Nanocrystalline silicon carbonitride thin films prepared by plasma beam-assisted deposition

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Abstract

Nanocrystalline silicon carbonitride thin films were prepared by reactive co-sputtering of graphite and silicon on Si(111) substrates. Asymmetrical RF biasing of the plasma served to sputter the target at high energy (>2 keV) and to simultaneously bombard the growing film at moderate energy (up to 180 eV). The films grown with pure nitrogen gas are exclusively amorphous. Nanocrystallites of 400–490 nm in size were observed by atomic force microscopy in films deposited with a mixture of N$_2$+Ar. Films of greater carbon content were polymerized, displaying a lamellar morphology. A maximum Vickers hardness of 14.1 GPa was measured in crystalline specimens. The films were further characterized by X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy and X-ray diffraction. Quantification of the XPS data proceeded with relative sensitivity factors established on stoichiometric 4H-SiC and α-Si$_3$N$_4$ standards ($S_{Si}/S_{C}$ = 1:1.37, $S_{Si}/S_{N}$ = 1:1.16). The results measured are briefly discussed with reference to the deposition parameters. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon carbonitride; Plasma processing and deposition; Nanostructures; Ion bombardment

1. Introduction

The family of covalent materials from light elements, i.e. boron, carbon, nitrogen and silicon, as well as aluminum, has manifested many extraordinary physical, chemical and mechanical properties. Often they are semiconductors of wide bandgap, chemically inert and superhard due to the nature of the strong covalent bonds [1]. A great demand exists to explore the exceptional properties of known materials in this family for many significant applications and to push the limits of currently available materials. In the past decades, many efforts have been devoted to the synthesis of materials belonging to this family [1–4]. Remarkable examples of this enterprise are the fabrication of cBN and the hypothetical β-C$_3$N$_4$ (for a critical comment on the history of β-C$_3$N$_4$, see Badzian et al. [5]), for which a number of deposition techniques have been employed.

As a reward, some novel deposition methods have emerged and a gradual deepening of the understanding of the materials science for this family of materials has occurred.

Since the 1970s, ceramists have energetically investigated the properties of the Si–C–N system and SiC–Si$_3$N$_4$ composites [6]. The existence of ternary Si–C–N compounds, however, has been vaguely proposed, but is difficult to verify with certainty because of the tendency of SiC and Si$_3$N$_4$ to undergo nanophase separation. Large (up to 10s of μm), well-faceted silicon carbonitride crystals (not the SiC–Si$_3$N$_4$ composite) have only been successfully fabricated in recent years in the laboratories of Badzian [5,7] and Chen [8,9] utilizing the microwave plasma-enhanced chemical vapor deposition (MW-CVD) method. Deposition of polycrystalline SiCN using magnetron sputtering and hot-filament CVD has also been reported [10–12]. Interestingly, a source of Si in form of a precursor gas or target is not always necessary; simply the silicon substrate, when deposited with C and N under suitable...
conditions, would give rise to the formation of SiCN crystallites [7,12]. As expected, SiCN is a wide bandgap semiconductor, a direct bandgap of ca. 3.8 eV was determined by piezoreflectance spectroscopy and UV absorption measurements [7,8]. A microhardness of $2777 \pm 87 \text{ kg mm}^{-2}$ was measured in MW-CVD-deposited SiCN [5], but this is believed to be significantly below the upper limit it may reach, since the presence of second-phase soft materials in the matrix may significantly reduce its resistance to deformation.

The synthesis of crystalline SiCN is still a new enterprise, leaving much to be carried out in determining the phase diagram of this ternary system, in inferring the growth mechanism of possible crystal forms, and so on. Trying other deposition methods and further study of the properties of the deposits obtained represent an appreciable effort. It is reasonable to believe, as experienced in synthesizing cBN, that SiCN has to overcome a high energy barrier to initialize nucleation. Therefore, it is essential to introduce sufficient momentum into the growing film by growing SiCN under low-pressure low-temperature (LPLT) conditions. This can be achieved by bombarding the growing surface with an ion or plasma beam at moderate energy.

