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Effect of chemical sputtering on the growth and structural evolution of magnetron sputtered \( \text{CN}_x \) thin films

Niklas Hellgren, Mats P. Johansson, Esteban Broitman, Per Sandström, Lars Hultman, Jan-Eric Sundgren

Abstract

The growth and microstructure evolution of carbon nitride \( \text{CN}_x (0 \leq x \leq 0.35) \) films, deposited by reactive d.c. magnetron sputtering in \( \text{Ar/N}_2 \) discharges has been studied. The substrate temperature \( T \) varied between 100 and 550°C, and the \( N \) fraction in the discharge gas varied from 0 to 100%. It is found that the deposition rate and film morphology show strong dependence on \( T \) and nitrogen fraction. For growth temperature of 100°C, the films are amorphous, and essentially unaffected by the nitrogen fraction. For \( T > 200°C \), 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 \( \text{CN}_x \), 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 \( \text{CN}_x \) thin films have been reported to exhibit highly interesting properties, well suited, e.g. for wear protection applications [1]. In fact, \( \text{CN}_x \) 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 \( \text{CN}_x \) films, depending on nitrogen concentration and growth temperature \( T \)[2]. For growth tem-peratures below \( \sim 200°C \), the structure is homoge-neously amorphous, and the film properties are essen-tially unaffected by the nitrogen incorporation. For higher temperatures, however, a transition from a me-chanically soft graphite-like material, to a much harder ‘fullerene-like’ structure was observed when increasing the nitrogen concentration from \( \sim 5 \) to \( 15 \) at.%[2]. The maximum achievable nitrogen concentration was in the range 25–30 at.%, found when growing at \( T = 100°C \). 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\textsubscript{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\textsubscript{x} (0 ≤ x ≤ 0.35) films magnetron sputtered in various N\textsubscript{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\textsubscript{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\textsubscript{x} films were deposited onto Si(001) substrates by unbalanced reactive d.c. magnetron sputtering in mixed Ar/N\textsubscript{2} discharges. The total pressure was fixed at 3 mTorr, with the N\textsubscript{2} fraction varied from 0 (pure Ar) to 100% (pure N\textsubscript{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 size of \(0.1\) 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 microscopy (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 \(R_D\) and film composition for different growth conditions. Fig. 1 shows \(R_D\) as a function of the N\textsubscript{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\textsubscript{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\textsubscript{2} is mixed in the gas (up to ~5%). When more N\textsubscript{2} is added, the decrease in \(R_D\) is 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\textsubscript{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 \(T_s = 100°C\), where the increase in \(R_D\) can directly be correlated to an increase in N\textsubscript{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\textsubscript{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 sputtering could hardly contribute to the decrease in \( R_\text{D} \), since the energies of the ions impinging onto the growth surface was only in the order of \( \sim 10–15 \) 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 (\( \text{C}^+, \text{C}_2^+, \text{C}^{2+} \)) appear due to sputtering from the graphite target, but in addition also carbon nitrogen species are visible (\( \text{C}_2\text{N}^+, \text{CN}^+, \text{C}_2\text{N}^+ \)), indicating that reactions take place in the deposition chamber. Dominating among the new species is \( \text{C}_2\text{N}_2^+ \) at mass 52, which has more than one order of magnitude larger signal than, e.g. \( \text{C}^+ \). 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.

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 \( \sim 26 \) at.% \( ([\text{N}] / [\text{C}] \sim 0.35) \), but for \( T_s = 550°C \) this value dropped to \( \sim 17 \) at.%. 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 \( \text{CN}_x \) 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 \( \text{N}=\text{N} \) bond is formed and the inert \( \text{N}_2 \) 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 \( \text{C}=\text{N} \) 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 \( \sim 15 \) and 40 at.% were predicted. Very good agreement between experimental and simulated nitrogen concentration profiles in the films was found. However, since the \( \text{C}=\text{N} \) dimer is not a stable satu-
rated molecule, it is more reasonable to assume that
cyanogen \( \text{C}_2\text{N}_2 \) molecules are being emitted, as observed in our study. Also other groups have experi-
mentally verified the presence of \( \text{C}_2\text{N}_2 \) during sputtering or ion beam deposition of \( \text{CN}_x \) thin film[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 im-plant ed, 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( ~ 10–15 eV) implies that the ions would hardly penetrate below the first atomic layers. Ther-
mally 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. Sub-stantial nitrogen-loss is typically observed when annealing
\( \text{CN}_x \) films a few hundred degrees above the deposi-tion temperatu-ral[14–17].

In sputtering depositions, the most important parti-cles that can contribute to the growth, as detected by
mass-spectrometry, are \( \text{C}^+, \text{N}_x^+, \text{N}^+ \) and \( \text{C}_2\text{N}_x^+ \). Neutral carbon atoms will also take part in the growth,
whereas
neutral \( \text{N}_2 \), as discussed above, are unlikely to con-trIBUTE due to the stability of the molecule. The same is
probably also true for neutral \( \text{C}_2\text{N}_2 \) molecules (dissociation energy ~ 5.5 eV[11]).

At impact, the \( \text{N}_2^+ \) ions can dissociate and become loosely bound physisorbed N atoms. At low tempera-
tures the diffusion rate is low and the atoms directly come to rest, and consequently an amorphous mi-crostructure
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 \( \text{N}_2 \) molecule which can desorb is rather high, even at low temperatures. Thus, a nitrogen concen-tra-
tion exceeding ~ 33 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 con-centration exceeding 40 at.% are, however, very rare.

For the deposition of diamond-like carbon(DLC) films, it is well known that for temperatures higher than ~
200°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 \( \text{CN}_x \) films above that temperature, we can assume that N atoms, and possibly also –C≡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 tem-perature, 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.
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$_2$N$_2$ 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≡N dimers are formed, either by dissociation of C$_2$N$_2^+$ ions at impact at the growth surface, or by reactions between C and N on the film surface. These dimers can encounter other –C≡N dimers when diffusing on the surface, to form volatile C$_2$N$_2$ 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≡N in the as-deposited films have been observed by infrared and Raman spectroscopy[2], which indicates that the creation of C$_2$N$_2$ is reasonable. The formation of C$_2$N$_2$ 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 micrographs, 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°C.

For the pure carbon films grown at $T_s = 350°C$ 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 (~ 1.7 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 consists of much smaller, densely packed nodules. No columnar features can be observed. The films grown at 550°C showed a similar microstructure trend as those grown at 350°C, however, with an even more porous structure for low nitrogen concentrations. When grown at 100°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 microcopy images from films grown at 350°C in pure Ar (Fig. 4a, 5% N, 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 $T_s = 350°C$. 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.](attachment:image.jpg)
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\% \( \text{N}_2 \), 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 when 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 \( \text{CN}_{0.15} \) (b), and a \( \text{CN}_{0.25} \) 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 \( \sim 3.5 \text{ Å} \). 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\% \( \text{N}_2 \) were all homogeneously amorphous independently of the nitrogen incorporation. When \( T_S \) was increased up to 550\% \( \text{N}_2 \), the formed 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 \( \text{CN}_x \) 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 \( \text{N}_2 \) and \( \text{C}_2\text{N}_2 \) 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...
of a denser and smoother film. The growth rate and nitrogen incorporation, however, decreases consider-ably.

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 incor-poration.

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