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Thresholds for the phase formation of cubic boron nitride thin films

H. Hofsäss, H. Feldermann, M. Sebastian, and C. Ronning
Fakultät für Physik, Universität Konstanz, Postfach 5560, D-78434 Konstanz, Germany

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We introduce a phase diagram for boron nitride film growth. It is based on studies of the influence of the ion energy and substrate temperature on the phase formation using mass-selected ion-beam deposition of B^+ and N^+ ions. For the formation of the cubic phase we find threshold values of 125 eV for the ion energy and 150 °C for the substrate temperature. Furthermore, we find a characteristic ion energy and substrate temperature dependence of the compressive stress, yielding low stress values for high energies and/or temperatures. *c*-BN nucleation and growth is attributed to a subsurface process qualitatively described by the subplantation model. [S0163-1829(97)05519-7]

Regarding mechanical and electronic applications, cubic boron nitride (*c*-BN) may leave diamond far behind, because it is chemically inert against iron and oxygen at high temperatures,[1] and because it can be *p* and *n* type doped.[2] So far, low pressure synthesis of *c*-BN thin films is only possible with a variety of ion-assisted physical and chemical vapor deposition techniques.[3] These films are usually nanocrystalline, with a textured *h*-BN interface layer. Attempts to grow *c*-BN by chemical processes alone have failed so far.[4] It is therefore generally accepted that ion bombardment is necessary for *c*-BN nucleation and growth; however, a satisfactory understanding of the underlying mechanisms is still lacking. An unwanted side effect is the ion-induced high compressive film stress, which limits the achievable film thickness to only a few hundred nm, insufficient for most tribological applications. The growth of low-stress *c*-BN films is therefore highly desirable.

The *c*-BN growth conditions for ion-beam-assisted deposition (IBAD) were investigated in systematic studies.[3,5] With IBAD, films are usually grown using evaporated boron atoms and additional ion bombardment, typically with a mixture of ${N_2}^+$, N^+, and Ar^+ ions. In addition, the ion angle of incidence may vary for different deposition systems. IBAD growth is therefore rather complex, and a variety of different processes such as condensation and thermal desorption, implantation of ions, recoil implantation of atoms deposited on the surface, and sputtering have to be considered. The *c*-BN growth regime is thus a complex function of three parameters: substrate temperature, ion energy, and the flux ratio of ions to neutral (boron) atoms.[3,5] Furthermore, *c*-BN growth takes place at conditions close to the resputter limit due to the intense heavy ion bombardment. Kester *et al.* introduced the average momentum transferred to the boron atoms deposited on the surface as a more universal parameter to characterize *c*-BN growth.[5] Sputter yield and nuclear stopping are quantities which depend on the square root of the ion energy (or the ion momentum) to a first approximation. On the other hand, nuclear stopping itself determines the range of low-energy ions in matter, the energy transfer to recoil atoms, and the deposited energy density. As a consequence, several models for *c*-BN nucleation and growth were developed, basing on selective sputtering of *h*-BN and *c*-BN,[3] static stress induced by the ion bombardment,[6] dynamic stress evolution,[7] or subplantation.[8] The difficulty to interpret the existing *c*-BN growth data within the one or the other model has to do with the complex deposition conditions outlined above.

Recently, we have shown that *c*-BN films can be grown by mass-selected ion-beam deposition (MSIBD) of boron and nitrogen ions.[9] In this case, the deposition parameters, like ion energy, ion flux ratio of different ion species, and the substrate temperature, are well defined and independently controllable. The major differences to IBAD techniques are that (i) both nitrogen and boron are deposited as singly charged ions with energies of several hundred eV, and (ii) no noble gas or other ions nor other neutral atoms or molecules are involved in the deposition process.

With this paper we introduce an unadulterated diagram for the phase formation in BN film growth. This diagram is based on experimental studies on the influence of the ion energy E_{ion} and the substrate temperature T_S on the growth of BN films by MSIBD. We also present results for the compressive film stress dependence on E_{ion} and T_S, revealing the possibility to grow low stress *c*-BN films. Finally, we measure the ratio of incorporated atoms to deposited ions, and find that sputter effects are of minor importance.

