

Crystalline SiCN: a hard material rivals to cubic BN

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Abstract

Growth and mechanical properties of SiCN materials prepared by microwave plasma enhanced chemical vapor deposition (CVD) as well as electron cyclotron resonance plasma CVD are reported. Large (several tens of microns), well-faceted ternary SiCN crystals were grown by microwave plasma-enhanced chemical vapor deposition, whereas amorphous SiCN films were deposited by ECR-CVD. The ternary crystalline compound (C; Si)_xN_y exhibits a hexagonal structure and consists of a network wherein the Si and C are substitutional elements. While the N content of the crystalline compound is about 50 at.%, the extent of Si substitution varies and can be as low as 10 at.%. The amorphous SiCN films contain only about 30 at.% N. Nano-indentation studies were employed to investigate the mechanical properties of the SiCN materials. From the load versus displacement curves, we estimated the hardness and the effective modulus of the SiCN crystals to be around 30 and 321.7 GPa, respectively. The corresponding values for the amorphous SiCN were around 22 and 164.4 GPa, respectively. These values are well above most reported values for CN films. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystalline SiCN; Cubic BN; Chemical vapor deposition; Growth and mechanical properties

1. Introduction

Covalently bonded crystalline carbon nitride (*c*-CN), preferably in the β -C₃N₄ structure that is isomorphic to β -Si₃N₄, has long been predicted to have a bulk modulus comparable to that of diamond [1–4]. However, growth of binary *c*-CN with crystal sizes large enough to enable measurement of its properties has not been achieved so far. Interestingly, exceptional hardness and yield strength have been reported for some CN films even with a very limited degree of crystallinity [5–9]. Hardness of CN films up to 20 GPa has been reported experimentally. Whereas a value about 73 GPa for β -C₃N₄ has been estimated by using an empirical model [10], in which the hardness and bulk modulus are derived from the average period number of constituent elements (*P*), the inter-atomic distance (*D*) and the degree of bond covalence (*C*). According to this PDC model, estimated hardness values for diamond, cubic BN, Si₃N₄, SiC and Si are 76.9, 62.5, 34.7, 33.1 and 14 GPa, respectively. Measured values are usually lower than calculated ones due to imperfection of crystals. Variation in the hardness of the same material prepared under different process conditions is also observed.

In contrast to the binary CN system, large (several tens of

microns), well-faceted ternary silicon carbon nitride (SiCN) crystals have been successfully grown by microwave plasma-enhanced chemical vapor deposition (MWCVD) [11–16]. Bendeddouche et al., and Gomez et al., proposed that a SiCN based alloy should have properties between silicon nitride and carbon nitride [17,18]. In other words, it should be a hard material with a wide band gap. Indeed, optical investigation of the polycrystalline SiCN films indicated a direct band gap of about 3.8 eV and a strong optical emission around 2.8 eV [14,19]. Thus, the ternary SiCN compound constitutes an important addition to the wide band gap material with gap energies within the blue-UV spectral region. In this article, we present nanoindentation measurements and further demonstrate the promising mechanical properties of crystalline SiCN.

The area of research in the mechanical properties of the ternary SiCN system is fairly open. Amorphous SiCN films have been deposited by electron cyclotron resonance (ECR) plasma-enhanced CVD, charge-coupled plasma CVD and pulsed laser ablation [18,20,21]. For the amorphous samples prepared by charge-coupled plasma CVD, microhardness was measured to be about 10–20 GPa dependent on the film composition [20]. Riedel et al., used polyorganosilyl-carbodiimides as precursor materials and have successfully produced nanocrystalline Si₂CN₄ [22]. However, no mechanical data for their materials were given. To our

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knowledge, the present work is a first report on the mechanical property of crystalline SiCN.

2. Experimental

The SiCN films were deposited on Si(100) substrates in an AsTex 5 kW microwave reactor. A mixture of semiconductor grade H_2 , CH_4 , N_2 and SiH_4 (5% SiH_4 in N_2 dilution) gases in various proportions was used for deposition of these films. Typical flow rates were 80 sccm for H_2 , 20 sccm for CH_4 , and 80 sccm for N_2 while the flow rate for SiH_4 was varied between 0–10 sccm. For any given microwave power, the chamber pressure was tuned so that the plasma was most stable. For instance, typical chamber pressure was maintained at 8 kPa when the microwave power was kept at 2 kW. The range of substrate temperature was varied between 400–1200°C. An independent RF heater was used to control the substrate temperature. During deposition, a single-color optical pyrometer was used to read the temperature from the front surface of the substrate.

