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Effect of Chemical Sputtering on the Growth and Structural Evolution of Magnetron Sputtered CNx Thin Films

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Effect of chemical sputtering on the growth and structural evolution of magnetron sputtered CN_x thin films

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Abstract

The growth and microstructure evolution of carbon nitride CN_x ($0 \leq x \leq 0.35$) films, deposited by reactive d.c. magnetron sputtering in Ar/N_2 discharges has been studied. The substrate temperature T varied between 100 and 550°C, and the N_2 fraction in the discharge gas varied from 0 to 100%. It is found that the deposition rate and film morphology show strong dependence on T_s and nitrogen fraction. For growth temperature of 100°C, the films are amorphous, and essentially unaffected by the nitrogen fraction. For $T_s > 200^\circ C$, however, the nitrogen fraction has more significant effect on the growth and structural evolution of the films. The pure carbon films appear porous and have a high surface roughness. For increasing nitrogen fraction the films become denser and the roughness decreases by one order of magnitude. It is suggested that a chemical sputtering process, during which desorption of volatile N and CN-species, predominantly C_2N_2 , is important not only for the deposition rate and the nitrogen incorporation, but also for the resulting film structure. The chemical sputtering process becomes more pronounced at elevated temperatures with higher nitrogen fractions.

1. Introduction

Diamond-like carbon and carbon nitride CN_x thin films have been reported to exhibit highly interesting properties, well suited, e.g. for wear protection applications [1]. In fact, CN_x compounds having very high hardnesses can be produced under conditions where pure carbon materials would exhibit rather poor properties. We have previously reported that basically three different phases can be observed in magnetron sputtered CN_x films, depending on nitrogen concentration and growth temperature T_s [2]. For growth temperatures below $\sim 200^\circ C$, the structure is homogeneously amorphous, and the film properties are essentially unaffected by the nitrogen incorporation. For higher temperatures, however, a transition from a mechanically soft graphite-like material, to a much harder 'fullerene-like' structure was observed when increasing the nitrogen concentration from ~ 5 to 15 at. %[2]. The maximum achievable nitrogen concentration was in the range 25–30 at. %, found when growing at $T_s = 100^\circ C$. This relatively low nitrogen incorporation level is consistent with several other reports, and has gener-

ally been attributed to chemically enhanced desorption of nitrogen-containing species. This process is commonly referred to as chemical sputtering.

The effect of chemical sputtering on the deposition rate and nitrogen incorporation has been discussed in the literature, especially during ion beam deposition of CN_x thin films [3–10]. The knowledge of how chemical sputtering influences the film structure and morphology has, however, been lacking. In this paper we present results from CN_x ($0 \leq x \leq 0.35$) films magnetron sputtered in various N_2/Ar mixtures and at temperatures between 100 and 550°C. We present evidence that a thermally activated chemical sputtering process becomes important as soon as a minute N_2 fraction is mixed into the discharge gas. Furthermore, the correlation between the chemical sputtering and the resulting microstructure and surface morphology is discussed.

2. Experimental details

CN_x films were deposited onto Si(001) substrates by unbalanced reactive d.c. magnetron sputtering in mixed Ar/N_2 discharges. The total pressure was fixed at 3 mTorr, with the N_2 fraction varied from 0 (pure Ar) to 100% (pure N_2), and with substrate temperatures of 100, 350 or 550°C. The details of the film growth have been reported elsewhere [2]. The film deposition rates R_D were measured by a surface profilometer at a step formed on the film by masking the substrate. The surface morphology of the as-deposited films were studied by scanning electron microscopy (SEM) using a LEO 1550 instrument operating with a 2-keV electron beam and with a lateral resolution of ~ 3 nm. Cross-sectional samples for the SEM were prepared by cleaving the Si substrates when cooled to liquid nitrogen temperatures. The films surface roughnesses were measured by a Digital Instruments Nanoscope IIIa atomic force microscope (AFM), operating in the tapping mode. Root mean square (rms) roughnesses were evaluated from $1 \mu m \times 1 \mu m$ scans. Furthermore, the microstructure of the as-deposited films was characterized by high resolution transmission electron microscopy (HREM) using a Philips CM 20 UT transmission electron microscope operated at 200 keV. Fractured cross-sectional HREM samples were prepared by mechanical cleaving of the coated Si substrates, whereas plan-view samples were obtained by floating off ~ 20 -nm-thick films deposited on NaCl crystals in de-ionized water. The films were then collected onto Cu microscopy grids.