Boron nitride thin films were grown by mass-selected ion-beam deposition using an UHV deposition system described in detail elsewhere.[10] B^+ and N^+ ions were produced in a plasma ion source using B_2O_3 vapor and N_2 gas. After acceleration to 30 keV and magnetic mass separation, the isotopically pure $^{14}N^+$ or $^{11}B^+$ ion beam is guided into the deposition chamber, where the ions are decelerated down to energies adjustable between 20 eV and 1 keV and deposited onto Si(100) substrates at temperatures between room temperature and 400 °C. The pressure during deposition was below 3×10^{-7} Pa. Prior to deposition the substrates were sputter cleaned by 1-keV Ar^+ ions. The amount of deposited ions is accurately measured by the ion charge, which is used to switch the separation magnet periodically to select $^{11}B^+$ or $^{14}N^+$. During each cycle, 10^{15} ions with an ion ratio of $B^+/N^+=1$ were deposited to ensure the growth of homogeneous and stoichiometric films.[9] The typical ion current was 20–30 μA on an area of 1.8 cm^2, and for a total deposited ion charge of 0.3 °C–0.5 °C we obtain a film thickness be-

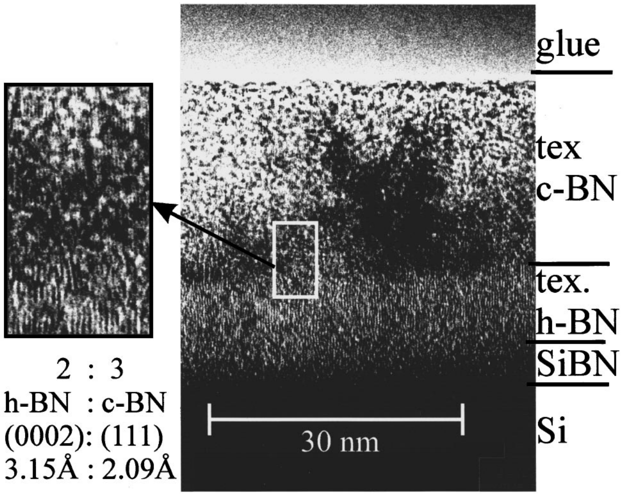

FIG. 1. HRTEM picture of a 35-nm-thick boron nitride film deposited at $T_S = 350$ °C and $E_{\text{ion}} = 500$ eV. c-BN crystallite sizes are around 10 nm. The 2:3 lattice matching between c-BN and the textured h-BN is clearly visible in the inset.

tween 60 and 100 nm. Films were characterized *in situ* by Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS), as well as *ex situ* by infrared spectroscopy (FTIR) and Rutherford backscattering spectroscopy (RBS). Some samples were prepared for transmission electron microscopy (TEM) and diffraction (TED).

AES measurements indicate contamination-free and almost stoichiometric BN films. The c-BN and h-BN phases were identified by FTIR measurements, using the characteristic c-BN reststrahlen band around 1080 cm^{-1} and the absorption lines at 1380 and 750 cm^{-1} due to h-BN stretching and bending vibrations. The c-BN content was calculated from the ratio of areas of the c-BN and h-BN absorption lines. As additional evidence for the c-BN phase, we measured the σ plasmon energy by reflection EELS using 2-keV primary electron energy. For all films showing the c-BN reststrahlen absorption, we measured plasmon energies of 31–32 eV. In contrast, for h-BN films we obtain lower values between 25 and 27.5 eV. From EELS measurements using primary electron energies down to 100 eV, we found that the surface region of all investigated BN films, including c-BN films, is sp^2 bonded. For c-BN films we estimate a thickness of 1–2 nm of the sp^2-bonded surface layer.

Some samples were also prepared for TEM and TED analysis. The cross-sectional TEM picture of a c-BN film deposited at 350 °C and with 500-eV ions is shown in Fig. 1. Starting from the Si substrate, a disordered Si-B-N mixed layer is formed, followed by a textured h-BN layer with the c axis parallel to the substrate surface. The mixed interface layer in our samples is rather broad and its thickness is comparable to the ion range of the 500-eV N^+ and B^+ ions used. On top of the textured h-BN the nanocrystalline cubic phase is formed. Zooming into the h-BN/c-BN interface we see that the c-BN layer is also textured with a 2:3 lattice matching of the h-BN (0002) and the c-BN (111) planes. In order to obtain a perfect matching, the h-BN planar distance has to be compressed from 0.33 to 0.315 nm, i.e., by 4.5%. Because of the large bulk modulus of c-BN it is unlikely that the (111) planar distance of c-BN is expanded. The texture of the c-BN is also seen in TED pictures, as they exhibit a structure in the c-BN diffraction rings.[9] The observed layered film structure is identical to the one obtained by IBAD.[11] Thus the same nucleation and growth processes occur in both deposition techniques. Possibly the 2:3 lattice matching and the formation of textured h-BN favor the nucleation of c-BN.

