

Annealing behavior and hardness enhancement of amorphous SiCN thin films

S. L. Ma,^{a)} B. Xu, and K. W. Xu

State Key Laboratory for Mechanical Behaviors of Materials, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

X. L. Wu

National Laboratory of Solid State Microstructures, and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

Paul K. Chu

Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

(Received 2 March 2007; accepted 25 June 2007; published 1 August 2007)

Amorphous silicon carbon nitrogen (SiCN) films deposited on stainless steel by radio frequency magnetron sputtering are annealed at different temperatures in hydrogen to investigate the phase transformation kinetics and the impact on film hardness. The SiCN films with polycrystalline structure are formed after annealing at 900 °C and the polycrystalline structures contain SiC, Si₃N₄, and C₃N₄ phases. The polycrystalline transformation is discussed using a thermodynamics mechanism. Our results reveal that the emergence of homogeneous particle reinforced composite SiCN structure and polycrystalline phases related to SiC, Si₃N₄, and C₃N₄ may be responsible for the hardness enhancement of the annealed SiCN films. © 2007 American Vacuum Society.

[DOI: 10.1116/1.2764080]

I. INTRODUCTION

Silicon nitride (Si₃N₄) and silicon carbide (SiC) thin films have been widely studied due to their attractive properties^{1,2} such as wear resistance, chemical inertness, high refractive index, and wide band gap that bode well for optical, electronic, and tribological applications in tough environment.^{3,4} Recently, silicon carbon nitrogen (SiCN) films have also spurred much interest because the materials possess mechanical properties that are even better than those of single crystal Si₃N₄ and/or SiC films.⁵ Furthermore, crystalline SiCN is similar to β-C₃N₄ that has hardness comparable to that of diamond as theoretically predicted by Liu and Cohen.^{6,7} So far, various methods such as microwave plasma chemical vapor deposition,⁸⁻¹² magnetron sputtering,¹³ ion or plasma sputtering,¹⁴ and ion implantation¹⁵ have been proposed to prepare SiCN films. The microstructure of the materials is, in most cases, amorphous, and only a few laboratories have reported the synthesis of very tiny crystals on the nanometer or submicrometer scales. These nano- and microcrystals are embedded in an amorphous matrix wherein the volume of the crystalline phase accounts for only about 5% of the total volume of the materials.¹⁶ Crystalline SiCN films have significantly different physical and mechanical properties from amorphous SiCN (*a*-SiCN) films. The current challenge is to release the excess internal energy stored in amorphous films deposited in nonequilibrium conditions and relax them back to the thermal equilibrium state in order to obtain crystalline SiCN thin films. However, no related work was reported so far.

In this study, we investigate annealing behavior of *a*-SiCN films in hydrogen ambient. We found that initial crystallization of *a*-SiCN film forms tiny β-C₃N₄ crystal-embedded SiCN film. With the temperature rising, crystalline β-C₃N₄ component decreases, but the hardness obviously increases. We attribute the result to the formation of particle reinforced composite polycrystalline SiCN component. This work presents a possible way to obtain crystalline SiCN film with high hardness.

II. EXPERIMENTAL DETAILS

The SiCN films were grown on stainless steel at 300 °C by radio frequency magnetron sputtering using a 99.999% pure silicon target. The chamber was evacuated to a base pressure better than 5 × 10⁻⁶ Pa before a gas mixture containing 60% N₂ (99.999%)/40% Ar (99.999%) and CH₄ (99.999%) was introduced to a working pressure of 1 Pa. The stainless steel substrates were plasma etched for 5 min *in situ*. The flow rates of N₂ and CH₄ were 30 and 15 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. Sputtering was carried out with a power of 25 W and bias voltage of 500 V. The deposition time was 4 h and the film thickness was measured using a profilometer to about 2.3 μm.