3. Results and discussion

3.1. Film growth and evidence for chemical sputtering

Important information about the growth process can be obtained by studying the film deposition rate R_D

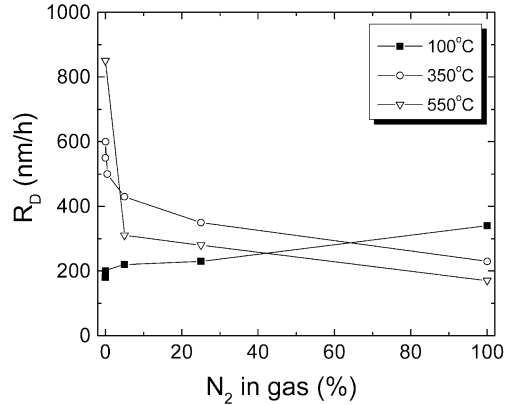


Fig. 1. Deposition rate R_D of the film grown at temperatures of 100, 350 and 550°C, as a function of the N_2 fraction in the discharge gas.

and film composition for different growth conditions. Fig. 1 shows R_D as a function of the N_2 fraction in the discharge gas for various temperatures. It can be seen that the trends are quite different for high and low deposition temperatures, respectively. For the pure carbon films, R_D is more than a factor of three higher when grown at 350°C compared with at 100°C, and for even higher temperatures temperature, R_D increases further. The effects of N_2 incorporation on R_D are also quite different for the studied temperatures. For the films grown at the higher temperatures, R_D decreases rapidly when only a small amount of N_2 is mixed in the gas (up to $\sim 5\%$). When more N_2 is added, the decrease in R_D continuous, but is less pronounced. The films deposited at the lower temperature, however, show a different behavior. In this case R_D increases, almost linearly, with the fraction of N_2 in the gas.

There are mainly three factors that can cause such variations in the growth rate depending on temperature and gas mixture: (i) since nitrogen from the gas phase is incorporated in the film, the reactive process results in that more material contribute to build up the film in the presence of nitrogen. This effect can likely explain the behavior at $T_s = 100^\circ C$, where the increase in R_D can directly be correlated to an increase in N_2 partial pressure; (ii) since surface profilometry only measures the film thickness, an increased film porosity or lower density would result in an increase of the apparent growth rate. This is an important effect for the films grown at elevated temperatures, as will be discussed in more detail later. RBS data were used to evaluate the deposited mass (number of atoms) per unit area, and it was found that the large variations in R_D would be somewhat less pronounced if all films were dense.

However, even if the effect of density variation is taken into account, there is still a decrease in the amount of deposited material when increasing the N_2 partial pressure for elevated growth temperatures. Therefore, also a third possibility must be considered;

(iii) a chemical sputtering process, which results in desorption of the deposited particles. This mechanism appears to be the most reasonable explanation, as also has been proposed by other authors [3–10]. Physical resputtering could hardly contribute to the decrease in R_D , since the energies of the ions impinging onto the growth surface was only in the order of ~ 10 – 15 eV, and did not vary significantly when varying the nitrogen fraction. Furthermore, a physical sputtering process would not show a temperature dependence as observed here. However, a chemical sputtering process would be expected to be strongly temperature dependent.