The present article reports on the plasma beam-assisted deposition of nanocrystalline SiCN films. By applying plasma-beam bombardment, the ion energy is free of shift caused by the notorious charging effect that accompanies ion-beam bombardment of insulating materials. Thus, it allows the film growth to proceed under ion bombardment at a well-defined energy. This is essential for understanding the role of ion bombardment in initiating and enhancing the nucleation process. The atomic concentration of Si in the films was controlled to be less than 10 at.%, since it was originally the possible promotion of crystallization of CN by Si (the coupling with 3d orbitals may stabilize the structure) that was of interest. The deposits were then inspected by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to characterize the chemical composition, bonding states, crystallographic order and the surface morphology. Fourier-transform infrared spectroscopy (FT-IR) and indentation measurements were also performed to test the optical and mechanical properties. In discussing the bonding states from XPS data, a short discussion of the limit of XPS in identifying the subtle differences in chemical environments in CN and SiCN is given.

2. Experimental

Film deposition was conducted in a custom-designed UHV chamber, in which the electron-cyclotron-wave-resonance (ECWR) plasma was inductively generated at 27.12 MHz in a glass cylinder. There are evident merits in applying ECWR-plasma to the deposition of SiCN films: (a) the very low pressure and post-ionization process ensure that ionic species arriving at the substrate are predominantly atomic ions; (b) the reaction processes are relatively simple in a hydrogen-free atmosphere; and (c) it allows changes in ion energy without significantly altering the plasma conditions. Detailed arrangements of the experimental set-up are described elsewhere (see [13] and references therein). Briefly, the silicon (111) substrate was mounted on the ground plate at one end of the glass cylinder, with a metal rod covered by graphite and silicon as target at the opposite end of the cylinder. A capacitive biasing voltage at 54.4 MHz was supplied between the target and the ground-plate holding the substrate. Since the ground-plate is much larger than the target ($>4:1$), a dominant portion of the potential drops across the sheath in front of the smaller electrode, the target [14]. Therefore, while the energy of ions sputtering the target was as high as over 2 keV, the ion energy for the bombardment of the growing films was maintained at a few 10s to 180 eV. The ion energy values given here refer to the center of the Gaussian profiles, which show a typical full-width at half-maximum (FWHM) of 4 eV, as determined using a custom-designed retarding-field energy analyzer. The sputtered Si and C atoms are post-ionized on their way through the plasma, and together with the nitrogen ions they are accelerated towards the substrate and deposited on the fresh surface. The energetic ions striking the surface introduce the surplus momentum necessary to overcome the barrier to nucleation and to elevate the mobility of deposited atoms.

The base pressure in the UHV chamber was better than $4 \times 10^{-7}$ Pa. During operation of the ECWR plasma, the pressure in glass cylinder was maintained at ca. 10 Pa, while the pressure outside the glass cylinder was only $8 \times 10^{-3}$ Pa. High-purity (4N) nitrogen and argon were introduced into the chamber at a well-controlled flux ratio. The films were grown at a typical deposition rate of approximately 4 μm h$^{-1}$ for 15–20 min. In order to suppress the loss of weakly bonded nitrogen atoms, the substrate temperature was raised to only 300°C. The films were taken out to the ambient environment for ex situ characterization only after gradual cooling to room temperature in the vacuum chamber, otherwise exfoliation ensued.

A rigorous determination of the film thickness by a stylus method was hampered by bending of the substrate due to accumulated stress in the films. Generally, the films have a thickness of 1.0–1.2 μm. Therefore, by determining the microhardness with an indentation method (Nano Indenter™ II, MTS), the measurement was performed at a constant displacement of 200 nm to exclude the influence of the substrate. AFM (Park Instrumentation II) was applied to examine the surface morphology of the deposits. All images were obtained in the contact mode in ambient conditions. For those
films exhibiting crystallites in AFM images, XRD (Rigaku, D/Max 2400) was conducted with the CuKα line to obtain more crystallographic information. FT-IR spectroscopic measurement was performed on a Nicolet MX-I apparatus to study the optical property of the deposits. The spectrum was recorded in the transmission geometry at a resolution of 4 cm⁻¹ per step in the range 400–4000 cm⁻¹. After recording a spectrum of the film on a substrate, the contribution of the substrate was numerically ratioed out.

