Fundamental role of ion bombardment for the synthesis of cubic boron nitride films

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Boron nitride film growth from B and N ion deposition is studied. We observe growth of the cubic phase (c-BN) between 75 eV and 5 keV and a transition to sp^2-bonded BN growth between 5 and 10 keV, as predicted by the cylindrical spike model. Atomic rearrangements in thermal spikes are identified as the mechanism responsible for c-BN formation and suppression of defect accumulation. The onset of defect accumulation eventually enhances the growth of sp^2-bonded BN. The results highlight the fundamental role of the balance between thermal spikes and defect accumulation in ion deposition processes.

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Cubic boron nitride (c-BN) thin films have attracted much attention because of their outstanding diamondlike properties.[1–4] Low-pressure, low-temperature synthesis of sp^3-bonded c-BN films is possible with various methods, however, only if energetic ions or atoms are involved. Without energetic particle bombardment only sp^2-bonded phases such as hexagonal BN (h-BN) or turbostratic BN (t-BN) are formed. In general, ion bombardment strongly influences film growth in several ways. First of all, it leads to the penetration of atoms below the film surface causing a local densification. Other effects related to ion bombardment are sputtering, electronic excitation, and ionization, Frenkel-defect production in ballistic displacement collisions, and excitation of target atom vibrations. Defect production in displacement collisions occurs on a time scale of femtoseconds immediately upon ion impact. In the following picosecond, the excitation of target atom vibrations causes a local rearrangement of atomic positions and bonds. It is precisely this latter process which one describes as a thermal spike.[5] The dominant contribution of such rearrangements has become evident in recent molecular-dynamics studies.[6] Unfortunately, the term ''displacements'' rather than ''rearrangements'' was used in a later publication, which may be interpreted misleadingly as collisional displacements.[7] It is the balance between these ion bombardment-related effects which controls the final film structure. Because of the competing sp^2-bonded and c-BN phases, BN film growth is particularly suited to study this balance and to extract the fundamental processes responsible for the phase formation.

Boron nitride thin films most often exhibit a layered structure consisting of an interfacial layer containing substrate and deposited atoms, followed by an oriented interlayer of turbostratic BN (t-BN) of several nm thickness, followed by also oriented, nanocrystalline c-BN, and a thin sp^2-bonded surface layer.[2,8] It is accepted that the t-BN interlayer texture is essential for the nucleation of c-BN. Threshold values for the ion energy and the substrate temperature to trigger the nucleation of c-BN have been identified.[2,9] For the direct deposition of B and N ions, these thresholds are 125 eV and 150 °C.[4,8] Nucleation and growth of c-BN are, however, characterized by different threshold values.[9] Once nucleated, the growth of c-BN can be maintained at room temperature[10] and at energies as low as 60 eV, well below the nucleation threshold.[11,12] For most BN growth methods, film growth at higher ion energies is not possible because of resputtering. This limitation does not exist for direct B and N ion deposition and a possible upper energy limit for c-BN nucleation and growth definitely lies beyond 1.5 keV.[4,8] Such a limit may be correlated to the instability of c-BN under ion irradiation because a transformation to sp^2-bonded BN can be induced by heavy ion irradiation at doses corresponding to a critical defect concentration of about 1 ballistic displacement per target atom (dpa).[13–15]

