Structural and Hardness Studies of CNₓ/TiN Composite Coatings on Si (100) Substrates by Laser Ablation Method

A. Kumar, H.L. Chan, and N.B. Dahotre

CN$_x$/TiN composite coatings were deposited on Si (100) substrates using the pulsed laser deposition (PLD) method. Previous results showed that a seed of titanium nitride (TiN) layer between silicon substrates and a top layer of carbon nitride increased the hardness and modulus values of overall composite coatings (Ref 1). This paper describes the same approach to growing carbon nitride composite coatings with varying thicknesses of different kinds of buffer layers and carbon nitride films on Si (100) substrates at different temperatures and pressures. Preliminary results showed the presence of carbon nitride films by the Fourier transform infrared spectroscopy (FTIR) method. The mechanical properties of the films were characterized using the nanoindentation technique. The crystallographic properties of the films were characterized using the x-ray diffractometer method.

1. Introduction

In the last few years, there were numerous attempts to synthesize crystalline β-C$_3$N$_4$ by various techniques (Ref 2-5). The theoretical study by Liu and Cohen (Ref 5) suggested that the bulk modulus of a hypothetical material, β-C$_3$N$_4$, that has the same structure as β-Si$_3$N$_4$, can have equal or greater hardness than that of a diamond. Hardness is a complex property that contains both elastic and plastic deformation. For an ideal system without defects, the hardness is determined by the bulk modulus, that is, by the strength of the chemical bonding. In this case, β-C$_3$N$_4$ should have a higher hardness than a diamond.

These β-C$_3$N$_4$ materials attracted the attention of various investigators worldwide. Several attempts were made to produce and identify this compound. The production methods include shock compression of nitrogen-containing organic materials, pyrolysis of organic compounds with high nitrogen contents under high temperatures and pressures, and several physical vapor deposition (PVD) methods, such as radio frequency (rf) sputtering of a graphite target in a nitrogen ambient and ion beam methods (Ref 6, 7). It is difficult to obtain the proper carbon-to-nitrogen ratio. Recently, W.D. Sproul et al. (Ref 8) reported the formation of CN$_x$/TiN coatings using dual-cathode magnetron sputtering. Titanium nitride (TiN) provides a lattice-matched structural template to seed the growth of carbon nitride crystallites (Ref 1). Recently, pulsed laser deposition (PLD) was used to prepare high quality TiN films (Ref 9, 10).

In this paper, the PLD technique was used to fabricate both TiN (as a buffer layer) and carbon nitride coatings on Si (100) substrates. The detailed evaluation of mechanical properties by the nanoindentation method of composite CN$_x$/TiN films on Si

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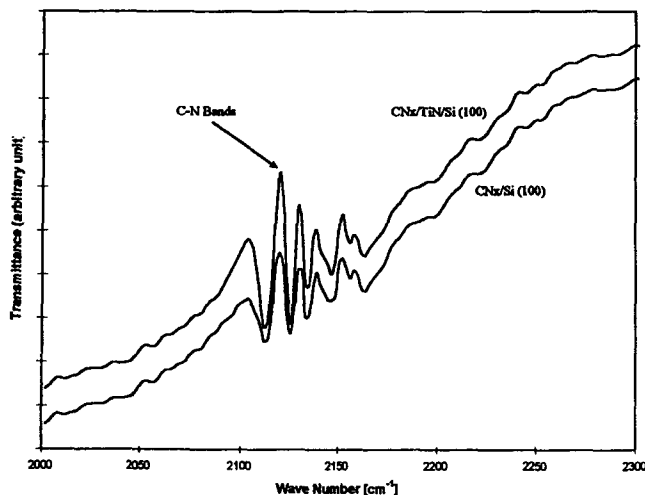
(100) substrates prepared under a wide range of conditions by the PLD technique was reported in this investigation.