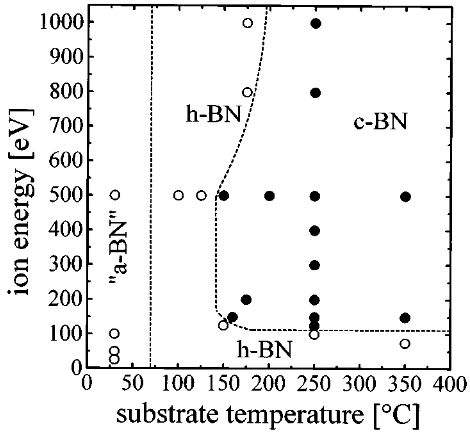

FIG. 2. Phase diagram for ion beam deposited boron nitride films. The c-BN content is plotted as a function of the ion energy and the substrate temperature. Filled symbols represent samples with a c-BN content exceeding 75%, whereas open symbols represent h-BN or disordered a-BN samples.

The results of EELS and FTIR analyses of BN films grown for different values of E_{ion} and T_S are summarized in the diagram for BN phase formation shown in Fig. 2. We observe c-BN formation above rather sharp threshold values of $T_S \geqslant 150$ °C and $E_{\text{ion}} \geqslant 125$ eV. Except for $E_{\text{ion}} > 500$ eV, these threshold values seem to be independent of each other. In the following we will discuss the details of the observed energy and temperature dependence.

The energy dependence of c-BN formation is plotted in Fig. 3(a) for substrate temperatures of 250 °C. At a threshold energy of 125 eV the c-BN content rises to about 85% and remains nearly constant for higher ion energies. The observed threshold energy is much lower compared to published data for IBAD growth.[3,5] The sharp energy threshold indicates a subsurface nucleation process requiring a certain ion range, and a certain critical deposited energy density. Such a process is qualitatively described by the subplantation model introduced by Lifshitz, Kasi, and Rabalais to explain the formation of tetrahedrally bonded amorphous carbon (ta-C).[12] A quantitative description on an atomic scale is provided by the thermal spike model of ion impact and rapid energy dissipation.[13] An energy of 125 eV is sufficient to create an energy density high enough to enable a complete rearrangement of the atoms within the thermal spike volume. The resulting bond structure is then essentially determined by the boundary conditions. This is opposite to Robertson's interpretation that a large number of rearrangements always leads to the formation of a low-density phase.[8]

The c-BN content of films deposited with 500-eV ions as a function of T_S is plotted in Fig. 3(b). It is clearly seen that the temperature threshold for c-BN formation of 150 °C is also rather sharp. A similar sharp temperature threshold around 150 °C was observed for ion-assisted pulsed-laser-

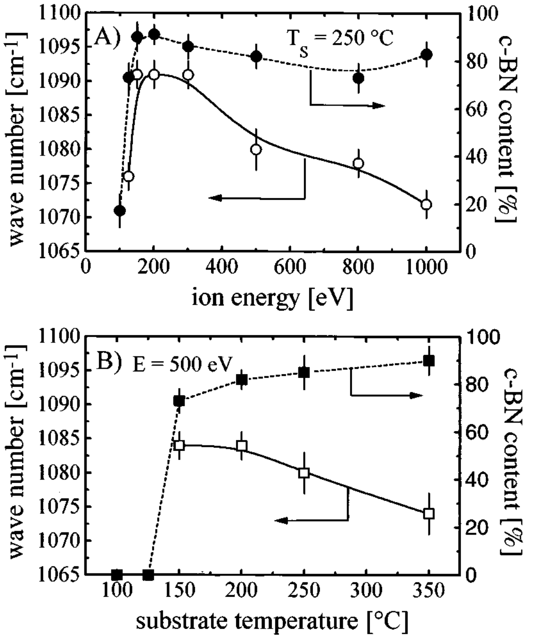

FIG. 3. *c*-BN content (filled symbols) and wave number of the peak position of the *c*-BN reststrahlen absorption (open symbols) as a function of (a) the ion energy for films deposited at 250 °C and (b) the substrate temperature for films deposited with 500-eV ions.

deposited BN films.[14] In contrast, Kester and Messier reported an extended temperature regime where mixed *h*-BN and *c*-BN phases were formed.[5]

Another transition temperature lies between room temperature and about 100 °C, indicated by the dashed line in Fig. 2. Samples deposited at room temperature have an IR spectrum similar to *h*-BN; however, the *h*-BN peaks are broader compared to bulk *h*-BN, and their positions are shifted to lower wave numbers.[15] This indicates bond disorder and weaker bonding but not necessarily an amorphous phase. Nevertheless, we use the term *a*-BN for these disordered *h*-BN films deposited at low temperatures. $T_S \approx 100$ °C is sufficient to obtain BN films exhibiting an IR-absorption spectrum of crystalline *h*-BN. The fact that a crystalline phase is formed at such rather low temperatures can be attributed to the ionicity of the BN bond.[16]