Several models were developed to explain the role of ion bombardment in c-BN formation, in particular the low energy threshold for nucleation and growth. These models link the c-BN formation either to the generation of ion-induced compressive stress[16,17] or to defect generation and relaxation processes following subplantation.[18] Thin film growth models based on the subplantation concept were originally developed to describe the formation of highly tetrahedral amorphous carbon (ta-C).[5,7,18–20] For the case of amorphous carbon, the subplantation-type models predict a maximum sp^3 bond fraction at a certain ion energy and a continuous transition from mainly sp^3-bonded to sp^2-bonded carbon with increasing ion energy, the latter being attributed either to thermal spike induced relaxation processes[18] or to defect accumulation.[19,20] For the case of boron nitride, most of the models do not consider a high energy limit for c-BN growth, probably because such a limit is experimentally obscured by resputtering processes, as stated above. Furthermore, the restrictions of models based on stress-induced c-BN formation have already been discussed in Ref. 2. One of the above subplantation models has been applied to c-BN formation[18] and predicts a behavior similar to sp^3-bonded amorphous carbon. However, according to Eq. (15) of Ref. 18 one would expect a transition to sp^2-bonded BN well below 1 keV. The applicability of the other subplantation model[19,20] to c-BN formation will be discussed later. None of the above c-BN growth models predicts a high-energy limit for c-BN growth beyond the experimentally verified energy of 1.5 keV.

Recently, we introduced the cylindrical spike model to describe diamondlike film formation by ion deposition.[5] The cylindrical spike model considers atomic rearrangements in thermal spikes to be the essential process leading to the formation of sp^3-bonded diamondlike phases such as highly tetrahedral amorphous carbon (ta-C) and also c-BN. The model introduces the ratio n_T/n_S as a key parameter, where

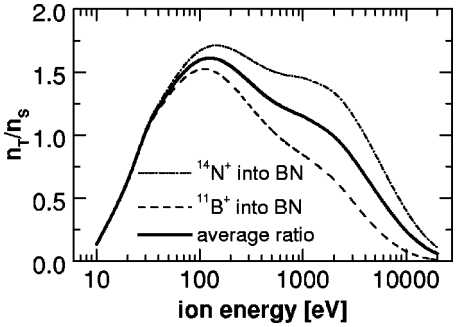

FIG. 1. Parameter n_T/n_S calculated for ^{11}B and ^{14}N ion deposition into boron nitride (from Ref. 8).

n_T is the number of thermal spike induced rearrangements in the collision cascade volume, which is approximated by a cylindrical volume containing n_S atoms. A ratio $n_T/n_S>1$, i.e., complete rearrangement, is seen as a requirement for diamondlike film formation. For the case of B and N ion deposition, the average ratio n_T/n_S exceeds unity between 30 eV and 2 keV, which represents a prediction for the *c*-BN growth regime (see Fig. 1). If only the N ions are considered, the upper limit for n_T/n_S exceeding unity shifts to about 4 keV. At higher ion energies, n_T/n_S rapidly decreases, predicting a transition back to sp^2 BN growth. An experimental confirmation of such a transition in the predicted ion energy regime would provide a critical test of the cylindrical spike model and clarify the role of ion irradiation for the stability of *c*-BN. This was the driving motivation for the experiments presented in this work.

Boron nitride films were grown by mass selected deposition of B^+ and N^+ ions of defined ion energy as described elsewhere.[8,10] In order to eliminate the influence of *c*-BN nucleation processes, we studied the growth of BN on previously nucleated *c*-BN films. In a first step, *c*-BN films of about 1 cm^2 were grown on *p*-type Si (100) substrates with an ion energy of 600 eV, a substrate temperature of 250 °C and a total deposited ion charge of 0.2 C. These initial BN films were about 50 nm thick including about 20–25 nm of a *t*-BN interfacial layer. Thus, the *c*-BN layer thickness is larger than the ion range of 10 keV N and B ions (15–20 nm). In a second step, ion deposition was continued in vacuo at different ion energies between 50 eV and 10 keV and with unchanged substrate temperature. An additional 30 nm was grown in this second step by deposition of 0.2 C total ion charge on an area of about 1.5 cm^2. The larger area was chosen to ensure that the initial film is completely overgrown. For all films, *in situ* Auger electron spectroscopy confirms stoichiometric and contamination-free BN films. Sputter losses are in accordance with TRIM simulations with a maximum sputter yield of $s\approx 0.5-0.6$ between 1 and 3 keV.[21] Therefore, a resputter limit does not exist, in contrast to most ion beam assisted deposition (IBAD) methods.