Chemical composition of individual crystal was studied using a Perkin Elmer scanning Auger nanoprobe system (SAN 760) at an electron primary energy of 3 keV. Auger electron spectra were obtained in the usual derivative mode, and the Si:C:N ratio was determined from the peak-to-peak Auger intensities, scaled by the relative sensitivity factors [23]. In addition, depth profiling with a probe size smaller than the crystal dimension is used.

To evaluate the mechanical behavior of the SiCN films, nanoindentation tests were carried out by using a TriboScope instrument made by Hysitron Inc. Indentations were made by a Berkovich (3-faced pyramid) diamond tip using a single loading-unloading cycle. A 5-second constant-load hold segment was used at maximum load to allow any thermal drift of the instrument to be estimated and corrected for. Indentations were made with a maximum load of 500 μN , with at least 6 indent sequences for each load. The indenter tip shape had been calibrated following the procedure described by Oliver and Pharr [24] and a quartz standard was used to check the calibration of hardness measurement. The upper part of the loading curve was fitted by a power-law to determine the hardness and Young's modulus [24].

3. Results and discussions

Up to a deposition temperature of about 550°C and a SiH_4 flow rate of about 4 sccm, the coatings were amorphous. Above 800°C and 8 sccm SiH_4 , the coatings were completely crystalline. If a mixture of crystalline and amorphous phases was observed in the same film, the latter one appeared as a smooth background coating on the substrate (Fig. 1). In general, the higher the SiH_4 flow ratio, the lower the substrate temperature it required to form crystalline phases in the films. In the extreme case that no SiH_4 was provided, SiCN crystallites were formed primarily by

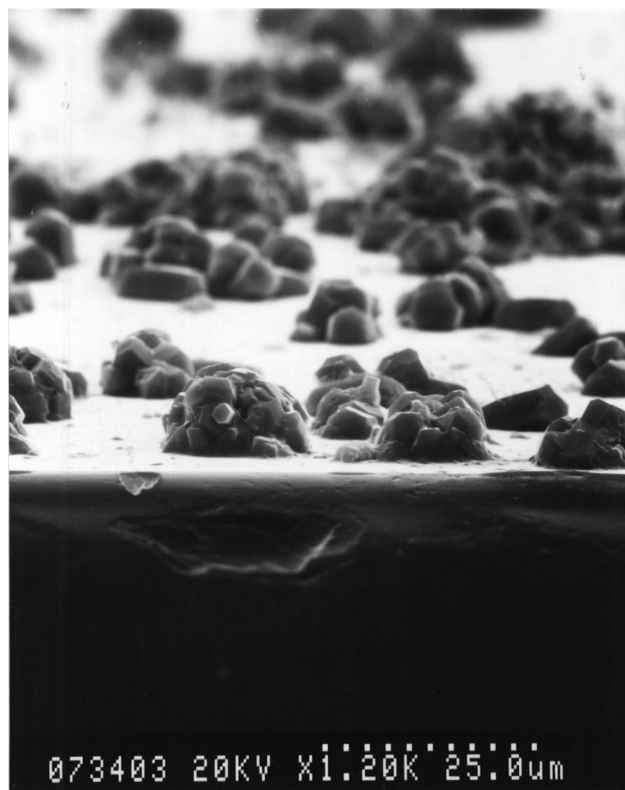


Fig. 1. Typical SEM micrograph of a SiCN film prepared under the conditions where mixtures of amorphous and crystalline phases are observed.

chemical reactions between the Si substrate and gaseous species in the plasma at high temperature. Silicon incorporation in the growth of CN crystal via solid-gas reaction occurred at substrate temperatures above 1000°C.

It is noted that samples prepared with low SiH_4 flow ratio or without any SiH_4 addition exhibited low nucleation density, leading to the growth of scattered SiCN crystals on the substrates. In contrast, samples deposited with high SiH_4 flow ratio exhibited high nucleation density, leading to the growth of nearly continuous films. Further enhancement in the nucleation density can be achieved by using two-step growth wherein a buffer layer was first deposited by ECR-CVD technique before the microwave CVD process [25]. However, the average grain size of the polycrystalline film with improved continuity was somewhat smaller due to growth limited by impingement.