The deposited samples were furnace annealed under hydrogen for 60 min at temperatures of 700, 800, and 900 °C. The binding energies were determined by an x-ray photoelectron spectroscopy (XPS) (Axis Ultra with Al Kα radiation). X-ray diffraction (XRD) (Philips PW 1700× with Cu Kα radiation), high-resolution transmission electron microscopy (HRTEM) (JEM-3010), and energy dispersive

^{a)}Author to whom correspondence should be addressed; electronic mail: slma@mail.xjtu.edu.cn

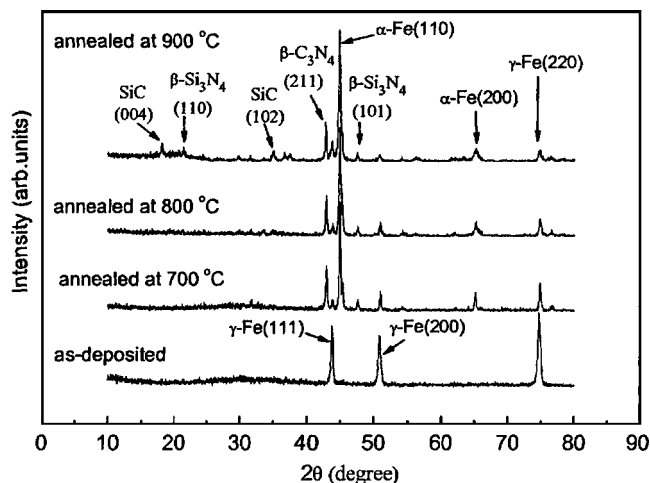


FIG. 1. XRD patterns of the as-deposited SiCN films and SiCN films annealed at 700, 800, and 900 °C.

x-ray spectrometry (EDS) (JSM-6700F) were employed to determine the chemical composition, structure, and morphology of the SiCN films.

III. RESULTS AND DISCUSSION

XRD shows that crystalline transformation in the as-deposited *a*-SiCN films takes place after annealing at 700 °C. The XRD spectra of the as-deposited $a\text{-Si}_{38.83}\text{C}_{27.38}\text{N}_{33.79}$ (determined by EDS) and annealed films are depicted in Fig. 1. Compared to the as-deposited *a*-SiCN films, the C_3N_4 crystalline phase can be observed after annealing at 700 °C suggesting that C_3N_4 is the key phase in the annealed SiCN films, especially when the annealed film consists of three crystal phases of SiC, Si_3N_4 , and C_3N_4 , as shown in Fig. 1 is formed at 900 °C. This C_3N_4 phase seems easy to be formed under annealing in hydrogen. Since the C_3N_4 has hardness comparable to diamond as predicted theoretically, we measured the microhardness (Hv) of the as-deposited and annealed SiCN films. The hardness values of the SiCN films annealed at 700, 800, and 900 °C are 33, 38, and 40 GPa, respectively, which are significantly higher than that of the as-deposited amorphous SiCN film with a hardness of 30 GPa. In comparison, the hardness of CN_x films is about 30–60 GPa depending on the chemical composition and microstructure.^{17–19}

The large hardness increase from 33 to 38 GPa in the two films annealed at 700 and 800 °C is interesting. We can see from the XRD results that the diffraction intensity of the C_3N_4 phase is slightly lower in the 800 °C annealing film than in the 700 °C annealing film. This indicates that the C_3N_4 phase is not a main factor causing the hardness enhancement of the annealed SiCN films. Interestingly, accompanied with further decrease of the C_3N_4 phase diffraction intensity and appearance of many diffraction peaks related to SiC and Si_3N_4 crystalline phases in the film annealed at 900 °C, the film hardness only increases by 2 GPa. This implies that the existence of local crystalline phases related to SiC and Si_3N_4 only slightly increases the hardness of the

film, whereas large hardness enhancement mainly arises from the formation of a homogeneous particle reinforced composite structured SiCN film. In our current work, such composite SiCN structure appears in the film annealed at 800 °C.

The XRD results reveal nucleation and growth of the crystalline grains during annealing in hydrogen. It is probably due to the unstable *a*-SiCN films deposited at nonequilibrium plasma deposition conditions. As a result, thermodynamically stable (in equilibrium) crystalline SiCN structure will be formed based on thermodynamics especially at a higher temperature such as 800 °C (some diffraction peaks related to crystalline phase weakly appear). In addition, the structural instability of the amorphous clusters increases the nucleation rate favoring the formation of the homogeneous nanoscale grain structure. It is possible that such a grain structure is difficult to be detected by XRD due to too small crystalline sizes. The structural change from amorphous to microcrystalline in hydrogenated amorphous silicon-rich bulk alloys after thermal annealing has been reported by Basa and Smith,²⁰ and the transition in stoichiometric alloys from the amorphous to polycrystalline phase occurs via nucleation and growth of crystallites formed during the nucleation process, as observed by Calcagno *et al.*²¹ In our case, the transformation kinetics from amorphous to crystalline is observed to evidently depend on the annealing temperature. For the film annealed at 900 °C, homogeneous SiCN grain structure has been formed, but the appearance of other crystalline phases leads to slight increase of the film hardness.