In the presence of the silicon substrate, the composition of the SiCN system deposited could not be resolved in a straightforward manner using the energy-dispersive X-ray (EDX) analysis that provides reliable bulk information. Fortunately, no strong segregation is expected in covalent SiCN systems, and thus the XPS peak intensities can be taken with confidence to calculate the atomic concentrations of C and Si varied rather irregularly. The carbon concentration reached the maximum value of 67.9 at.% at η = 0.45, whereas the largest silicon concentration, 10 at.%, was achieved at η = 0.25. This is quite understandable, since the concentrations of Si and C depend in a complex manner upon many factors, e.g. the target, the energy and species of ions striking the target, the ionization process in the bulk plasma and the bombardment behavior of the growing film.

The spectral profiles of the Si 2p, C 1s and N 1s lines were recorded at high resolution to investigate the chemical bonding states (Fig. 2). Since the SiCN compound is a good insulator with electrical resistivity being too high to be measured, charging effects inevitably come into play under X-ray irradiation. All spectral lines were calibrated with respect to the Ar 2p₃/₂ line set at 241.9 eV [15]. The binding energy of the Si 2p line was found slightly below that for Si in α-Si₃N₄, scattered in a range between 102.2 and 102.6 eV. The weak satellites at 99.0 eV were contributed from the exposed Si substrate edge. Although the C 1s line, centered between 285.2 and 285.7 eV, was broadened (FWHM = 2.7 eV) compared to that in 4H-SiC (FWHM = 2.5 eV), its profile remained unchanged in various SiCN samples. An evident splitting of the C 1s line has not been observed as in [10]. The position of the N 1s line varied between 389.2 and 400.0 eV. It is

3. Characterization

Some 30 SiCN deposits were prepared at different bombarding ion energy and varying gas mixtures. The maximum bombarding ion energy applied for this experiment was 180 eV. XPS spectroscopy was first employed to determine the composition of the deposits and the chemical states of the constituent elements. The relative sensitivity factors for the Si 2p, C 1s and N 1s lines were inferred from measurements on stoichiometric 4H-SiC and α-Si₃N₄ standards. In Table 1, the compositions for a series of samples deposited at constant nitrogen fraction η, η = Fₙ/(Fₙ + Fₐ), are compiled. With increasing ion energy up to 140 eV, the atomic concentrations of C and N decreased by less than 2.5 at.%; at 153 eV, the N concentration decreased to 26.0 at.%, while the C concentration experienced an abrupt increase of 7.4 at.%, reaching 67.7 at.%. Fig. 1 represents the N concentration in a series of specimens prepared at a fixed bombarding energy of 142 eV. It exhibits a general trend of diminishing nitrogen incorporation in the film when the plasma is operated at a low nitrogen fraction. However, in the vicinity of η = 0.35, the N concentration displayed an evident local maximum. This has significant implications in relating the film properties to plasma conditions, as will become clear later. The concentrations of C and Si varied rather irregularly. The carbon concentration reached the maximum value of 67.9 at.% at η = 0.45, whereas the largest silicon concentration, 10 at.%, was achieved at η = 0.25. This is quite understandable, since the concentrations of Si and C depend in a complex manner upon many factors, e.g. the target, the energy and species of ions striking the target, the ionization process in the bulk plasma and the bombardment behavior of the growing film.

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### Table 1

Atomic concentrations of Si, C and N in the deposits prepared with varying bombarding energy

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Ion energy (eV)</th>
<th>Concentration (at.%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>E.1</td>
<td>80</td>
<td>4.4</td>
</tr>
<tr>
<td>E.2</td>
<td>93</td>
<td>5.5</td>
</tr>
<tr>
<td>E.3</td>
<td>110</td>
<td>6.8</td>
</tr>
<tr>
<td>E.4</td>
<td>124</td>
<td>8.1</td>
</tr>
<tr>
<td>E.5</td>
<td>140</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Nitrogen fraction in gas mixture is fixed; N₂ flow rate 2.0 sccm, Ar flow rate 1.0 sccm.
Accordingly, from the XRD diffraction spectrum, only very fine crystallites below the resolution of the AFM. Simply amorphous or, if crystallized, contained only barding energy even up to 180 eV, the deposits were FWHM of 2.7 eV.

