Plasma enhanced deposition of silicon carbonitride thin films and property characterization

Z.X. Cao*

National Laboratory for Surface Physics, Institute of Physics, The Chinese Academy of Sciences, P.O. Box 603, 100080 Beijing, PR China

Received 5 January 2001; accepted 30 May 2001

Abstract

Silicon carbonitride thin films were elaborated by reactive co-sputtering of graphite and silicon onto Si(111) substrates. The low-pressure electron cyclotron wave resonance (ECWR) plasma was radio-frequency biased both to sputter the target and to bombard the growing film at moderate energies (up to 180 eV). X-Ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and atomic force microscopy (AFM) were applied to characterize the deposits. While films grown with pure nitrogen are exclusively amorphous, nanocrystallites are observed in specimens deposited with N$_2$ + Ar mixture and the grain size can be well controlled. Depending on the processing parameters, the films displayed a variety of surface morphologies. The Vickers hardness for amorphous samples is roughly 17 GPa, slightly larger than the maximum value 13.8 GPa measured in crystalline specimens. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silicon carbonitride; Plasma beam assisted deposition; Hard material; Surface morphology

1. Introduction

A few decades of efforts have been devoted to the synthesis and property exploration of ultra-hard materials, namely the diamond and cubic boron nitride (cBN) and a large family of hard materials including carbides, nitrides and borides of silicon, titanium and aluminum, etc. [1]. These materials have attracted interest of researchers from diverse disciplines because they, besides hardness, have also manifested many other extraordinary properties, e.g. the wide band-gap character as dielectric and semiconductor, the enhanced oxidation/corrosion resistance as well as the expected tunability of band-gap. Note, however, that it is nowadays still difficult to obtain single crystalline diamond in large dimensions and the maximum thickness reported for cBN films is only 3 μm [2], this has considerably limited the applicability of these superior materials. In the case of the hypothetical β-C$_3$N$_4$, it is expected to be ‘harder-than-diamond’, even no spur of crystallization could have ever been experimentally ascertained [3]. At the present time, it is desirable to explore some easy-to-made materials that have physical properties approaching cBN, namely of hardness over 3000 kg/mm$^2$ and a band-gap of approximately 4 eV. A few ternary phases of light elements, among which one is the silicon carbonitride, promise to meet these requirements. In recent years, intensive research activities have been executed to the synthesis of materials belonging to this family on conditions that can be achieved as facilely as possible [4–11].

The properties of the ternary Si–C–N system, in particular those of the SiC–Si$_3$N$_4$ composite, have been thoroughly investigated by ceramists since the early 1970s [12]. However, the existence of ternary Si–C–N compounds has been vaguely proposed but it is difficult
to verify with certainty because of the phase separation of SiC and Si$_3$N$_4$ at a nanometer scale. The large (up to tens of microns), well-faceted silicon carbonitride crystals have been successfully synthesized only recently utilizing the chemical vapor deposition (CVD) and reactive magnetron sputtering methods [3,4,8–10]. Interestingly, a Si source in form of precursor gas or target is not always necessary, simply the diffusion from heated silicon substrate would give rise to SiCN crystallites by the undertaking of CN synthesis [13]. As reported by Badzian and Chen, SiCN is a wide band-gap semiconductor, a direct band-gap of approximately 3.8 eV was determined by piezoreflectance spectroscopy and UV absorption measurements [3,10]. Until now on the maximum micro-hardness of only 2777 ± 87 kg/mm$^2$ was measured for SiCN in a MW-CVD deposit [3], the presence of second-phase soft materials in matrix has significantly reduced its resistance to deformation. From the theoretical aspect, SiCN crystals were created on the basis of α- or β-Si$_3$N$_4$ structure with Si partly substituted by C. The mostly investigated forms are Si$_2$CN$_4$ and SiC$_2$N$_4$ to preserve the bonding sp$^3$ character, with the lattice constant occasionally allowed relaxing to the equilibrium configuration [14]. The author has built up the virtual Si$_2$CN$_4$ and SiC$_2$N$_4$ in such a way and eventually raised the lattice symmetry to P3m1, but could not derive a band-gap as large as 3.8 eV from the band structure calculation. This is, of course, not a negation to the experiment but rather a hint of other stoichiometry for SiCN crystallite, or it reminds us of the fact that carbon atoms also exist as interstitials in the Si$_3$N$_4$ network.