XPSs were performed to determine the bonding energy of the SiCN film annealed at 900 °C. Figure 2 shows high resolution XPS scans of the core levels of C 1s, N 1s, and Si 2p. The N(1s) peak in Fig. 2(b) consists of three components at 397.2, 398.6, and 400.0 eV which can be assigned to N–Si bond (397.2 eV),²² C≡N bond (398.6 eV),²³ and N=C bond (400 eV), respectively.²³ The photoelectron peak of C 1s shown in Fig. 2(a) is composed of four components according to fitted Gaussians centered at 283.1, 284.6, 286.0, and 288.5 eV, which can be assigned to C–Si bond (283.1 eV),²⁴ C–C bond (284.6 eV),²⁵ C (sp^2)=N bond (286 eV),²³ and C≡N(sp) bond (288.5 eV),²³ respectively. In the photoelectron peak of Si 2p in Fig. 2(c), the peak centered at 100.9 eV is attributed to Si–C bond (100.9 eV),²⁴ and the peak centered at 102.0 eV is assigned to Si–N bond (102 eV).²² Therefore, the SiCN film annealed at 900 °C possesses a multiphase structures.

The plan-view HRTEM images and corresponding electron diffraction patterns of the as-deposited and annealed SiCN films annealed at 700 and 900 °C are displayed in Fig. 3. The TEM samples were prepared by a standard preparation technique that included dimpling and subsequent 3 keV Ar^+ ion milling at low incident angles. As shown in Fig. 3(a), the as-deposited SiCN film has a random atomic arrangement and a dim halo is observed in the electron diffraction pattern, suggesting that the as-deposited SiCN film has an amorphous structure. In the TEM bright field image of the