A broad spectral line peaked at 2θ = 2θ, corresponding to an interplanar distance of d = 2θ, was assigned to SiCN (Fig. 5). At the current stage, it is still impossible to confirm the crystal structure possibly responsible for this peak. From the shift of the Si(004) peak with respect to the position for strain-free silicon at 2θ = 44.72°, the strain was estimated to be 4.12 × 10⁻², and hence the stress in the substrate resulting from the deposits was 68 MPa. This may be due to the excess momentum caused by ion bombardment and to the rapid cooling of the substrate when the plasma was turned off. The strain in the substrate caused the Si(002) peak to appear at 2θ = 33.02°, and the intensity ratio I_{002}/I_{004} was 5.6%.

The microhardness of the deposits was tested by indentation at a constant displacement of 200 nm into the specimens. The eventual values presented here are the average of some 20 measurements on each specimen, scattering within ±5%. Generally, the hardness has a value lower than 2777 kg mm⁻² (or 27.2 GPa) recorded on the samples in [5]. The maximum Vickers hardness was 14.1 GPa for the deposits prepared with a mixture of N₂ + Ar, and it was found that the Vickers hardness was sensitive to the deposition parameters. Fig. 6a shows the variation in hardness with bombarding ion energy. The data points refer to the AFM images in Fig. 3. For samples showing crystallites, the Vickers hardness decreased slightly with increasing grain size, in agreement with the Hall–Petch relation. At still higher energy, when the sample surface was covered by large islands.

Fig. 2. (a) The Si 2p line profiles in the XPS spectra from a series of SiCN samples specified in Table 1. The Si 2p line profiles in α-Si₃N₄ and 4H-SiC (dashed line) are also presented for comparison. (b) Typical N 1s and C 1s line profiles.

When prepared with pure nitrogen plasma at bombarding energy even up to 180 eV, the deposits were simply amorphous or, if crystallized, contained only very fine crystallites below the resolution of the AFM. Accordingly, from the XRD diffraction spectrum, only the Si(002) and Si(004) peaks were identified. The AFM images obtained on an area of 10 × 10 µm in these samples did not display any distinct features. The surface was very flat, with a typical root mean square (RMS) roughness of 1.4 nm. However, these amorphous films are considerably hard. The average Vickers hardness measured with indentation was as high as 17 GPa.

In the presence of Ar in the working gas, crystallization took place in the deposits. The AFM images show rich features. Fig. 3 shows the AFM height image in SiCN samples deposited at different energy, while the flow rate was fixed. In Fig. 3a,b, the surfaces showed much broader (FWHM = 3.1 eV) than the N 1s line in α-Si₃N₄ (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 with a FWHM of 1.4 eV and the other at 399.8 eV with a FWHM of 2.7 eV.

In the presence of Ar in the working gas, crystallization took place in the deposits. The AFM images show rich features. Fig. 3 shows the AFM height image in SiCN samples deposited at different energy, while the flow rate was fixed. In Fig. 3a,b, the surfaces showed regular, crystalline aggregates with an aspect ratio of nearly 1:1. The grain size, either defined as the average intercept length along a random line, or as the average section diameter on a planar section, took nearly the same value. This increased from ca. 400 nm in Fig. 3a to ca. 490 nm when the ion energy was elevated. At the same time, the surface became flatter and the RMS roughness decreased from 24.5 to 11.6 nm. In Fig. 3c, the surface instead consisted of rotund islands separated by distinct boundaries, yet the RMS roughness changed only slightly, being 14.1 nm. When the ion energy was increased to 153 eV, the surface morphology of the deposits drastically changed. A lamellar structure of ca. 1 µm in width dominated on the surface in Fig. 3d. In this sample, the larger carbon content conferred a polymerized character on the film. Ignoring Fig. 4d for the moment, the surface morphology of the series of SiCN compounds deposited at constant energy demonstrated a clear trend of a polymerized surface with decreasing nitrogen fraction (Fig. 4). The surface developed from a compact one through a stage of granular structures to the lamellar structure in Fig. 4e. The abnormal flatness of the surface in Fig. 4d is ascribed to the high N⁺ portion in the plasma at that nitrogen fraction.