The enterprise of crystalline SiCN synthesis is still in its infancy. Much work has to be done in determining the phase diagram of this ternary system, in inferring the growth mechanism of possible crystal forms and so on. It will be appreciable to try out other deposition methods to obtain large crystalline samples, thus further to enable investigation of a wide spectrum of material properties. The phase separation tendency of SiC and Si$_3$N$_4$ may imply that a higher energy barrier has to be overcome to initialize nucleation when preparing SiCN with vapor condensation methods. An effective way for this is to introduce sufficient momentum during film growth. This can be achieved by bombarding the growing surface with ion beam or plasma beam at moderate energies, or even with high-energy electron beam [15,16]. The present article reports the plasma-beam-assisted deposition of nanocrystalline SiCN films. By applying plasma-beam bombardment the nefarious charging effect in insulating materials under ion bombardment can be avoided, hence the film grows under ion bombardment at a well-defined energy. This is fundamental for the understanding of mechanisms relating to bombardment induced phase evolution. The deposits would be inspected with AFM, XPS and XRD methods for the characterization of chemical composition, bonding states, crystallographic order and surface morphology. Also FTIR and indentation measurements were performed to test the optical and mechanical properties.

2. Sample preparation

The films were prepared in a custom-designed UHV chamber, in which the electron cyclotron wave resonance (ECWR) plasma was inductively generated in a glass cylinder at 27.12 MHz. Detailed arrangement of the experimental setup was described elsewhere [17], here only the target was replaced by a slab of silicon on pyrolytic graphite support. By varying the RF-biasing voltage at 54.4 MHz the ion energy can be changed at ease without significantly altering the plasma conditions. Since the ground-plate holding the Si(111) substrate is much larger than the target (> 4:1), the plasma sheath in front of the target shares a dominant portion of the applied voltage. Therefore, while ions sputter the target at over 2 keV, those ions striking the substrate are only of a few tens to 180 eV, depending on the amplitude of the RF-biasing. Before coming to the growing surface, the sputtered Si and C atoms would be post-ionized by the hot electron gas in plasma. The energetic ions striking the surface increased the mobility of atoms at film surface, a favorable condition for the generation of dense phases. Note that the energy for ions extracted from a plasma obeys the Gaussian distribution, the energy values given in the context refer to the center of energy profiles. The full width at half maximum (FWHM) of the energy profile is generally 4 eV in this experiment, as verified using a custom-designed retarding field energy analyzer.

The base pressure in the UHV-chamber was better than 4 × 10$^{-7}$ Pa. During operation of the ECWR plasma, the pressure in glass cylinder was maintained at approximately 10 Pa, while the pressure outside the glass cylinder was only 8 × 10$^{-3}$ Pa. High purity (4 N) nitrogen and argon were introduced into the chamber at well-controlled flux ratios. The films were grown at a typical deposit rate of approximately 4 μm/h for 15–20 min. In order to depress the loss of weakly bonded nitrogen atoms the substrate temperature was raised only to 300°C.

3. Characterization of deposits

Two series of samples were prepared: one in pure nitrogen plasma at varying bombarding energies (up to 180 eV); and the other in plasma of argon and nitrogen mixture with different flux ratios. All the other relevant parameters for plasma operation retained. The samples
were estimated to be $1.0 - 1.2 \mu m$ in thickness by using a stylus method, substrate bending was observed due to accumulated stress in the film.

XPS measurements were first performed for composition and chemical state characterization, using the achromatic MgK$_\alpha$ line in an ESCA-Lab (MarK II, VG) operated at a passing energy of 22 eV. The samples were found containing over 60 at.% carbon, approximately 30 at.\% nitrogen and less than 10 at.\% silicon, depending on the gas mixture and bombarding energy, the concentration fluctuated within approximately 5 at.\% for each component. Prior to the XPS measurement Ar$^+$-sputtering at 1 keV was applied to remove any contaminants during ambient handling. To the chemical state characterization all the spectral lines were calibrated with respect to the Ar$_{2p}$ line set at 324.5 eV, which was well resolved with respect to the N$_{2p}$ line at a distance of 2.1 eV. The binding energy of Si$_{2p}$ line was found slightly below that for Si in $\alpha$-Si$_3$N$_4$ but over that for 4H-SiC, scattered in a range between 102.2 and 102.6 eV see Fig. 1. It shifts slightly to the low energy end at elevated bombarding energy, accompanying the subdued incorporation of nitrogen in film. This suggests the presence of inter-bonded Si–C–N covalent structures in the deposit. Although the C$_{1s}$, centered between 285.2 and 285.7 eV, was broadened (FWHM = 3.56 eV) compared to that in 4H–SiC (FWHM = 2.5 eV), the profile of this spectral line, however, remained unchanged in various SiCN samples. An evident splitting of the C$_{1s}$ line has not been observed as in ref. [8]. The position of N$_{1s}$ line scattered between 399.2 and 400.0 eV. It is much broader (FWHM = 3.1 eV) than the N$_{1s}$ line in $\alpha$-Si$_3$N$_4$ (FWHM = 1.8 eV), showing a hump on the high binding energy side. It can be resolved into two Gaussian profiles, one centered at 398.6 eV and the other at 399.8 eV. The nature of the broad peak at 399.8 eV is rather complicated, it can be attributed to various possible C–N bonds as in amorphous CN$_x$ films [18].