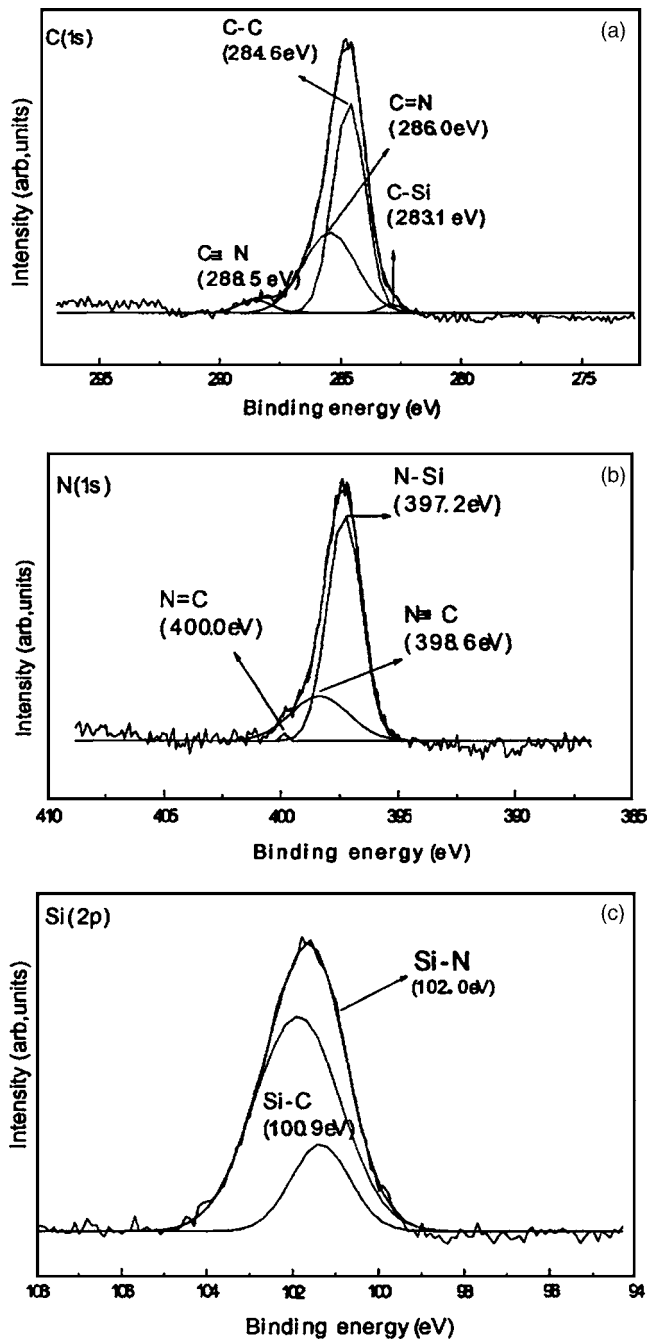


FIG. 2. XPS spectra of the SiCN films annealed at 900 °C: (a) C 1s core level, (b) N 1s core level, and (c) Si 2p core level.

SiCN film annealed at 700 °C exhibited in Fig. 3(b), small particles manifesting as black dots within an amorphous matrix can be observed. Meanwhile, a small quantity of speckles can be observed from the corresponding electron diffraction pattern suggesting the existence of the crystalline C_3N_4 phase after annealing at 700 °C. The TEM bright field image of the SiCN film annealed at 900 °C in Fig. 3(c) discloses polycrystalline particles of SiC, Si_3N_4 , and C_3N_4 with various sizes which are confirmed by the corresponding electron diffraction patterns. This TEM results agree well with our XRD measurement.

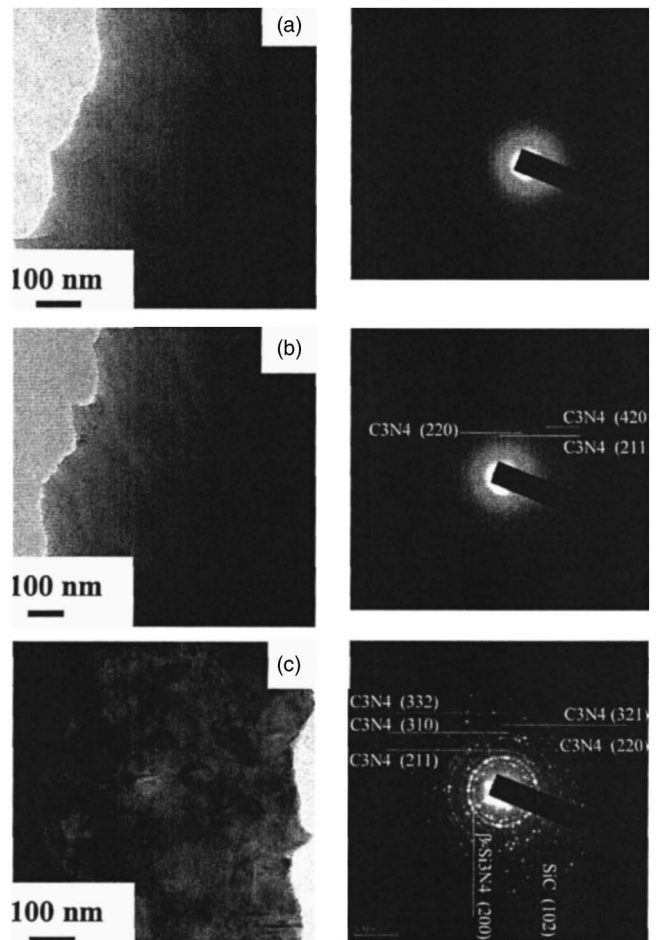


FIG. 3. HRTEM images and corresponding electron diffraction patterns acquired from (a) as-deposited SiCN film, (b) SiCN film annealed at 700 °C, and (c) SiCN film annealed at 900 °C.

IV. CONCLUSIONS

In summary, thermal annealing in hydrogen improves the characteristics of amorphous SiCN films due to the formation of a homogeneous particle reinforced composite SiCN structure, which leads to a large increase of the film hardness. The process is thermodynamically driven. Moreover, the emergence of polycrystalline structure of SiC, Si_3N_4 , and C_3N_4 is observed in the annealed SiCN films at 900 °C and appears to be responsible for slight increase in the hardness. We believe that the technique presented here can be expanded to the fabrication of other superhard nanocrystalline materials.

ACKNOWLEDGMENTS

This work was supported by Grant Nos. 50671079 and 50531060 from the National Natural Science Foundation of China, the National Key Basic Research Projects Nos. 2004CB619302 and 2006CB921803 of China, and City University of Hong Kong Direct Allocation Grant No. 9360110.

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