A typical scanning electron microscopy (SEM) micrograph of our crystalline sample shows large crystallites of dimensions on the order of tens of microns (Fig. 2). Many rod-shaped crystals exhibit hexagonal cross-sections. Auger spectra taken on the crystals indicated the presence of Si, C, and N, whereas O was observed as a minor impurity element. It should be mentioned that the probe size used for Auger analyses was smaller than the crystal size to ensure that all the signals were generated within an individual crystal. A typical Auger depth profile of the crystal is shown in Fig. 3, where the atomic concentration of each

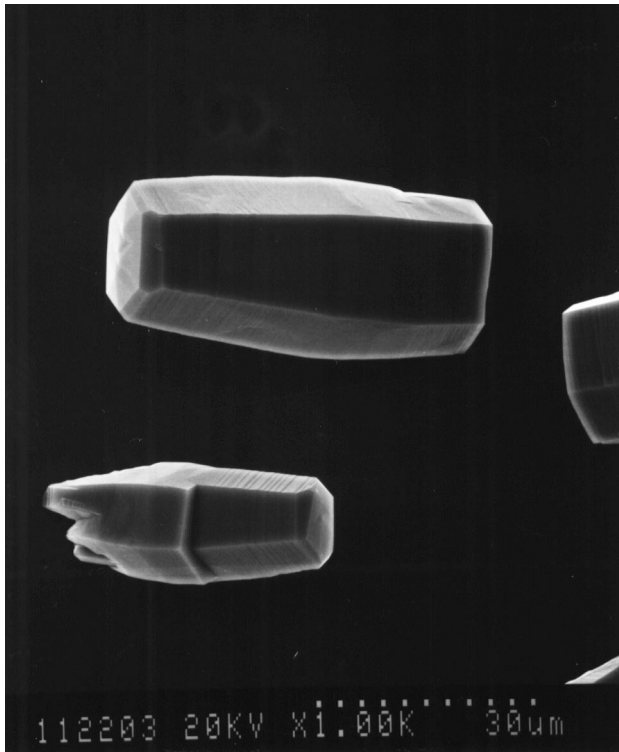


Fig. 2. SEM image of rod-shaped SiCN crystals exhibiting a six-sided cross-section.

constituent element is shown. For this particular crystal, [N] varies between 45–55 at.%, [C] between 30–40 at.%, and [Si] between 10–20 at.%. The scanning Auger studies also confirmed that any of the large crystals are neither ‘pure’ Si_3N_4 nor ‘pure’ C_3N_4 . Apart from some crystal-to-crystal variations in Si:C:N, all three elements are present in all the crystals we investigated. Hence, it is quite clear that the formation of this new compound can not be attributed to the intermixing of two binary phases such as Si_3N_4 and SiC, nor the graphite immersed in a Si_3N_4 matrix.

For comparison, an Auger depth profile of amorphous

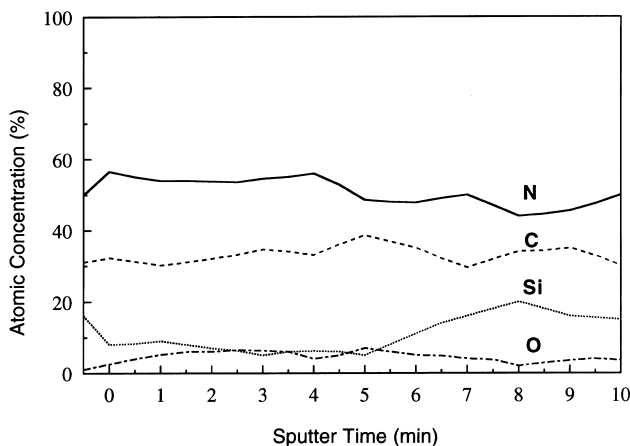


Fig. 3. Typical scanning Auger depth profile of a SiCN crystal.

SiCN is shown in Fig. 4. There is virtually no fluctuation in the composition of the amorphous film. The results of composition determined for a number of crystallites and various amorphous regions of SiCN films grown at 900°C are depicted in Fig. 5. It is noted that the nitrogen content in the amorphous film was lower than that in the crystalline counterpart. The average [N] for the crystalline phase was about 50 at.%, only slightly less than the theoretical value for the C_3N_4 or Si_3N_4 . Furthermore, variation in the nitrogen content for crystalline SiCN was also less than that in the silicon and carbon contents, exemplifying the substitutional nature of the Si and C atoms in the network. As can be seen from Fig. 5, the C:Si ratio varied between 5:1 and 1:1 with a mean value at around 2:1.