In order to get further insight into the growth process, mass-spectrometry was used to monitor the gas phase species during growth. Fig. 2 shows typical mass-spectra from a deposition in a pure N_2 discharge. The solid bars represent the gas composition before deposition, and the open bars are the additional signals appearing when turning on the discharge. It can be seen that various carbon signals (C^+ , C_2^+ , C^{2+}) appear due to sputtering from the graphite target, but in addition also carbon nitrogen species are visible ($C_2N_2^+$, CN^+ , C_2N^+), indicating that reactions take place in the deposition chamber. Dominating among the new species is $C_2N_2^+$ at mass 52, which has more than one order of magnitude larger signal than, e.g. C^+ . At the low pressure used in this study, it is unlikely that the CN species would form in the gas phase, since it would require multiple body interactions. Instead, most of them are presumably created at the target surface, but reactions are also likely to take place on the substrate surface, as well as at the chamber walls. It should be noted that our mass-spectrometer was in a remote position from the most intense plasma, so short-lived species could not be detected. However, Kaltofen et al. [6–8] have, by a mass-spectrometer positioned at the substrate position during an r.f. magnetron sputtering process, identified the same species of importance as we do here.

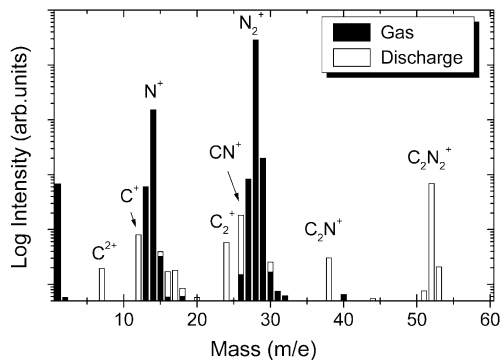


Fig. 2. Typical mass-spectra from a deposition in 3 mTorr pure N_2 . (■) Gas composition before igniting the discharge, (□) additional signals appearing from the plasma during deposition.

We have previously reported [2] that the nitrogen concentration in the film increases rapidly when mixing small amounts of N_2 in the discharge gas, but then starts to saturate already when $\sim 10\%$ of N_2 is added. When further increasing the N_2 fraction only a slight increase in the film nitrogen concentration was observed. For films grown at 100°C , the nitrogen concentration saturated at ~ 26 at.% ($[N]/[C] \sim 0.35$), but for $T_S = 550^\circ\text{C}$ this value dropped to ~ 17 at.% [2]. By comparing the flux of N_2 molecules impinging on the growth surface with the resulting N concentration in the film, we estimate that the nitrogen sticking coefficient was less than 10^{-6} , i.e. only a very small fraction of the nitrogen is actually incorporated in the film. Since N_2 is a very stable molecule with a dissociation energy of 9.8 eV [11], thermalized molecules will most likely immediately bounce off when hitting the surface. Ionized N_2^+ , on the other hand, has the possibility to dissociate provided that the energy of the ions impinging onto the growth surface is higher than 9.8 eV, and thereby they can take part in the growth. However, the sticking coefficient of N_2^+ is also found to be very low ($\sim 10^{-3}$). This indicates that the nitrogen supply to the growth surface is not a limiting factor for the total nitrogen incorporation, but rather structural instability and desorption of volatile nitrogen-rich species are responsible for the low nitrogen concentration.

3.2. Mechanisms for chemical sputtering

The fact that the deposition rate decreases considerably in the presence of nitrogen, and that the film nitrogen concentration saturates at rather low values, indicates that chemical effects, accompanied by desorption of both carbon and nitrogen, takes place during growth. Todorov et al. [3] performed ballistic TRIM-based computer simulations for modeling ion beam deposition of CN_x film. They were not able to reproduce the experimentally obtained nitrogen concentrations, unless a mechanism for preferential nitrogen loss was included in the simulations. However, by stipulating that whenever two nitrogen atoms become nearest neighbors, a $N\equiv N$ bond is formed and the inert N_2 molecule can migrate to the surface where it desorbs. Furthermore, it was assumed that if a C atom was implanted in such a way that it became surrounded by a certain number of N atoms, it would form a strong $C\equiv N$ bond with one of them and be re-emitted as a CN molecule. Depending on the number of N neighbors required for these reactions, the maximum achievable nitrogen concentration would be defined, and values between ~ 15 and 40 at.% were predicted. Very good agreement between experimental and simulated nitrogen concentration profiles in the films was found. However, since the $C\equiv N$ dimer is not a stable satu-

rated molecule, it is more reasonable to assume that

cyanogen C_2N_2 molecules are being emitted, as observed in our study. Also other groups have experimentally verified the presence of C_2N_2 during sputtering or ion beam deposition of CN_x thin films [4–8,12,13].