The observed temperature thresholds, indicated as dashed lines in Fig. 2, are closely related to the phase formation process during ion deposition, because they are not observed in annealing studies of BN films carried out for both *c*-BN and *a*-BN films.[15] In these studies, *c*-BN films were found to be stable up to 900 °C for annealing in air, and up to 1200 °C in vacuum. *a*-BN films are stable up to 1100 °C for annealing in vacuum. Above these temperatures the films disintegrate and evaporate from the Si substrates. For *a*-BN films a gradual shift of the absorption peak toward the bulk *h*-BN value and a narrowing of the absorption line was observed. No phase transformation of the films from *c*-BN to *h*-BN, or vice versa, takes place.

Nucleation of *c*-BN above the temperature threshold of 150 °C can be explained by the ordering of the *h*-BN phase so that the basal planes are parallel to the surface normal. This ordering requires a certain temperature and is driven by ion-induced stress.[17] Furthermore, stress may reduce the basal-plane separation, until eventually a 2:3 matching of the *h*-BN (0002) and *c*-BN (111) planar spacing is satisfied (Fig. 1). This provides boundary conditions which favor *c*-BN nucleation during recrystallization of the thermal spike volume following an ion impact.

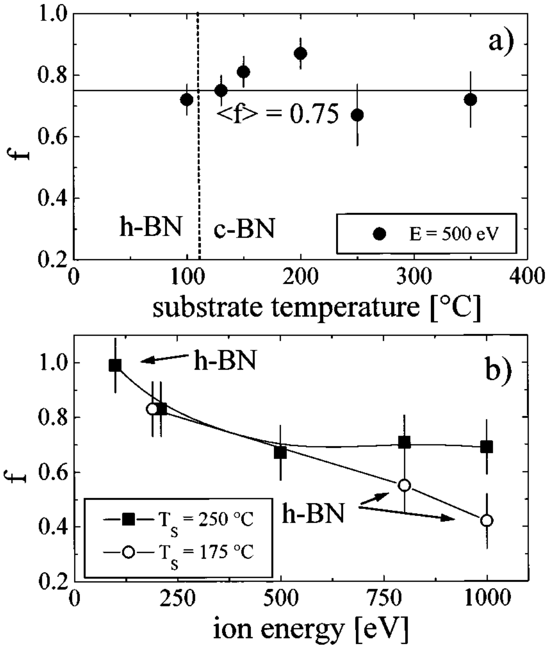

FIG. 4. Fraction *f* of deposited B and N ions actually incorporated into the films as a function of (a) the substrate temperature and (b) the ion energy.

Compressive stress in *c*-BN films leads to a shift of the peak position of the reststrahlen IR absorption to higher wave numbers.[18] This peak position is therefore a measure of the compressive film stress. In our films the reststrahlen absorption peak shifts to lower wave numbers with increasing T_S and particularly E_{ion} (open symbols in Fig. 3), indicating the decrease of compressive stress. A low value of the peak position is also observed for $E_{\text{ion}} = 150$ eV, slightly above the energy threshold. This suggests a relation between stress and E_{ion} very similar to the one observed for ta-C films, with maximum stress values occurring around $E_{\text{ion}} \approx 200$ eV.[19] To grow low-stress *c*-BN films one would thus choose high values of T_S and E_{ion}. Here we would like to emphasize that this requires a deposition method such as MSIBD, where both B and N are deposited as energetic ions. With the IBAD method film growth at higher ion energies is confined by the resputter limit.

It was proposed by the sputter model that a high sputter yield close to the resputter limit, as well as differences in the sputtering yields for *h*-BN and *c*-BN, determine the growth of *c*-BN thin films.[3] However, for our experiments we estimate a sputtering yield of at most 30% for N and B-ion bombardment of BN with energies below 1 keV, using the Monte Carlo simulation program TRIM.[20] A surface binding energy of 3 eV was chosen to reproduce the resputter limit at 500 eV observed with IBAD for Ar^+ and N_2^+ with $\text{Ar}^+/\text{N}_2^+ = 1$, incident on BN films at an angle of 45°.[5] Furthermore, the fact that the surface region of our *c*-BN films is always sp^2 bonded, and the observed low-energy threshold for *c*-BN formation are not consistent with the sputter model.