We find the low energy threshold for *c*-BN growth between 50 and 75 eV, in accordance with results of other groups.[11,12] On the other hand, three films were grown at ion energies of 3.5, 5, and 10 keV, respectively. The infrared absorption (FTIR) spectra of the films are displayed in Fig. 2. The 3.5 and 5 keV films show pronounced absorption

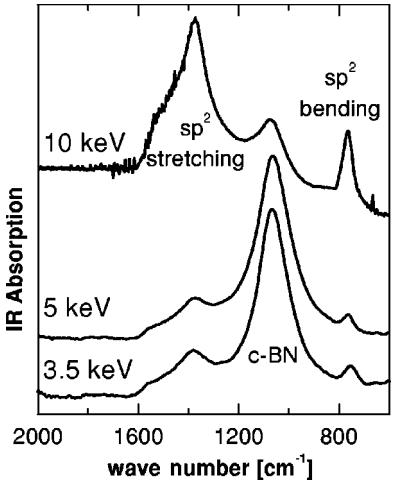

FIG. 2. FTIR spectra of BN films grown on *c*-BN with ion energies of 3.5, 5, and 10 keV, respectively. The stretching and bending absorption peaks at 1380 and 750 cm^{-1}, respectively, are typical for sp^2-bonded BN. The absorption peak around 1070 cm^{-1} is due to the characteristic *c*-BN reststrahlen band.

peaks due to *c*-BN at about 1070 cm^{-1}, whereas strong absorption peaks at 750 and 1350 cm^{-1} due to sp^2-bonded BN are seen for the 10 keV film. For this sample, a small absorption around 1070 cm^{-1} is also visible, possibly due to a residual *c*-BN layer from the initially grown *c*-BN film. The cross-sectional transmission electron microscopy (TEM) and electron diffraction images of the 5 keV film displayed in Fig. 3 confirm the high *c*-BN content an show *c*-BN crystallites extending almost up to the film surface. Thus, *c*-BN growth at 5 keV is unambiguously demonstrated. The TEM analysis of the 10 keV film reveals a *t*-BN film extending up to the film surface. Furthermore, most of the initially nucleated *c*-BN film has been converted to *t*-BN. Both results are in accordance with the FTIR data in Fig. 2. Evidently, *c*-BN growth with an ion energy of 10 keV is not possible and, in addition, ion irradiation of *c*-BN with 10 keV B and N ions leads to a transformation to *t*-BN.

Our experiments clearly demonstrate that the upper energy limit for *c*-BN growth by direct B and N ion deposition is at least 5 keV and definitely below 10 keV. This is in reasonable quantitative agreement with the predictions made by the cylindrical thermal spike model.[5] Thermal spikes are usually treated as spherical spikes, assuming instantaneous pointlike energy deposition and neglecting any energy loss and energy transfer mechanisms. In contrast, the cylindrical spike model treats thermal spikes under more realistic assumptions, including an estimate of the fraction of the ion energy transferred to atom vibrations (phonon excitations). Furthermore, the energy transfer is assumed to occur within a cylindrical collision cascade volume rather than as a pointlike energy deposition. The initial phonon energy density distribution is assumed to be uniform along a length given by the ion range with a Gaussian radial distribution. The width of this distribution is energy dependent and is related to the number of secondary collision events. The model compares the number n_T of atomic rearrangements in such a cylindrically symmetric volume with the number of atoms n_S in this