In Todorov's model, the bonding configuration and probability of re-emission was only dependent on the chemical environment of an atom after being implanted, and the assumption that at least one of the atoms in the re-sputtered molecules must be set into motion ballistically. The present results, however, clearly indicates that the chemical sputtering effect is not only induced by ion bombardment, but is also thermally activated. The low ion energies used in our experiment ($\sim 10\text{--}15\text{ eV}$) implies that the ions would hardly penetrate below the first atomic layers. Thermally activated surface mobility can thus be expected to dominate the structural evolution during deposition of the carbon nitride films. Further evidence showing that ballistic effects are not necessary for chemically induced desorption of volatile nitrogen-containing species can be found from annealing experiments. Substantial nitrogen-loss is typically observed when annealing CN_x films a few hundred degrees above the deposition temperature [14–17].

In sputtering depositions, the most important particles that can contribute to the growth, as detected by mass-spectrometry, are C^+ , N_2^+ , N^+ and $C_2N_2^+$. Neutral carbon atoms will also take part in the growth, whereas

neutral N_2 , as discussed above, are unlikely to contribute due to the stability of the molecule. The same is probably also true for neutral C_2N_2 molecules (dissociation energy $\sim 5.5\text{ eV}$ [11]).

At impact, the N_2^+ ions can dissociate and become loosely bound physisorbed N atoms. At low temperatures the diffusion rate is low and the atoms directly come to rest, and consequently an amorphous microstructure lacking of long-range order will form. In agreement with Todorov's model, it is reasonable to assume that whenever a nitrogen atom has another nitrogen as nearest neighbor, the probability of forming a volatile N_2 molecule which can desorb is rather high, even at low temperatures. Thus, a nitrogen concentration exceeding $\sim 33\text{ at.}\%$ would be hard to achieve, assuming a cubic arrangement where each nitrogen atom is surrounded by C atoms on all sides in the surface plane. In reality, the average number of nearest neighbors is probably lower than it would be in a cubic structure, and thereby the nitrogen concentration can reach slightly higher values. Reports on nitrogen concentration exceeding $40\text{ at.}\%$ are, however, very rare.

For the deposition of diamond-like carbon (DLC) films, it is well known that for temperatures higher than $\sim 200^\circ\text{C}$, the surface mobility is sufficient for forming the more energetically favorable graphitic structure, over the amorphous phase found at lower temperatures [18]. When depositing CN_x films above that temperature, we can assume that N atoms, and possibly also $-C\equiv N$ molecules, will diffuse on the growth surface until they either become bound in a low-energy lattice site, or react with other particles to form volatile molecules which can desorb. At higher temperatures the diffusion rate becomes higher, so more reactions are likely to take place. Furthermore, bulk diffusion becomes more important at higher temperature, so N from the subsurface region could diffuse toward the surface, and there recombine or react and eventually desorb. This can thus explain the reduced nitrogen incorporation with increasing temperature.