To quantify the sputtering yield during MSIBD BN film growth, we determined the sputter losses using RBS measurements of the area density of B and N film atoms for known film areas as well as measurements of the deposited ion charge. The latter quantity can be determined very accurately in MSIBD and is used to calculate the area density of deposited atoms. As a result, we obtain the fraction f of atoms actually incorporated into the film. The measured values f as a function of T_S and E_{ion} are plotted in Fig. 4. For c-BN films, we obtain high values $f \approx 0.7-0.85$ almost independent of T_S and E_{ion}. These values are in good agreement with the sputter yield estimated by TRIM, and show that sputter effects play a minor role for the growth of c-BN films. For h-BN films, f decreases gradually from $f \approx 1$ at 100 eV to $f \approx 0.4$ at 1 keV. However, for films deposited at ion energies below 200 eV we find no significant differences in f for h-BN and c-BN films. This, together with the observed low sputter yield, clearly demonstrates that the sputter model cannot be used to describe the growth of c-BN thin films.

The experimental facts presented in this paper prove that the nucleation and growth of c-BN thin films is a volume process occurring in the subsurface region at a depth given by the ion range. c-BN nucleates above well-defined threshold values for the ion energy and the substrate temperature. We interpret the energy threshold as the minimum energy needed to create a sufficiently high-energy density to enable complete rearrangement of the atoms within the thermal spike volume. Due to the ionicity of the BN bond, a crystalline h-BN phase is formed even at low substrate temperatures. At higher temperatures, ion-induced compressive stress causes an ordering of the h-BN basal planes, so that the c axis is parallel to the surface. This provides boundary conditions which favor c-BN nucleation during recrystallization of the thermal spike volume. This implies that further growth of c-BN should be possible at temperatures below the threshold if c-BN seed crystals are present. Such an effect was recently reported.[21] On the other hand, because of the subsurface nucleation process, it should not be possible to maintain c-BN growth by lowering the ion energy significantly below the energy threshold. Another important result is the observed decrease of compressive stress at high ion energies and high substrate temperatures. Under such deposition conditions, it should be possible to grow thick c-BN films with good adhesion.

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[1] Mater. Sci. Forum **54&55** (1990), special issue on synthesis and properties of boron nitride, edited by J. J. Pouch and S. A. Alterovitz.

[2] O. Mishima *et al.*, Science **238**, 1818 (1987).

[3] S. Reinke, M. Kuhr, and W. Kulisch, Diam. Relat. Mater. **4**, 272 (1995).

[4] S. Bohr, R. Haubner, and B. Lux, Diam. Relat. Mater. **4**, 714 (1995).

[5] D. J. Kester and R. Messier, J. Appl. Phys. **72**, 504 (1992).

[6] D. R. McKenzie *et al.*, Phys. Rev. Lett. **67**, 773 (1991); Diam. Relat. Mater. **2**, 970 (1993).

[7] P. B. Mirkarimi *et al.*, J. Mater. Res. **9**, 2925 (1994).

[8] J. Robertson, Diam. Relat. Mater. **5**, 519 (1996).

[9] H. Hofsäss *et al.*, Appl. Phys. Lett. **67**, 46 (1995).

[10] H. Hofsäss *et al.*, Diam. Relat. Mater. **3**, 137 (1994).

[11] D. J. Kester *et al.*, J. Mater. Res. **8**, 1213 (1993).

[12] Y. Lifshitz, S. R. Kasi, and J. W. Rabalais, Phys. Rev. Lett. **62**, 1290 (1989).

[13] H. Hofsäss and C. Ronning, in *Proceedings of the Second International Conference on Beam Processing of Advanced Materials*, edited by J. Singh, S. M. Copley, and J. Mazumder (ASM International, Materials Park, OH, 1996), pp. 29–56.

[14] P. B. Mirkarimi *et al.*, Appl. Phys. Lett. **66**, 2813 (1995).

[15] C. Ronning *et al.*, Diam. Relat. Mater. **6** (to be published).

[16] N. E. Christensen, S. Satpathy, and Z. Pawlowska, Phys. Rev. B **36**, 1032 (1987).

[17] D. G. McCulloch *et al.*, Nucl. Instrum. Methods Phys. Res. Sect. B **106**, 545 (1995).

[18] P. Widmayer *et al.*, Diam. Relat. Mater. (to be published).

[19] P. J. Fallon *et al.*, Phys. Rev. B **48**, 4777 (1993).

[20] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Ranges of Ions in Solids* (Pergamon, New York, 1985).

[21] K. T. McCarty *et al.*, Diam. Relat. Mater. **5**, 1295 (1996).