) and when grown on top of (001)Si wafers, the most widely used substrate, a complicated sequence of layers is observed, starting with an amorphous layer right at the substrate interface followed by a randomly oriented h-BN layer topped by strongly oriented h-BN with the hexagonal basal planes perpendicular to the substrate. This highly textured h-BN layer seems to be the starting point for the growth of preferentially (111) oriented c-BN [11,12]. Another general feature of c-BN films, which is closely related to the ion bombardment during their growth [6,13], is the large

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compressive stress (typically between 5 and 10 GPa) leading to serious problems with adhesion. This stress continuously builds up with increasing film thickness until eventually the film delaminates from the substrate. Thus, to avoid this catastrophic event, the total film thickness has to stay below a certain limit depending on the deposition details as well as on the adhesion, but typically being of the order of some hundred nanometers, which is too small for many applications.

In the following, a procedure will be described how to avoid delamination exploiting the possibility to release the compressive stress of c-BN films by irradiating them with inert ions of some hundred keV without destroying the cubic phase.

EXPERIMENTAL

The c-BN films were prepared onto (001)Si substrates by ion beam-assisted sputter deposition (IBAD) at 420 °C using two Kaufmann sources. Elemental boron (99.9 %) was sputter-eroded using 1.5 keV Ar⁺ ions from the first source, while the growing film was simultaneously irradiated with a mixture of argon and nitrogen ions (ion energy 280 eV) resulting in a deposition rate of 1.7 nm/min. The cleanliness at the surface of the individual layers in the as-prepared state as well as before any additional deposition step was checked by *in situ* Auger electron spectroscopy (AES) confirming also the stoichiometry within the near-surface region of the sample. Additional *in situ* characterization is performed after each growth step applying electron energy loss spectroscopy in reflexion (REELS) with a primary electron energy of 1.5 keV. This method has proven especially useful to distinguish the cubic from the hexagonal BN phase by monitoring the corresponding characteristic plasmon losses [14,15]. Rutherford back-scattering (RBS) has been employed to check for any contaminations due to heavier elements within the films. Transmission infrared spectroscopy (FTIR) was applied to estimate the volume fraction of the cubic phase and to analyze the position of the c-BN TO mode which can be taken—within certain limits—as a measure for the compressive stress. To corroborate these FTIR stress measurements especially in the case of ion-induced stress relief, additional direct stress measurements were accomplished by determining the stress-induced substrate bending using Newton interferometry.

As will be shown below, an important role to reduce the film stress is played by ion bombardment. For this purpose, inert ions, in the present work exclusively Ar⁺, with an incoming energy of 350 keV are used as projectiles. The beam is scanned horizontally as well as vertically in order to obtain a homogeneous irradiation. For reasons which will become clear below, the ion fluences Φ are restricted to below 10¹⁵ cm⁻² with typical currents of the order of μ A.

RESULTS AND DISCUSSION

The method we have developed to overcome the above-mentioned stress problems is based on the experimental finding, that medium-energy (some hundred keV) ion bombardment can be used to significantly reduce compressive stresses without destroying the cubic phase. Taking advantage of this observation, thick films of c-BN can be grown by the repeated deposition of thin top-layers (180 nm) followed by an *ex situ* irradiation step with, e.g., 350 keV Ar⁺ ions. To make this sequential procedure clear, a scheme of the different steps involved is presented in Fig. 1.

As has been demonstrated in [16], to guarantee that the ion-bombarded c-BN phase does not transform into h-BN, the total ion fluence must be limited to below 10¹⁵ cm⁻² corresponding to approximately 0.5 displacements per target atom (dpa) under the above irradiation conditions. Two remarks are important. First, it turned out that the cleaning step after the *ex situ* ion treatment as indicated in Fig. 1 is essential to obtain an undisturbed immediate growth of c-BN on top of c-BN without an additional h-BN interlayer. This fact has been proven recently by high-resolution transmission electron microscopy (HRTEM) [12]. In the context of cleaning, the possibility to control the surface *in situ* by Auger and REELS was found especially useful. The reason for this is the inevitable presence of carbon and oxygen contaminants due to any *ex situ* ion bombardment, which have to be completely

removed by presputtering. The second remark is related to stress. It was observed that each time a layer of c-BN was grown on top of a clean, stress-relaxed c-BN film, compressive stress builds up again. This points to ion-induced defects during film growth as causing the stress.

Applying the procedure described in Fig. 1, we were able to prepare thick ($>1.3\ \mu\text{m}$), high-quality c-BN films ($>80\%$ c-BN). Since these films, despite their thickness, exhibit stress values well below 1 GPa, they are mechanically stable even under ambient conditions (our first thick film has been stored under ambient since more than 12 months and it still shows no indication of a deterioration).