2. Experimental Procedures

Deposition of the films was completed using a state-of-the-art PLD method. A detailed description about the deposition system is described in Ref 11. For depositing of composite carbon nitride coatings, TiN films were first deposited as a buffer layer at 600 °C in high vacuum on Si (100) substrates at an energy density of 10 J/cm^2. Titanium nitride films were deposited at different thicknesses (~1000 to ~5000 Å). After depositing TiN films, the graphite target was ablated at an energy density of 3 J/cm^2. The films of CN$_x$ were deposited at 150 °C in partial pressure of 50 mTorr nitrogen atmosphere. The thickness of TiN films was increased to investigate the effects of mechanical properties of the composite films. The mechanical properties, such as hardness and Young's modulus, were measured using a Nano Indenter IIA (Nano Instrument Inc., Knoxville, TN). Microstructural features of these films were investigated to understand the effects of the processing parameters to correlate with the mechanical properties. The carbon-nitrogen bonding characteristics of the films were studied using Fourier transform infrared spectroscopy (FTIR). Structural parameters were measured using x-ray diffraction (Rigaku-USA, Inc., Danvers, MA, DMAX 2200 with thin film attachment) method.

3. Results

The bonding structure of the films was investigated with FTIR technique. Spectra were taken in transmission mode in the wave number range of 2100 to 2600 cm^{-1}. Figure 1 shows the infrared (IR) band for the CN$_x$ and CN$_x$/TiN composite films deposited on Si (100) substrates. Both IR bands were observed in the range 2100 to 2200 cm^{-1}, but the intensity of the IR band increased in the composite films (with TiN under layer) with a strong peak of C≡N bands, which indicates the formation of the dominant phase of CN$_x$. Figure 2 shows the IR

Fig. 1 Fourier transform infrared spectroscopy spectrum of CN_x and CN_x/TiN films deposited on Si (100) substrates

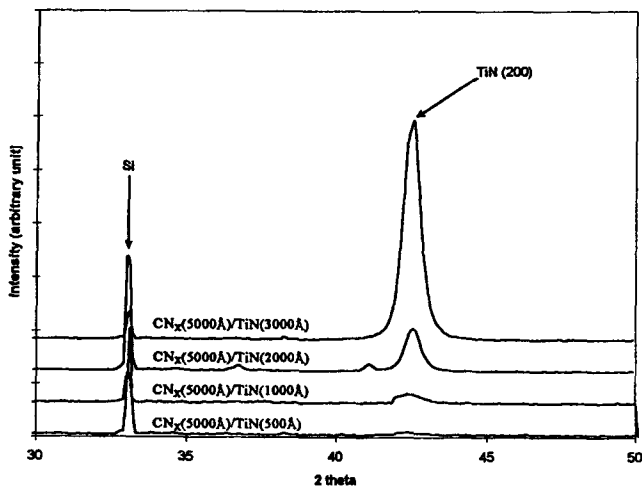
Fig. 3 X-ray diffraction pattern of CN_x/TiN composite films on Si (100) substrates at different thicknesses with TiN as an underlayer

Fig. 2 Fourier transform infrared spectroscopy spectrum of CN_x/TiN films on Si (100) substrates at different thicknesses with TiN as an underlayer

Table 1 Infrared absorption band of carbon nitride films

Observed IR bands, cm^{-1}	IR bands reported in literature, cm^{-1}(a)	Nature of bonding
2100-2200	2170	C≡N
...	2150	C≡N
...	2000-2300	C≡N
...	2190	C≡N
...	1530	C=N
...	1555	Graphitelike sp^2 domains
...	1575	Graphitelike sp^2 domains
...	1300	C-N
...	1360	Disordered sp^2 domains
...	1370	Disordered sp^2 domains
...	706	Graphitelike sp^2 domains
...	3200-3300	NH$_2$
...	2850-3300	C-H

(a) From Ref 12

absorption band of the CN_x/TiN composite films with different thicknesses of the TiN layer. Their locations are listed and compared with the published data in literature (Ref 12) and are tabulated in Table 1. In this case, the IR band was observed in the range between 2100 and 2200 cm^{-1}, which is attributed to the stretching mode of C≡N bonding. It can also be inferred from these FTIR results that there is no single sharp peak in the range between 2100 and 2200 cm^{-1}. This suggests that the formation of CN_x phases is a low percentage.