The specimens showing distinct crystallites in the AFM images were investigated by X-ray diffraction. A broad spectral line peaked at 2θ = 44.72°, corresponding to an interplanar distance of d = 2θ, was assigned to SiCN (Fig. 5). At the current stage, it is still impossible to confirm the crystal structure possibly responsible for this peak. From the shift of the Si(004) peak with respect to the position for strain-free silicon at 2θ = 69.127°, the strain was estimated to be 4.12 × 10⁻², and hence the stress in the substrate resulting from the deposits was 68 MPa. This may be due to the excess momentum caused by ion bombardment and to the rapid cooling of the substrate when the plasma was turned off. The strain in the substrate caused the Si(002) peak to appear at 2θ = 33.02°, and the intensity ratio I_{002}/I_{004} was 5.6%.

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or even polymerized, the microhardness became drastically reduced. For the sample with a lamellar surface, the microhardness is nearly 300-fold lower. In Fig. 6b, the variation in the microhardness, together with the RMS roughness, is plotted vs. the fraction of nitrogen in the working gas. These two quantities showed opposite trends. In general, the samples became softer with increasing nitrogen fraction, but in the vicinity of $\eta = 0.35$, the hardness value showed a marked local maximum. The RMS roughness displayed a minimum in this range.

The optical properties of the deposits were investigated with Raman and FT-IR spectroscopy. No distinct Raman lines could be observed in the deposits due to the intense atomic disorder. Fig. 7 depicts a typical infrared spectrum. A broad main absorption band with the peak at 1520 cm$^{-1}$ was located between 530 and 1750 cm$^{-1}$. For comparison, the main absorption band was between 880 and 1100 cm$^{-1}$ for $\alpha$-Si$_3$N$_4$ and between 780 and 1170 cm$^{-1}$ for polycrystalline Si–C–N with the carbon concentration below 6.0 at.% [5]. Ta–C films deposited using the same technique also displayed an absorption band in this range, but centered at 1240 cm$^{-1}$. Three other additional peaks are identified at 579 (having been reported for $\alpha$-Si$_3$N$_4$ [16]), 801 and 1086 cm$^{-1}$. The strong, distinct absorption peak at 2200 cm$^{-1}$ has been observed in pure CN films and was assigned to the C≡N bond, but the situation is not so simple. Many other components, such as C–N$^+$≡C– and $\cdot$C≡N≡N– may also contribute to the absorption band in this region [3]. An unambiguous assertion about the nature of this peak requires more meticulous work.

4. Discussion

Plasma beam bombardment has proved to be an effective tool for incorporating momentum into the growing films to promote the ‘sp$^3$ bonding’ required for the nucleation of superhard phases. In the case of cBN synthesis, it is well established that the cubic phase appears in a definite energy window depending on other deposition parameters, and cBN has been successfully produced both with a mixture of N$_2$ and an inert gas, and pure nitrogen at comparable ion energy values [18].
It is surprising to find that, under otherwise similar conditions, SiCN crystallites appeared (already at 80 eV) only under bombardment with the gas mixture. Even up to 180 eV, there was still no sign of crystallization in films deposited with pure nitrogen. A new atomic model is desirable to understand this behavior, since the current models for bombardment-enhanced crystallization essentially do not distinguish between the species of ions applied, although the energy windows might be changed when different ions are employed.

Amorphous samples prepared with pure nitrogen and those samples showing SiCN crystallites are hard materials, yet their hardness is lower than the value of 6500 kg mm$^{-2}$ for amorphous Si–C–N compounds found in [17] and the value of 2777 kg mm$^{-2}$ for polycrystalline SiCN in [5]. The reason is due to the extremely high
concentration of carbon (over 60 at.%) in samples prepared in this experiment; the mesophase structures embedded in amorphous materials have considerably abased the resistance to applied shear stress.