In contrast to the crystalline SiCN, the amorphous SiCN was nitrogen deficient and the deficiency in nitrogen was more pronounced at higher temperature. This observation is in consistent with literature results of amorphous CN films except that the loss of nitrogen at elevated temperature in binary CN system is even more dramatic. Therefore, it can be conjectured that silicon addition improves the retention of nitrogen in the film and stabilizes the crystal compound (C; Si_3N_4).

Fig. 6 shows a typical indentation response of a SiCN crystal prepared by microwave CVD with a microwave power of 2 kW and at a substrate temperature of about 1000°C . The hardness and effective modulus were estimated at 30 and 321.7 Gpa, respectively. For comparison, nano-indentation measurements were also performed on amorphous SiCN films prepared by ECR-CVD. This particular ECR sample contained a nitrogen content of about 29 at.% and a Si:C ratio of about 2:1. The loading-unloading curve is shown in Fig. 7. The corresponding hardness and effective modulus were 22 and 164.4 GPa, respectively. The remarkable change of mechanical properties due to different film deposition process and microstructure is best illustrated by comparing the load-displacement curves in Figs. 6 and 7. It is noted that the penetration in Fig. 6 is smaller, along with a negligible plastic deformation.

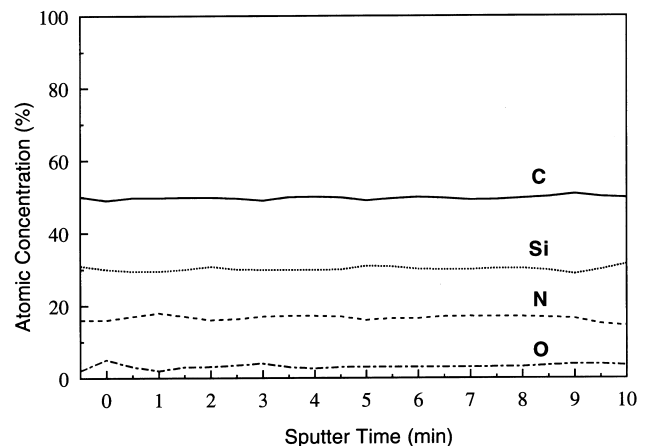


Fig. 4. Typical scanning Auger depth profile of an amorphous SiCN film.

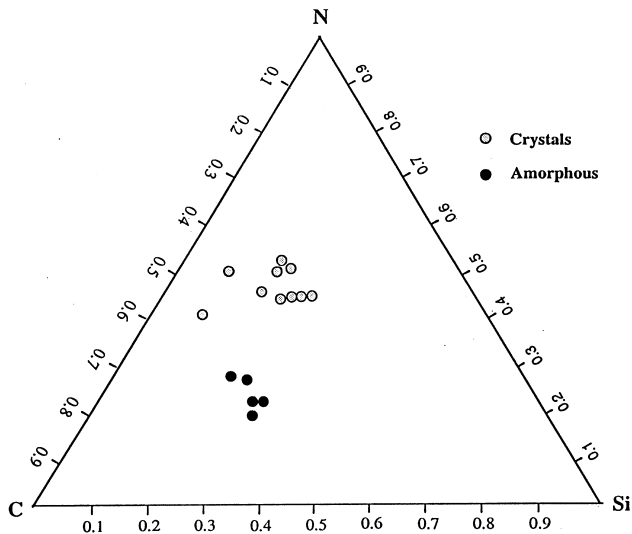


Fig. 5. The 'phase diagram' of Si-C-N system at 900°C.

Table 1 shows the hardness of SiCN, Si_3N_4 and SiC materials prepared by various methods together with that of diamond and cubic BN reported in the literature. The hardness of crystalline SiCN prepared in this work is comparable to that of Si_3N_4 and SiC prepared by pyrolytic CVD, but higher than that by reactive sintering at high temperatures. It should be mentioned that not only microhardness may vary according to the structure (phase) but also it may depend on the orientation of the crystal [26,27]. Directional variation of the microhardness for Si_3N_4 is quite substantial. The ratio between the high and low values in two different orientations is 1.81 for α - Si_3N_4 and 1.34 for β - Si_3N_4 . The high and low value is obtained by applying the load parallel and normal, respectively, to the c -axis. In our indentation measurements, the load was normal to the long axis (presumably the c -axis) since it was more convenient to measure in this orientation. Thus the value we obtained at 30 GPa for the crystalline SiCN is likely to be the low value.

