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Dependence of optical properties and hardness on carbon content in silicon carbonitride films deposited by plasma ion immersion processing technique

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Abstract

Materials with Si–C–N composition are of great interest due to their remarkable properties such as high hardness and oxidation resistance. In this study amorphous silicon nitride and silicon carbonitride films were deposited on glass, fused silica, and carbon substrates by the plasma immersion ion processing technique. Gas pressure during the deposition was kept around 0.13 Pa (1 mTorr) and SiH₄, N₂, Ar and C₂H₂ gas mixtures were used. Film hardness, composition and UV–visible optical absorption were characterized using nanoindentation, ion beam analysis techniques, and UV–visible spectroscopy, respectively. The films exhibit high transparency in the visible and near UV regions. Addition of the carbon to the films causes decrease in the density of the films, as well as decrease in hardness and transparency. These results suggest that in the low energy regime of PIIP the deposition of hard carbon composites with nitrogen and silicon does not take place.

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1. Introduction

Recently synthesis of the materials with Si–N–C composition drew increased attention. During the last decade, ternary Si–N–C phases have been prepared by different synthesis methods such as pyrolysis of polyorganosilazanes (POPOS), chemical vapor deposition (CVD), and physical vapor deposition (PVD). A detailed review can be found

elsewhere [1]. Important properties of amorphous Si–N–C have been reported such as oxidation resistance up to 1600 °C [2] and hardness of 38 GPa [3].

The other reason for the increased interest in the Si–N–C compounds was that based on theoretical calculations [4], a covalent bonded compound of carbon and nitrogen, preferably in the β-C₃N₄ structure that is isomorphic to β-Si₃N₄, might have a bulk modulus superior to that of diamond. The incorporation of silicon is thought to promote the formation of sp³ hybridization of the carbon, due to the affinity to silicon, to form sp³ bonding configurations with nitrogen.

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The dominant phases in the Si–N–C system are SiC and Si₃N₄. They are immiscible. There are no ternary phases shown in the Si–N–C phase diagram published in the 1995 compilation [5]. Incorporation of carbon into the Si₃N₄ lattice is a difficult task.

In this study, we created films with composition close to that of Si₃N₄ and attempted incorporation of carbon in the films not changing the amount of silicon and nitrogen. For film growth we used plasma ion immersion processing technique [6]. The advantage of this deposition method is that it allows non-line-of-sight deposition on the irregularly shaped substrates at low temperatures [7]. The films can be deposited even on plastics.

The films obtained in this study demonstrated deterioration of optical properties as well as hardness with the increased concentration of carbon.

2. Experimental

The film deposition experiments were conducted using the PIIP facility [6] at Los Alamos National Laboratory using RF inductive plasma of argon (Ar), silane (SiH₄), nitrogen (N₂) and acetylene (C₂H₂) gas mixtures. The experimental conditions are shown in Table 1. Substrates used in the experiments were fused silica from Rolyn Optics (17 × 17 × 1.7 mm) used in optical absorption and nanoindentation measurements, and carbon (10 × 10 × 1.2 mm) coated with 85 nm of niobium used in Rutherford backscattering measurements. Before deposition the substrates were

cleaned ultrasonically first in acetone and then in methanol.

The plasma was generated using two inductively coupled 0.46 MHz RF power sources. The plasma sources were located in mirror-symmetric positions with respect to the sample stage in the PIIP chamber to obtain uniform ion distribution. Each RF source was operated at 400 W. Pulsed bias voltage was –200 V during the deposition. Pulse width was 20 μs and pulse frequency was 10 kHz. The operating pressure was about 0.13 Pa (1 mTorr). The pressure in the PIIP chamber before deposition was below 1.3 × 10^{–4} Pa (10^{–6} Torr). The sample stage was cooled by air.

The thickness of the films was measured using surface profilometer Dektak IIA from Sloan Technology.

Hardness measurements were performed using a commercially available Nanoindenter II from Nanoinstruments, utilizing a continuous stiffness option. Hardness indents were made using a Berkovich triangular pyramid diamond indenter tip.