Of course, for applications it is necessary to prove the expected exceptional hardness of the c-BN films. In the case of thick films, hardness measurements can be safely performed by nanoindentation without the problem of the substrate severely influencing the results. An example is shown in Fig. 2, where the lateral hardness distribution of a $1.3\text{-}\mu\text{m}$ -thick c-BN film is presented together with the profile of the ion beam bombarding the growing film (nominal diameter 3 cm). Clearly, within the area of

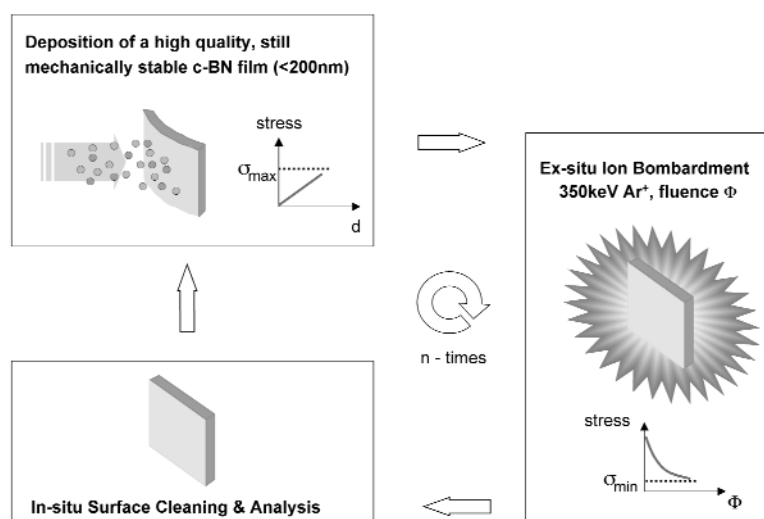


Fig. 1 Scheme of the sequential procedure to grow thick mechanically stable c-BN films.

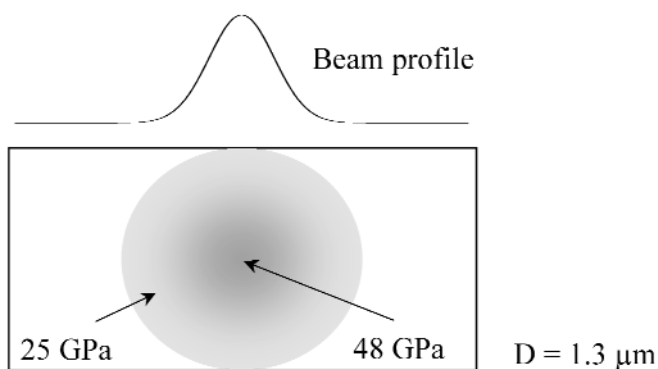


Fig. 2 Lateral hardness profile of a $1.3\text{-}\mu\text{m}$ -thick c-BN film together with the profile of the beam bombarding the film during its growth.

optimized ion bombardment during film growth, the obtained hardness of 48 GPa confirms the expected ultrahardness, while the outer area of lower ion flux exhibits a correspondingly smaller hardness of still 25 GPa.

To summarize, the significant progress made in preparing high-quality stress-relaxed c-BN films either by applying the procedure described above or, as has been reported quite recently [17], by relying on high temperature and high rate deposition processes, allows optimism with respect to future applications of this attractive material.

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REFERENCES

1. K. H. Müller. *J. Appl. Phys.* **58**, 2803 (1986).
2. J. Robertson. *Diam. Relat. Mater.* **5**, 519 (1996).
3. H. Hofsaess, C. Ronning, U. Griesmeier, M. Gross, S. Reinke, M. Kuhr. *Appl. Phys. Lett.* **67**, 46 (1995).
4. P. Ziemann, H.-G. Boyen, N. Deyneka, D. Schwertberger, P. Widmayer. *Adv. Solid State Phys.* **40**, 424 (2000).
5. M. Ben el Mekki, M. A. Djouadi, V. Mortet, E. Guiot, N. Mestres. *Thin Solid Films* **355–356**, 89 (1999).
6. W. Fukarek, C. Fitz, A. Kolitsch, W. Möller. *Mat. Sci. Forum* **437–349**, 256 (2000).
7. H. Wituschek, H. Stopka-Ebler, G. K. Wolf. *Surf. Coat. Technol.* **74**, 1 (1995).
8. J. Tian, L. Xia, X. Ma, Y. Sun, E. Byon, S. H. Lee, S. R. Lee. *Thin Solid Films* **355–356**, 229 (1999).
9. A. Lunk, P. Bachem, P. Scheible, L. Ulrich. *Appl. Phys. A* **72**, 557 (2001).
10. W. Kulisch. *Deposition of Superhard Diamond-like Materials*, Springer Tracts on Modern Physics, Heidelberg, Berlin (1999).
11. D. J. Kester, A. K. S. Ailey, D. J. Lichtenwalner, R. F. Davis. *J. Vac. Sci. Technol. A* **12**, 3074 (1994).
12. H.-G. Boyen, N. Deyneka, P. Ziemann, F. Banhart. *Diamond Rel. Mat.* **11**, 38 (2002).
13. G. Sene, D. Bouchier, S. Ilias, M. A. Djouadi, J. Pascallon, V. Stambouli, P. Moller, G. Hug. *Diam. Relat. Mater.* **5**, 530 (1996).
14. P. Widmayer, P. Ziemann, H.-G. Boyen. *Diamond Rel. Mat.* **7**, 385 (1998).
15. P. Widmayer, H.-G. Boyen, P. Ziemann, P. Reinke, P. Oelhafen. *Phys. Rev. B* **59**, 5233 (1999).
16. H.-G. Boyen, P. Widmayer, D. Schwertberger, N. Deyneka, P. Ziemann. *Appl. Phys. Lett.* **76**, 709 (2000).
17. W. J. Zhang and S. Matsumoto. *Appl. Phys. A* **71**, 469 (2000).