A typical Fourier-transform infrared (FTIR, Nicolet MX-1) spectrum taken on a specimen deposited at 142 eV, $F_{Ar}/F_N = 1:1$, is presented in Fig. 2. The strong, distinct absorption peak at 2200 cm$^{-1}$ features the FTIR spectra of these films. This absorption peak, also observed in CN films, has been assigned to the N=C bond, but other components such as C–N=C and –C=N=N– may also be responsible [18]. A broad absorption band peaked at 1520 cm$^{-1}$ was located between 530 and 1750 cm$^{-1}$. For comparison, the main absorption band was between 880 and 1100 cm$^{-1}$ in $\alpha$-Si$_3$N$_4$ and between 780 and 1170 cm$^{-1}$ in polycrystalline Si–C–N with the carbon concentration below 6 at.\% [3]. Three other additional peaks are identified at 579, 801 and 1086 cm$^{-1}$. The peak at 579 cm$^{-1}$ was reported for $\alpha$-Si$_3$N$_4$, originating in the Si–N bending vibration mode [19].

![Fig. 1. (a) The Si$_{2p}$ line profiles in a series of SiCN samples prepared with flux ratio $F_{Ar}/F_N = 1:2$ at varying bombarding energies. The weak satellites at 99.0 eV are contributed from the exposed Si substrate edge. Also the line profiles in $\alpha$-Si$_3$N$_4$ and 4H-SiC are shown for comparison. (b) Typical N$_{1s}$ and C$_{1s}$ line profiles.](image1)

![Fig. 2. Typical FTIR spectrum of the deposited SiCN films. The arrowed peak at 2200 cm$^{-1}$ indicated the existence of C–N chains.](image2)
below 140 eV, wherein the nitrogen content was above 30.0 at.%, see Fig. 3a. Roughly, the averaged size increased from 400 nm at 80 eV to ~490 nm at 110 eV. At energy above 140 eV, the distinct grains disappeared, the surface instead consisted of compact islands as shown in Fig. 3b. If the nitrogen fraction in the working gas was reduced, patterned morphology due to polymerization of the sample evolved following the increase of carbon content. In extreme cases when the nitrogen fraction is less than 0.35, lamellar structures approximately 100-nm wide dominated the surface morphology (Fig. 3d).

In the XRD (Rigaku, D/max 2400) diffraction spectrum of samples showing crystalline feature in AFM image, besides the strong Si(002) and Si(004) peaks from the substrate, only a broad spectral line peaked at $2\theta = 44.72^\circ$, corresponding to an interplanar distance of $d = 2.025 \text{Å}$, was identified and could be assigned to SiCN (Fig. 4). At this stage, it is clearly impossible to infer further structural information about the SiCN crystals. The appearance of the Si(002) diffraction, of intensity $I_{002}/I_{004} = 5.6\%$, indicated severe stress in Si substrate caused by film deposition. From the shift of the Si(004) peak in respect to the position for strain free silicon at $2\theta = 69.127^\circ$, the stress in substrate resulting from the deposits was estimated to be 68 MPa.

An expected property of crystalline SiCN is its high hardness. The films were tested with nanoindenter (Nano Indenter TM II, MTS) at a constant displacement 200 nm to determine their micro-hardness. In amorphous specimens prepared with pure nitrogen, the Vickers hardness is roughly 17 GPa, and moreover, it is not sensitive to the bombarding energy. In the series of samples deposited at $F_{\text{Ar}}/F_{\text{N}} = 2:1$, the Vickers hardness changes drastically with bombarding energy, as

Fig. 3. AFM revealed surface morphology of SiCN films deposited at (a) $E_b = 80 \text{ eV}, F_{\text{Ar}}/F_{\text{N}} = 2.0$, (b) $E_b = 153 \text{ eV}, F_{\text{Ar}}/F_{\text{N}} = 2.0$, (c) $E_b = 142 \text{ eV}, F_{\text{Ar}}/F_{\text{N}} = 0.8$ and (d) $E_b = 142 \text{ eV}, F_{\text{Ar}}/F_{\text{N}} = 1:3$. The scale to the left of each image indicates the height range that builds up the contrast. $E_b$ is the bombarding energy. The total gas flow is maintained at 4.0 sccm. In the case of (d), the sample contains 67% carbon and only 26% nitrogen.
Fig. 4. X-Ray diffraction pattern of a SiCN specimen prepared at 110 eV, nitrogen flow 2.0 sccm, Ar flow 1.0 sccm. This sample contains 61 at.% carbon, 32 at.% nitrogen and 7 at.% silicon.

presented in Fig. 5. The maximum Vickers hardness is 13.8 GPa measured in sample deposited at 80 eV (corresponding to Fig. 3a). In the sample deposited at 180 eV, the hardness is 300 times smaller, this situation is similar to those samples prepared at very low $F_{\text{Ar}}/F_{\text{N}}$ ratio corresponding to Fig. 3c–d.