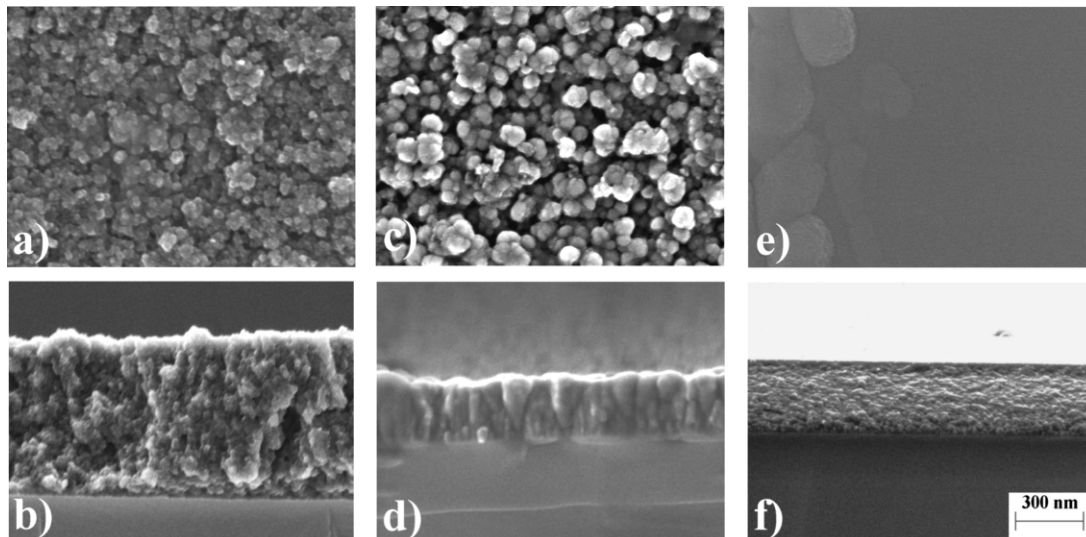


Fig. 3. Plan-view (top) and cross-sectional (bottom) SEM micrographs from films grown at $T_s = 350^\circ\text{C}$. (a,b) Pure carbon films, (c,d) a $CN_{0.09}$ film grown with $5\% N_2$ in the discharge gas, and (e,f) a $CN_{0.25}$ film grown in pure N_2 .

The desorption of N_2 , however, only suppresses the nitrogen incorporation, but not the total growth rate. The surface reaction processes must thus also involve desorption of carbon-containing species. Pure carbon are unlikely to be desorbed since that would require physical sputtering, but C_2N_2 and to some extent also other CN species, can be expected to be involved. The formation of these volatile molecules may happen in many ways. It is likely that first $-C \equiv N$ dimers are formed, either by dissociation of $C_2N_2^+$ ions at impact at the growth surface, or by reactions between C and N on the film surface. These dimers can encounter other $-C \equiv N$ dimers when diffusing on the surface, to form volatile C_2N_2 molecules. This type of a chemical sputtering process would result in a reduced growth rate, especially at elevated substrate temperatures. The presence of small residual amounts of $-C \equiv N$ in the as-deposited films have been observed by infrared and Raman spectroscopy [2], which indicates that the creation of C_2N_2 is reasonable. The formation of C_2N_2 molecules could also result in a lower total nitrogen concentration. However, since the surface is probably oversaturated by nitrogen, there would still be sufficient amounts of nitrogen for a high incorporation rate, unless the desorption of pure N_2 would also be significant.

3.3. Film morphology and microstructure

The chemical sputtering effect discussed above has implications not only on the growth rate and the film nitrogen concentration, but also on the resulting film structure and morphology. Fig. 3 shows SEM micro-graphs, both plan views and cross-sections, from a pure carbon film (a,b), a $CN_{0.09}$ film grown in 5% N_2 (c,d), as well as a $CN_{0.25}$ film grown in pure nitrogen discharge (e,f), all at a substrate temperature of $350^\circ C$.

For the pure carbon films grown at $T_s = 350^\circ C$ the material appears to be loosely packed (Fig. 3a,b). Raman spectroscopy has indicated that the structure is predominantly built up from nanometer-sized graphitic clusters, which becomes more ordered at higher T_s [2]. Even if the structure consists of graphitic clusters, the overall density of the film is well below that of graphite ($\sim 1.7 \text{ g cm}^{-3}$ for the film shown in Fig. 3a,b, to be compared with 2.25 g cm^{-3} for graphite), which is consistent with a rather porous structure. Hence, this can explain the apparently higher deposition rate for the pure carbon films deposited at elevated temperatures (cf. Fig. 1). The apparently porous structure can be explained by a low nucleation density at the higher temperature, and that the graphitic clusters due to the high diffusion rate grow so fast that the competing smaller grains were shadowed.

In Fig. 3c,d it can be seen that when nitrogen is added to the discharge gas, the structure becomes more columnar in appearance, and the clusters become more rounded, but the film still not appears to be fully dense. The films grown in pure nitrogen (Fig. 3e,f) show a substantially decreased surface roughness, and the film appears to consist of much smaller, densely packed nodules. No columnar features can be observed. The films grown at $550^\circ C$ showed a similar microstructure trend as those grown at $350^\circ C$, however, with an even more porous structure for low nitrogen concentrations. When grown at $100^\circ C$, all films appeared to be homogeneous and dense.