The film composition was measured by Rutherford backscattering spectroscopy (RBS) at Ion Beam Materials Laboratory of Los Alamos National Laboratory. For RBS we used an analyzing beam of 2 MeV ⁴He⁺ normal to the sample, with the detector located 13° from the normal.

Optical absorption of the films was measured using a Varian Cary 300 Bio UV–visible spectrophotometer. The absorbance spectra were taken in the range 190–900 nm (6.53–1.38 eV).

3. Results and discussion

The properties of Si–N–C films showed strong dependency on the amount of acetylene gas in the gas mixture. Fig. 1 shows dependence of the thickness of the films grown on glass on the acetylene content. The growth rate increases almost linearly with the acetylene gas fraction and varies from about 1.5 nm/min for a film with no carbon (sample #1) to 11.3 nm/min for a film with the highest carbon concentration used in our experiments (sample #6).

Table 1
Gas flow parameters used in the experiments

Sample number	Gas composition (sccm)			
	SiH ₄	N ₂	C ₂ H ₂	Ar
1	1.5	6	0	8
2	1.5	6	0.5	8
3	1.5	6	1	8
4	1.5	6	2	8
5	1.5	6	3	8
6	1.5	6	5	8

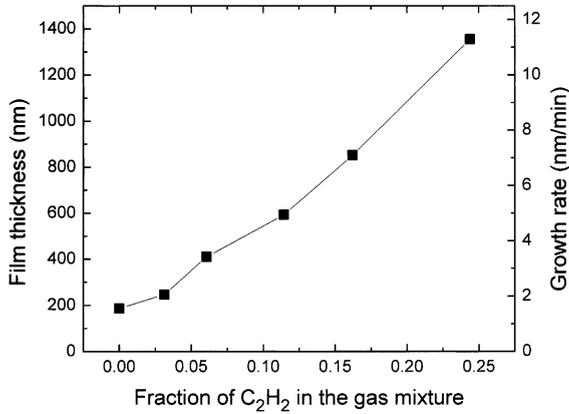


Fig. 1. Dependence of the film thickness and growth rate on the fraction of acetylene in the gas mixture.

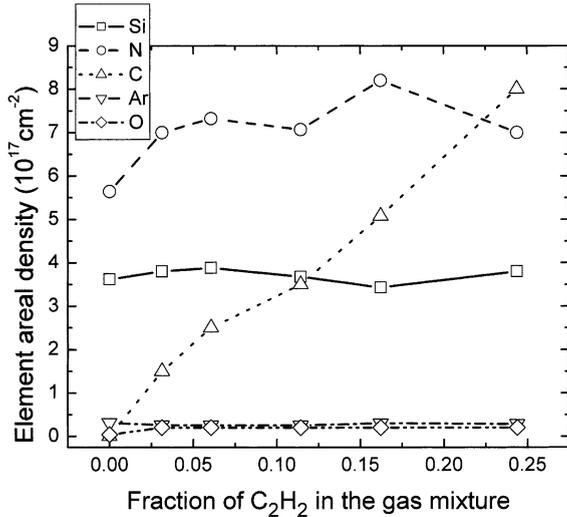


Fig. 2. Surface density of different elements in the films depending on the fraction of acetylene in the gas mixture.

The composition of the films changes significantly too. The RBS analysis results are shown in Fig. 2. The deposition rate for Si, N and Ar remains almost constant through the entire spectrum of the gas compositions used in the experiments, whereas the fraction of the carbon in the films grows almost linearly and mimics the behavior of the deposition rate. Therefore it is justified to suppose that the changes in the growth rate are caused entirely by the deposition of carbon on the surface.