4. Discussion

This work initially intended to study the effect of Si admixture on the structure and property of the CN-based materials, since the 3s3p-configuration was thought to be able to stabilize the sp$^3$ hybridized network. Therefore, the films are characterized by low silicon content. It is found that with Si content as large as 10 at.% the films have still insufficient nitrogen regarding the expected (Si,C)$_3$N$_4$ stoichiometry. Two factors are to be blamed. First, the carbon-rich structure could not maintain so large a nitrogen content. This is the main reason that impaired the β-C$_3$N$_4$ synthesis effort. On the other hand, energetic ions striking the surface cause heavy loss of nitrogen from the film, and consequently, reduce the nitrogen content in resulting deposits. It seems meaningful to pose the question that at what a content of carbon, either as substitute or interstitial, can the (Si, C)$_3$N$_4$ stoichiometry be fulfilled.

Though the Si atoms were incorporated into the complex C–N network, the films still contained largely doubly- or triply-bonded CN chained structures that terminate the zig-zag Si–C–N network required for the formation of SiCN crystal. The SiCN crystallites appeared only in films prepared at large nitrogen fraction in plasma and low bombarding energy when the nitrogen content is over 32 at.%. There are always secondary soft materials that considerably reduces the film hardness, renders it less than half the expected value approximately 30 GPa. In extreme cases when polymerization takes place, the films simply become soft. Since even the pure a-C films prepared with the same method was compact at surface and considerably hard, the soft material relating to the lamellar morphology in Fig. 3d was speculated to compose of mainly CN$_{<1}$ chains. The films prepared with pure nitrogen plasma perhaps composed of small grains of nanometer dimension, hence demonstrated a hardness larger than the crystalline SiCN samples. This is reasonable since in such small grains the propagation of dislocations is depressed.

The local atomic order and chemical bonding are very complex in SiCN, especially for carbon. In the amorphous or cluster phases, the carbon atoms can exist in any possible configurations with the bonding orbit containing rather arbitrary s- and p-component. It seems improper simply to refer a three-co-ordinated configuration sp$^2$-bonded and a four-co-ordinated sp$^3$-bonded. The multiple bonding states in the SiCN complex give rise to considerably widened XPS line profiles, but the chemical shift of Si2p line and the profile change of the Cls and N1s lines were not so strikingly large. The identification of chemical states with resolved component spectra should subject to elaborate contemplation.

Ion-assisted film growth is a tradeoff between deposition and sputtering. Clearly, a reduced nitrogen content due to N$^+$- or Ar$^+$-sputtering is detrimental to the synthesis of SiCN crystal. The etching effect also plays a role in the pattern formation on the polymerized surface of C-rich film. Intuitively, an ion source that is able to effectively incorporate momentum into growing surface while giving rise to only less severe sputtering may be most favorable. This condition can be achievable when the incident angle for the ion beam is larger.

Fig. 5. (a) Variation of the micro-hardness with bombarding energy in specimens prepared at $F_{\text{N}}/F_{\text{Ar}} = 2.0$. 
than 70° from the substrate normal. This adventure is currently being undertaken in our laboratory.

5. Conclusion

Preparation of SiCN thin films could proceed under control with ECWR-plasma beam assisted deposition. At a bombarding energy up to 180 eV the films are uniquely amorphous when deposited with pure nitrogen plasma. Nanocrystalline specimens ensued when a small fraction of argon was added and at low bombarding energy (< 140 eV). The grain varies in between 400 and 490 nm in size with deposition parameters. A maximum micro-hardness of 13.8 GPa was measured in crystalline specimens, slightly less than in amorphous films. The sample is expected to demonstrate larger hardness when the soft amorphous CN phases are reduced on properly chosen deposition conditions.

Acknowledgements

This work was supported by the National Natural Science Foundation (NNSF) of China grant no. 19974065, by the Volkswagen-Stiftung grant no. I74701 and by the Chinese Academy of Sciences. The author is indebted to Prof. H. Oechsner for his constructive advice in the due course of this program and for his allowing me to utilize the facilities in the Institut für Oberflächen-und Schichtanalytik, Kaiserslautern, Germany.

References