We can attribute this structural transition largely to the chemical sputtering process. In the presence of nitrogen, atoms not sitting in stable lattice sites have a high probability to react with nitrogen to form volatile molecules which can desorb. This is more likely to occur at edges where the atoms are more loosely bound, so protruding clusters will be rounded or completely etched away. Consequently, the films become both denser and smoother the more nitrogen is present, as can be seen in Fig. 3. This effect is further illustrated in Fig. 4, which shows atomic force microscopy images from films grown at $350^\circ C$ in pure Ar (Fig.

4a), 5% N_2 (b) and pure N_2 (c) [note that the z-axis scale is in (a) 200 nm per division whereas in (b) and (c), it is one order of magnitude less]. It is evident that

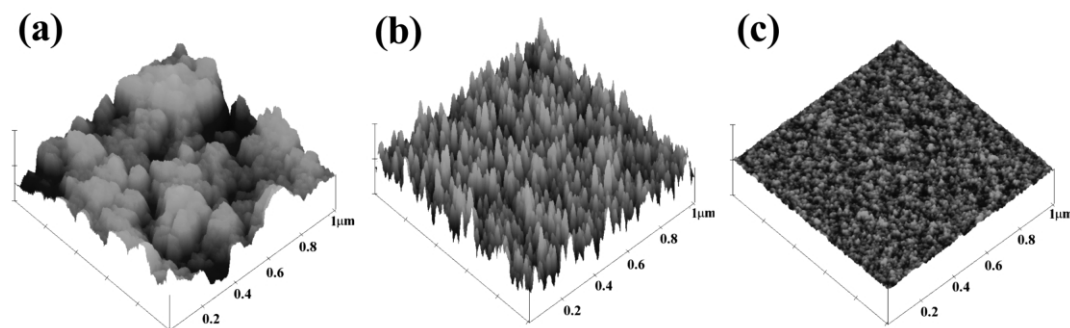


Fig. 4. AFM images from (a) a pure carbon film, (b) a $CN_{0.09}$ film grown in 5% N_2 and (c) a $CN_{0.25}$ film grown in pure N_2 . All films were grown at $T_s = 350^\circ C$. The scan size is $1 \times 1 \mu m^2$ in all images, but the z-scale is in (a) 200 nm per division, while in (b,c) the scale is 20 nm per division.

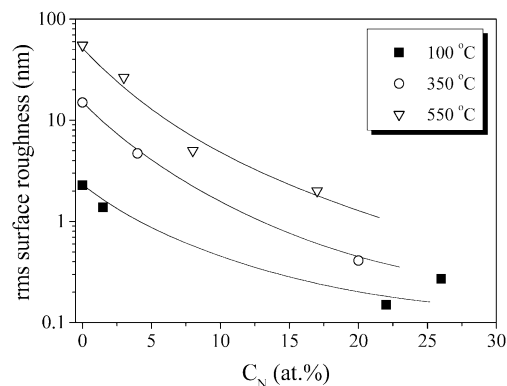


Fig. 5. Root mean square (rms) surface roughness of the as-deposited CN_x films as a function of the growth temperature and nitrogen concentration. The lines are drawn to guide the eye.

both the surface roughness and the surface morphology changes depending on the nitrogen partial pressure.

The rms surface roughness, as measured by AFM, is displayed in Fig. 5 as a function of nitrogen concentration and growth temperature. For all temperatures, the surface roughness decreases monotonically as C_N is increased, and the roughness is approximately one order of magnitude lower for the films grown in 100% N_2 , compared with the pure carbon films. For all nitrogen concentrations, the surface roughness increased with increasing growth temperature. It should be noted that some variations in the roughness can be expected due to differences in the film thickness, however, this effect is in our case negligible compared with the overall variation in the roughness.