Figure 3 shows the diffraction spectra taken from carbon nitride/titanium nitride composite films deposited on Si (100) substrates under different conditions. In all cases, the peak that appears in each scan can be indexed either to a silicon substrate or to TiN (200) underlayers. Therefore, it is suggested that the structure of carbon nitride films prepared in this study are amorphous.

The elastic modulus and hardness values of carbon nitride films on Si (100) substrates determined as a function of dis-
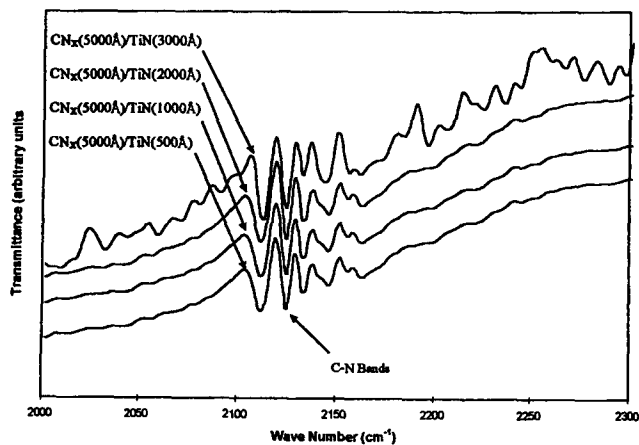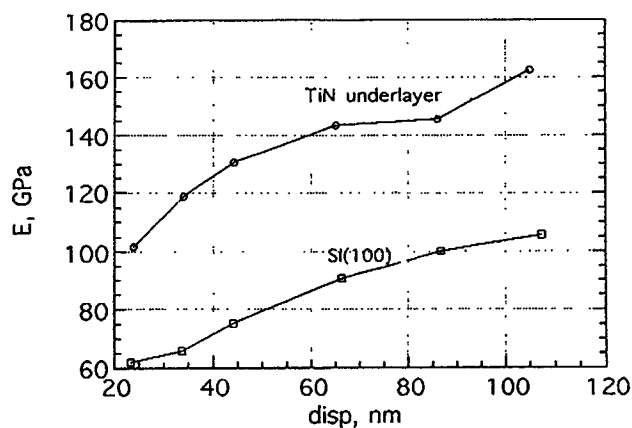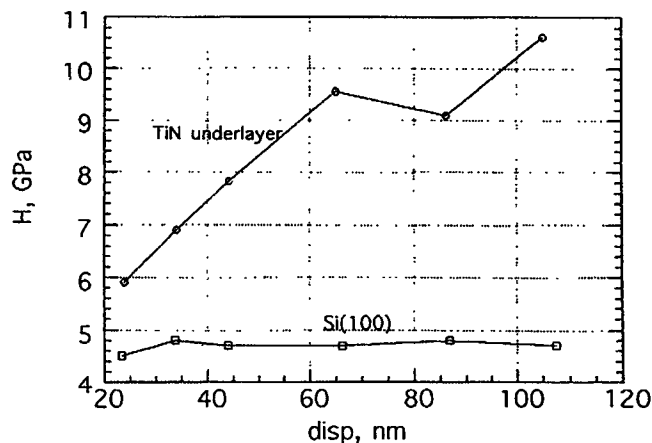
placement are presented in Fig. 4(a) and (b), respectively. In both figures, the substrate effect is absent. The deposition of the TiN layer increased the hardness values. A three- to four-fold increase in hardness values is found when carbon nitride film is deposited with TiN as an underlayer on Si (100) substrates. Recently, the overall hardness (~45 GPa) value of composite carbon nitride was enhanced with appropriate processing conditions and a suitable choice of buffer layers (Ref 13).

4. Conclusions

Infrared bands of carbon nitride films were observed in the range between 2100 and 2200 cm^{-1}, which is attributed to the C≡N bonding. It was demonstrated that using TiN as an underlayer on Si (100) substrates increases the hardness and modulus values of carbon nitride composite coatings three- to four-fold compared to the films of CN_x on Si (100) without any buffer layer.

Fig. 4 (a) Young's modulus of composite carbon nitride coatings on Si (100) substrate as a function of penetration depth.
(b) Hardness of composite carbon nitride coatings on Si (100) substrate as a function of penetration depth

Acknowledgments

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