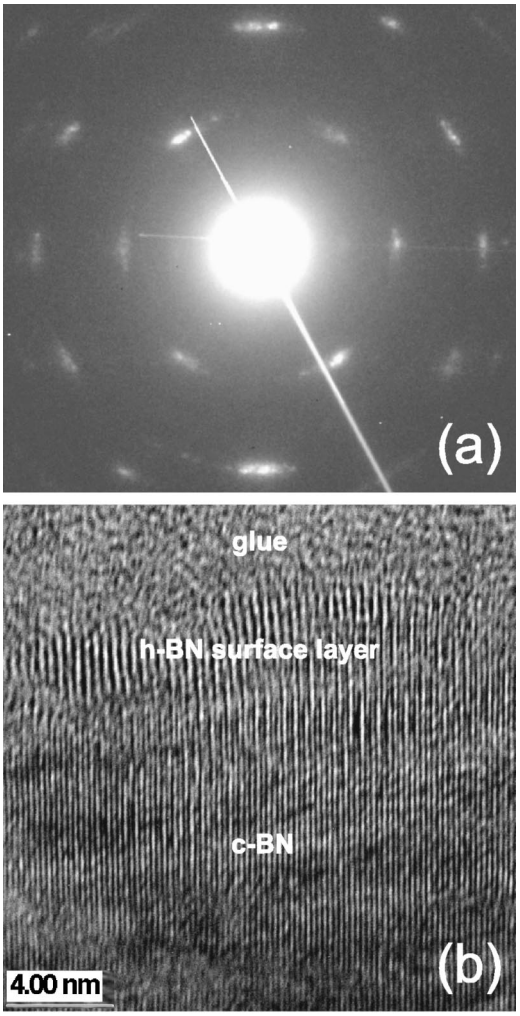

FIG. 3. (a) Electron diffraction image of the top half of the 5 keV BN film showing the typical c-BN pattern. (b) TEM cross-sectional view of the surface region of the 5 keV BN film, showing the c-BN planes extending up to the film surface covered only by a thin sp^2 surface layer.

volume. For a certain range of ion energies we find $n_T/n_S > 1$, corresponding to a complete rearrangement of the volume. At higher energies n_T/n_S strongly decreases, which is mainly related to an increasing collision cascade volume and a decreasing fraction of the ion energy transferred to phonon excitations. The experimentally observed c-BN growth regime is in reasonable agreement with the energy regime between about 30 eV and 2–4 keV where $n_T/n_S > 1$ (see Fig. 1), which is a strong indication of the validity of the cylindrical thermal spike model. Therefore, a complete rearrangement of atoms in individual collision cascade volumes seems to be a necessary condition for c-BN formation.

The dominant role of thermal spikes becomes evident if we apply the concept of a critical defect concentration due to ballistic displacements for an ion induced transformation of c-BN to sp^2-bonded BN and extrapolate this to the low energy regime. As stated before, a transformation of c-BN to sp^2-bonded BN can be induced by high-energy heavy-ion irradiation at a sufficiently high dose.[13–15] Whereas c-BN is

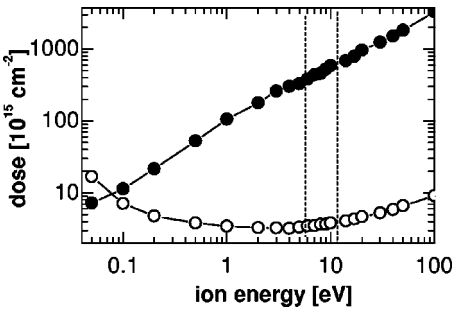

FIG. 4. Open circles: Required dose to accumulate a defect concentration of 1 dpa within the mean ion range by ion bombardment of a 3.5 g/cm^3 BN target with B and N ions. Solid circles: Required dose to grow a BN layer with thickness equal to the mean ion range with sputter losses included. The doses were calculated with TRIM (Ref. 21). The dashed lines indicate the c-BN to sp^2-bonded BN transition region.

stable under 350 keV Kr ion irradiation up to about 0.5 dpa,[13] a 1.1 MeV Xe irradiation causes a transition to sp^2-bonded BN around 1015 cm^{-2} corresponding to about 1 dpa.[14] In a recent study, c-BN could be converted to sp^2-BN by irradiation with 2×10^{15} Ar$^+$/cm^2 at 35 keV.[15] Thus, a dose producing a hypothetical defect concentration of about 1 dpa seems sufficient to induce such a transformation for a wide ion energy range and for different ion masses. It is important to note that ''dpa'' describes the accumulated defect concentration generated by ballistic displacements and neglecting any defect annihilation.