For the growth of pure carbon films, it is commonly observed that the rms roughness is very low when depositing at low temperatures, but it increases considerably when T_S is raised above $\sim 200^\circ\text{C}$, due to the increased mobility and a consequent formation of a sp^2 -rich material [18]. The present results also show that the smoothest surface is formed at low temperatures, but the chemical sputtering in the presence of nitrogen is an independent process serving to smoothen the surface during growth.

Fig. 6 shows plan-view HREM micrographs from a pure carbon film (a), a $CN_{0.15}$ (b), and a $CN_{0.25}$ film (c), all grown at $T_S = 350^\circ\text{C}$. It can be seen that the basic structure was the same for all films, i.e. a structure built up from graphitic basal planes, in average separated by $\sim 3.5 \text{ \AA}$. As discussed above, the structure of the pure carbon film consists of nanometer-sized graphitic clusters [2], as can be seen in Fig. 6a. However, when small amounts of nitrogen is added, longer continuous basal planes are observed, and when further increasing the nitrogen concentration, this process becomes more pronounced (Fig. 6b,c). The longer continuous basal planes observed in the nitrogen-containing films can likely also be explained by the chemical sputtering process, which results in a higher packing density, and that atoms not being incorporated in stable lattice sites (i.e. in the graphitic basal structure) are removed.

As discussed above, the films grown at 100°C were all homogeneously amorphous independently of the nitrogen incorporation. When T_S was increased up to 550°C , the structured resembled those presented in Fig. 6, however, the basal planes appeared to be even more curved, sometimes forming circular features.

4. Conclusions

The growth and structural evolution of CN_x thin films depend mainly on three parameters; availability of nitrogen, substrate temperature, and ion flux and energy. The presence of nitrogen results in chemical sputtering processes, involving the desorption of volatile N_2 and C_2N_2 molecules. The substrate temperature determines the mobility of the adatoms; for $T_S = 100^\circ\text{C}$, the mobility is low, and the structure becomes amorphous and dense. For $T_S > 200^\circ\text{C}$, the higher mobility provides for that the more energetically favorable graphitic structure can form. The higher mobility also results in a more pronounced chemical sputtering in the presence of nitrogen, which leads to the formation

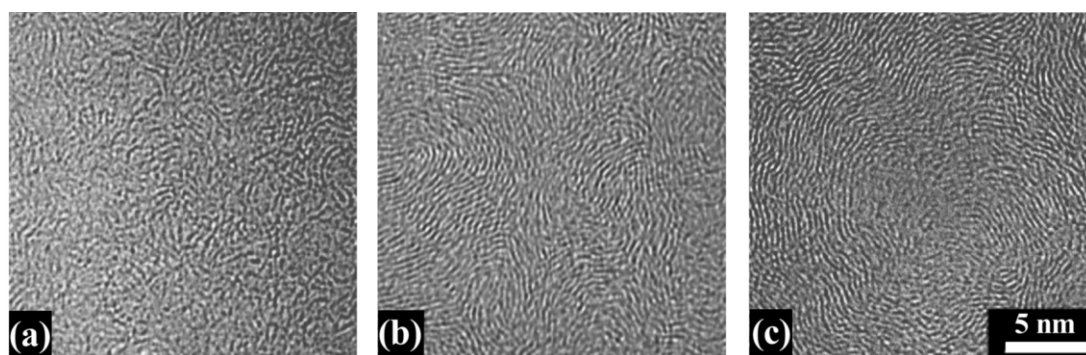


Fig. 6. Plan-view and cross-sectional HREM micrographs from (a) a pure carbon film, (b) a $CN_{0.09}$, and (c) $CN_{0.25}$ films (c), all grown at $T_S = 350^\circ\text{C}$. The same scale is used in all images.

of a denser and smoother film. The growth rate and nitrogen incorporation, however, decreases considerably.

The role of ion bombardment has not been analyzed in this study, but we can draw the parallel to previous studies [19,20] which indicate that the mechanisms for chemical sputtering are similar if the atomic mobility is enhanced by ion bombardment, instead of thermal energy. Consequently, a high ion energy leads to a reduced deposition rate and reduced nitrogen incorporation.

Acknowledgements

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