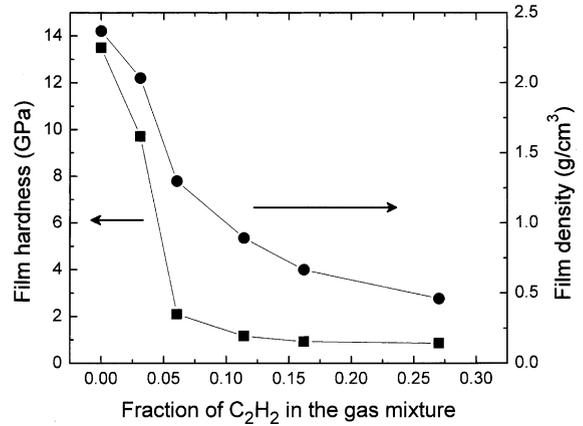


Fig. 3. Film hardness and film density as functions of the fraction of acetylene gas in the gas mixture.

As one can see from Fig. 3, hardness of the Si–N coating with no addition of carbon is almost 14 GPa. With the fraction of acetylene gas growing in the mixture of gases used for deposition, the film hardness rapidly decreases (Fig. 3). Very low hardness can, at least in part, be caused by the decrease in the density of the films taking place at the same time (Fig. 3). The density of the samples was calculated from RBS and profilometry results. The Vickers hardness of films grown by CVD was 24.5–28.2 GPa for SiC (varies with crystal face) and 16–18 GPa for Si₃N₄ [8].

Most of the films demonstrated excellent transparency (Fig. 4). The oscillations in the spectra result from multiple interference between beams reflected at the two interfaces (air–film, film–substrate) [9].

We used Tauc's formula [10] to estimate bandgaps of our films. According to Tauc's formula

$$(\mu E)^{1/2} \propto (E - E_g), \quad (1)$$

where μ is the absorption coefficient and E_g is the bandgap. We estimated that the bandgap of the films changes from about 5 eV for the Si–N sample (#1) to about 2 eV for the sample #6. The bandgap of Si₃N₄ is 5.0 eV [11], which indicates that our carbon free films may consist of Si₃N₄. The bandgap of SiC is equal to 2.86 eV [11]. This indicates that in our films with the addition of carbon formation of SiC may take place. However, since the

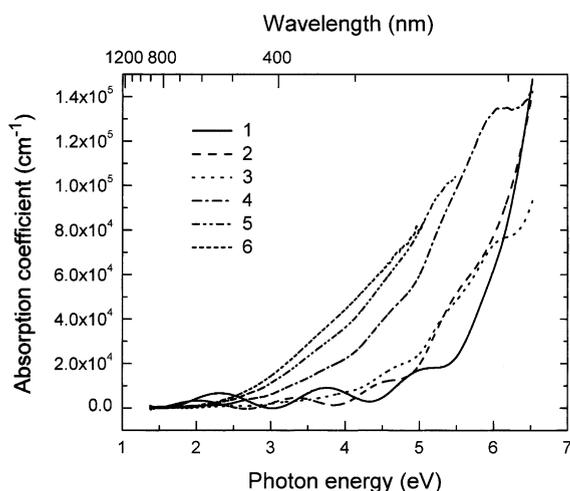


Fig. 4. Absorption coefficient of the samples. For samples description see Table 1.

bandgap falls below 2.86 eV we must consider other reasons for the bandgap changes. At higher concentrations of carbon we probably have polymerization of carbon in our films, which becomes more likely at low deposition energies [12,13], and which is consistent with the low densities observed. This can explain both the decrease in the hardness and the deterioration of optical properties. Softening of the carbon films with the addition of nitrogen has been observed before [14,15]. However, the decrease in hardness was not as dramatic as in our experiments. Given the severity of the density decrease in our films we conclude that the polymerization is the main process responsible for the decrease in the bandgap and hardness.

Further research is required to elucidate the structure of the obtained Si–N–C films.

4. Conclusions

Thin film with Si–N–C composition were grown using Plasma Ion Immersion Processing. The films exhibit good transparency in visible and near UV region. The band gap was estimated to be around 5 eV for films free of carbon. The hardness of the films falls with addition of carbon from about 14 GPa to around 1 GPa. This is most probably due to the decrease in density of the films and possible

polymerization of the films. The results indicate that in the low energy regime of PIIP the deposition of hard carbon composites with nitrogen and silicon does not take place. However, the films with no carbon and low carbon concentration demonstrate exceptional optical properties as well as high hardness.

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