The dose D to produce an average accumulated defect concentration of 1 dpa can be calculated using TRIM as a function of ion energy E_{ion} and is given as $D(E_{\mathrm{ion}}) \approx n_A \cdot \overline{r}(E_{\mathrm{ion}})/n_d(E_{\mathrm{ion}})$ with target atomic density n_A, mean ion range r, and number of displacements n_d. The calculated dose for 1 dpa is about 3×10^{15} cm^{-2} for B and N ion irradiation of a 3.5 g/cm^3 BN target and is rather constant in a broad energy window between 200 eV and 20 keV. Furthermore, the calculated dose is comparable to the doses in the above ion irradiation experiments. The required dose to grow a BN layer of thickness is about 5×10^{17} cm^{-2} for the energy regime of 5–10 keV, i.e., two orders of magnitude larger (Fig. 4). Therefore, the concept of a critical defect concentration breaks down for ion energies up to 5 keV, since we have demonstrated c-BN growth under such conditions. Obviously, the defect accumulation in this energy regime must be efficiently suppressed. At 10 keV ion energy we may have reached a situation where defect accumulation sets in, leading to a transformation to sp^2-bonded BN under continued ion bombardment. We propose thermal spike induced rearrangements as the mechanism that is responsible for efficiently suppressing defect accumulation. This is further supported by the following arguments.

Displacements are created within femtoseconds in the initial collisional stage of an ion impact process. Within a certain energy regime, the calculated number of rearrangements occurring in the subsequent thermal spike stage with picosecond duration is an order of magnitude larger[5] and rearrangement processes will completely override the effect of

ballistic displacements. This is also supported by recent molecular-dynamics simulations.[6] For BN ion deposition, this energy regime coincides with the *c*-BN growth regime. As soon as the number of rearrangement processes decreases, defect accumulation becomes possible and a transition to *h*-BN growth can occur. Exactly such a decrease is predicted by the cylindrical thermal spike model to occur in the keV energy range (Fig. 1).

Applying the picture we have developed for *c*-BN growth to the formation of diamondlike carbon, we first recognize that the critical accumulated defect concentration for the amorphization and sp^2-phase transformation of diamond is about 0.1 dpa, corresponding to critical doses of 10^{14}–10^{15} cm^{-2}.[22] The fact that highly tetrahedral *a*-C films (sp^3 fraction $\geqslant 50\%$) can be grown using carbon ions of 0.1–2 keV leads to a diagram similar to Fig. 4 and implies that defect accumulation must also be efficiently suppressed. Again, we explain this suppression with rearrangements in a thermal spike following the collisional stage. Indeed, the ratio n_T/n_S and the measured sp^3 fraction in ion deposited *a*-C films exhibit the same ion energy dependence.[5] With increasing ion energy, thermal spikes become less efficient and defect accumulation enhances the formation of sp^2-bonded carbon.

The semiquantitative subplantation model introduced by Marton *et al.* is a simple phenomenological model for low energy ion interactions with surfaces.[20] It was developed to model the ion energy dependence of certain figures of merit such as the sp^3 bond fraction of diamondlike carbon films. Let us now apply the semiquantitative subplantation model to BN ion deposition and extract the *c*-BN fraction as figure of merit. The aims of the exercise is to test the applicability of the model to *c*-BN formation and also to suggest how the model should be revised, in case it fails to predict the observed *c*-BN growth regime. In this model, the destruction of a dense diamond-like phase is directly correlated to damage production (i.e., ballistic displacements). The amount of damage is taken to be proportional to the accumulated number of ballistic displacements, and the conversion of sp^3 to sp^2 is assumed to be proportional to the sp^3 fraction itself. The model is able to describe the energy dependence of the sp^3 fraction f_{sp^3} in ion deposited *a*-C using the relation [Eq. (11) from Ref. 20],