The last point to be mentioned is that nitrogen deficiency

may affect the measured hardness value. Moriyama et al., [20] have studied the relationships between Vickers microhardness and atomic ratio of Si:N or Si:C in the binary systems of SiN_x and SiC_y . In both the systems, approximately stoichiometric composition of Si_3N_4 or SiC showed a maximum value in hardness. Our SiCN crystals exhibited an average nitrogen content at around 50 at.%, which is slightly less than the stoichiometric composition at 57 at.% for $(\text{C}; \text{Si})_3\text{N}_4$. Hence it is very likely that our measured hardness value can be higher if the nitrogen incorporation is improved further.

4. Conclusions

Large-sized SiCN crystals and polycrystalline as well as amorphous SiCN films can be grown by microwave CVD using SiH_4 , CH_4 , N_2 and H_2 gases as the raw materials. The relationships between the process parameters and the resultant structure are discussed. The composition of SiCN crystals can be described by $(\text{C}; \text{Si})\text{N}_x$, wherein $(\text{C}; \text{Si})$ denotes the substitutional nature of the carbon and silicon atoms in the structure and $x \approx 1$. Nano-indentation studies showed a value of hardness around 30 GPa for the crystalline SiCN, and 22 GPa for the amorphous counterpart. The corresponding effective modulus is 321.7 and 164.4 GPa for the crystalline and amorphous phases, respectively. Considering the anisotropy of the crystal and the nitrogen deficiency, the measured value of hardness at 30 GPa is likely to be in the low side. Nevertheless, these values are already remarkable. Hence the SiCN compound constitutes a new addition to the superhard material with a hardness value rivals to that of BN.

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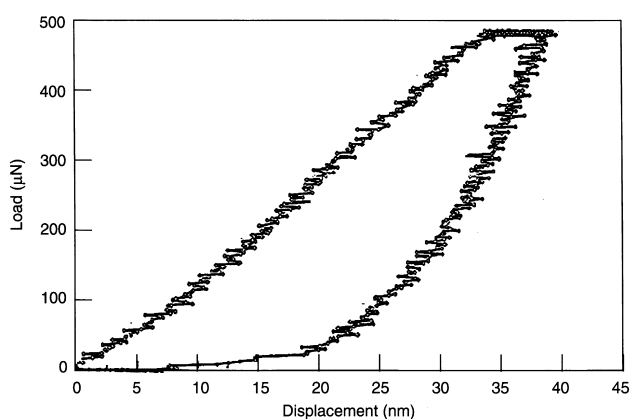


Fig. 6. A typical indentation response of SiCN crystal deposited by microwave CVD at 1000°C.

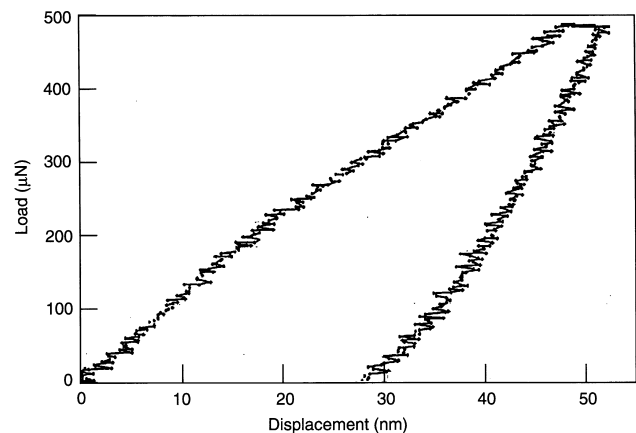


Fig. 7. A typical indentation response of amorphous SiCN film deposited by ECR CVD at 680°C.

Table 1
Microhardness data for SiCN, Si₃N₄ and SiC prepared by various methods

| Materials | Preparation method | Preparation temperature (°C) | Phase | Hardness, H_v (GPa) | References |
|--------------------------------|--------------------|------------------------------|-------------|-----------------------|------------|
| SiCN | Microwave CVD | 1000 | Crystalline | 30 | This work |
| | ECR-CVD | 680 | Amorphous | 22 | |
| Si ₃ N ₄ | CVD | 1300–1500 | α | 30.4–37.2 | [28] |
| | | 1100–1400 | Amorphous | 21.6–31.4 | |
| | Reactive Sintering | – | α | 21.6 | [20] |
| | | – | β | 16.7 | |
| Plasma CVD | 400 | Amorphous | 20.2 | | |
| SiC | CVD | 1500 | β | 33.0 | [29] |
| | Reactive sintering | – | – | 24.5–34.3 | [30] |
| | Plasma CVD | 400 | Amorphous | 12.2 | [20] |
| C | | 870 | Diamond | 70 | [31] |
| BN | | 1370 | cubic | 47 | [32] |

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