In the case of higher bombarding energy or low nitrogen fraction resulting in polymerization (Fig. 3d and Fig. 4e), the samples became significantly rough and soft. Although the ECWR plasma was operated at very low pressure, which is believed to depress the generation of $\mathrm{C}═\mathrm{N}^–$ like components, the samples still contain a large content of $\mathrm{C}═\mathrm{N}^–$ components, as revealed by the FT-IR spectrum. Higher bombarding energy would destroy the weak bonding of N atoms in these materials, and thus the crystallization environment for a stoichiometric deposit. The possible CN groups, such as $\equiv \mathrm{N}═\mathrm{C}═\equiv$, $\equiv \mathrm{C}═\mathrm{N}═\equiv$ and other similar groups, are linear and continuous, and they impose conditions on the structure of the material that may lead to polymerization. For the series of samples prepared at fixed bombarding energy with decreasing nitrogen fraction, the trend in the variation of surface morphology, roughness and phase-image features was in accordance with the microhardness. However, how to relate the topographical features to the mechanical properties of the samples is not well understood at present. The nitrogen content in films, and the hardness and surface morphology all displayed a local maximum and inflexion feature near $\eta = 0.35$. Similar behavior has also been observed for CN films deposited with a plasma beam in the measurement of the optical bandgap and microhardness [19]. This is correlated with the maximum $\mathrm{N}^+$ fraction in the ion species available in plasma at this gas composition. Deposition of CN and SiCN with a mass-separated plasma beam to distinguish the effects of $\mathrm{N}^+$ ions from molecular $\mathrm{N}_2^+$ ions is now being carried out in our laboratory.

The bonding states for Si and C are quite simple in the deposits; both the Si 2p and C 1s lines are only slightly broadened in comparison to those in 4H-SiC. This implies that the chemical environment for the Si atoms is quite homogeneous. The binding energy of the

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**Fig. 5.** X-Ray diffraction pattern of a SiCN specimen prepared at 140 eV, nitrogen flow rate 2.0 sccm, Ar flow rate 1.0 sccm.

**Fig. 6.** (a) Variation of the micro-hardness with bombarding energy in specimens specified in Table 1; (b) Variations of the micro-hardness (solid line) and RMS roughness (dashed line) with nitrogen fraction. Deposits in (b) were prepared at a bombarding energy of 142 eV.

**Fig. 7.** Typical FT-IR spectrum of the SiCN films deposited.
Si 2p line is slightly lower than in $\alpha$-Si$_3$N$_4$, as expected, since when surrounded by both C and N atoms, the charge transfer from Si atoms is less severe than in $\alpha$-Si$_3$N$_4$. In the N 1s profile, the small satellite at 403.734 eV is assigned to the N–N bond, and the component at 398.6 eV arises from the local Si–C–N bonding configuration. For comparison, the N 1s line in $\alpha$-Si$_3$N$_4$ is at 398.2 eV. The broad peak at 399.8 eV can be ascribed with certainty to the N–N bond, which is consistent with the measurements in CN films. Generally speaking, it is difficult to correlate the resolved component peak with a specific bonding state of an atom pair, since the chemical shifts in XPS spectra are not always large enough to allow two bonding states to be distinguished. For example, the C 1s line in ethyl trifluoroacetate (C$_2$H$_5$F$_3$O$_2$H$_4$) shows five distinct peaks spread over a range of 8 eV, but in various carbon allotropes, it lies in a very narrow region between 284.3 and 285.0 eV. For atoms in CN, BCN and SiCN systems, their XPS lines rarely exhibit separate peaks that allow unambiguous assertion of the chemical states that have often been termed sp$^3$ or sp$^3$ bonding in the literature.

5. Conclusions

Nanocrystalline SiCN can be prepared using ECWR plasma beam-assisted deposition, when the plasma is operated with a mixture of N$_2$+Ar. The deposits prepared with nitrogen plasma were amorphous at bombarding energy up to 180 eV in this experiment. A combination of surface analysis methods has been applied to characterize the deposits to measure the stoichiometry, chemical bonding and surface morphology, as well as to verify the reproducibility. A maximum microhardness of 14.1 GPa was measured in crystalline specimens. The sample is expected to demonstrate great hardness when the soft, amorphous CN phases are reduced under properly chosen deposition conditions.

In future work, the deposition of SiCN will be conducted with an enlarged Si target to increase the Si content in the deposits. Efforts will be devoted to clarifying the crystallization mechanism of SiCN under plasma beam bombardment, in particular to determine under which conditions SiCN films begin to crystallize when the plasma is operated with pure nitrogen gas.

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