$$f_{sp^3} = \alpha \ln(E/E_P) - \beta f_{sp^3}[(E-E_D)/E_D] + f_0, \qquad (1)$$

with ion energy E, fit parameters α and β, displacement energy $E_D \approx 36$ eV, penetration threshold energy $E_P \approx 8$ eV and constant $f_0 \approx 0.05$. According to Ref. 20, the first term in Eq. (1) describes the penetration probability and is assumed to saturate at about $8E_P = 64$ eV. The second term describes the defect production by introducing an efficiency factor β multiplied with the defect production rate $(E-E_D/E_D)$. In addition, the second term is multiplied by f_{sp^3} to take into account, that defect production is proportional to the abundance of sp^3 carbon. Finally, the third term describes an energy-independent sp^3 fraction. Let us now apply the model to *c*-BN growth by replacing f_{sp^3} with $f_{c\text{-BN}}$ and assuming a penetration probability $\alpha \ln(E/E_P) \approx 1$ and a residual energy-independent sp^3 fraction $f_0 \approx 0$. Inserting this into Eq. (1) we get

$$f_{c\text{-BN}} \approx \frac{1}{1+\beta[(E-E_D)/E_D]}. \qquad (2)$$

The number $(E-E_D)/E_D$ of displacements per ion is large, both for 5 and 10 keV. However, according to the experimental data presented in this work we have to set $f_{c\text{-BN}} \approx 1$ at 5 keV and $f_{c\text{-BN}} \approx 0$ at 10 keV. This would require a vanishing parameter β at 5 keV, but a β large enough to allow the cubic fraction to drop to zero at 10 keV. As an example, we set $f_{c\text{-BN}} \approx 0.9$ at 5 keV and $f_{c\text{-BN}} \approx 0.05$ at 10 keV and assume $E_D = 35$ eV. We then calculate from Eq. (2) $\beta < 7.8 \times 10^{-4}$ for 5 keV and $\beta > 6.7 \times 10^{-2}$ at 10 keV, about two orders of magnitude larger. Therefore, the semiquantitative subplantation model cannot explain the observed high energy limit for *c*-BN growth, because the assumption of the model that the defect production efficiency β is constant over a broad range of energies no longer holds. In other words, we have to introduce an additional efficient process suppressing the accumulation of defects at the lower energy in order to correct for the required different β values at 5 and 10 keV. We therefore propose the following revised mechanism for the semiquantitative subplantation model.[20] At ion energies high enough for the ions to penetrate below the film surface, thermal spikes enhance the formation of sp^3 carbon, because rearrangements make it possible to adjust the local microstructure, incrementally densified by the incoming ions, and at the same time efficiently suppress damage accumulation. At even higher ion energies, the onset of damage accumulation, rather than the damage production itself, controls the destruction of the sp^3 phase. Therefore, the parameter β in Eqs. (1) and (2) should be replaced by an energy dependent parameter also describing the suppression of defect accumulation. Obviously, such a parameter would be closely related to the term n_T/n_S of the cylindrical spike model and the physical processes underlying the cylindrical spike model and the revised Marton model appear quite similar.

We have demonstrated that *c*-BN growth using mass selected B and N ions is possible within an ion energy window between 75 eV and 5 keV. A transition from *c*-BN to sp^2-bonded BN growth takes place above 5 keV. Both results are in good agreement with the predictions of the cylindrical thermal spike model. An analysis of the defect production and energy transfer processes during ion impact clearly reveals that a significant amount of atomic rearrangements due to thermal spikes efficiently suppresses defect accumulation and enables a readjustment of the local microstructure. Thus, thermal spike induced rearrangements play the fundamental role in ion deposition processes leading to diamondlike film formation. The revealed mechanism is of

general importance for low energy ion beam processes such as ion beam synthesis and low energy ion implantation. In particular, the mechanisms of stress generation in thin films have to be reconsidered in light of an efficient suppression of defect accumulation.

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