JOURNAL OF MATERIALS SCIENCE **34** (1999) 1093–1098

# Structural, morphological, and mechanical properties of amorphous carbon and carbon nitride thin films deposited by reactive and ion beam assisted laser ablation

JANG-HWAN BAE, JAEKYONG CHO
*Department of Electronic Materials Engineering, ReCAPT, Gyeongsang National University, Gazwa-dong 900, Chinju, Gyeongnam 660-701, Korea*
*E-mail: jkcho@nongae.gsnu.ac.kr*

Amorphous carbon nitride thin films have been prepared on Si (100) wafers by nitrogen ion beam assisted Nd:YAG laser ablation techniques. Amorphous carbon and carbon nitride films have also been prepared by the conventional laser ablation techniques for comparison. Raman spectroscopy and spectroscopic ellipsometry have been performed for the films to analyze structural properties, atomic force microscopy to observe surface morphologies, and scratch, acoustic emission, and Vicker hardness test to examine mechanical properties. The amorphous carbon nitride films deposited by the ion beam assisted laser ablation techniques had generally better mechanical properties compared to the amorphous carbon films and amorphous carbon nitride films deposited in $N_2$ atmosphere. The amorphous carbon nitride films deposited at optimum ion beam current of 10 mA and laser power density of $1.7 \times 10^9$ W/cm$^2$ showed excellent mechanical properties: root mean square surface roughness of 0.33 nm, friction coefficient of 0.02–0.08, the first crack and critical load of 11.5 and 19.3 N respectively, and Vicker hardness of 2300 [Hv]. It is considered that the films have high potential for protective coatings for microelectronic devices such as magnetic data storage media and heads. 

## 1. Introduction

Amorphous carbon (a-C) and carbon nitride (a-CN) thin films have been extensively studied for applications as protective coatings of microelectronic devices like magnetic data storage media and heads. Because previous studies have shown that a-CN films have generally better mechanical properties with smaller internal compressive stress compared to a-C films [1–3], many efforts have been made to prepare a-CN films. a-CN films have been prepared by many vacuum techniques such as chemical vapor deposition [4], evaporation [5], arc deposition [6], sputtering [1–3], and laser ablation [7]. Of various film preparation techniques laser ablation have advantages; wide working pressure range, high energy of ablated particles, and pure nitrogen gas can be used to obtain dense films with high nitrogen content and to avoid hydrogen incorporation into the films which may deteriorate film quality. Previous studies have also shown that the ion beam assisted deposition techniques results in films with good adhesion to substrate, high density, and smooth surface [8].

In this study, we prepared a-C and a-CN films by a combined technique of laser ablation and ion beam assisted deposition. We also prepared a-C and a-CN films by conventional laser ablation techniques using pure nitrogen as reactive gas for a-CN film preparation. We investigated and compared the mechanical properties of the films depending on film preparation techniques and parameters.

## 2. Experiments

a-C and a-CN thin films were prepared by laser ablation techniques using Nd:YAG pulse laser with wavelength of 1064 nm. Table I summarizes film deposition conditions. a-C thin films were prepared by laser ablation with laser power densities of $3.5 \times 10^9$ and $1.7 \times 10^9$ W/cm$^2$ at high vacuum of $2.5 \times 10^{-7}$ torr. a-CN thin films were prepared by two techniques: $N_2$ gas introduced reactive laser ablation with laser power density of $3.5 \times 10^9$ W/cm$^2$ at chamber pressures of $1 \times 10^{-3}$, $4 \times 10^{-3}$ and $8 \times 10^{-3}$ torr and nitrogen ion beam assisted laser ablation with laser power densities of $3.5 \times 10^9$ and $1.7 \times 10^9$ W/cm$^2$ and ion beam current of 10, 20, 30, 40, 50 mA at $2.8 \times 10^{-5}$ torr. Before deposition the chamber was pumped down to a base pressure of $1.9 \times 10^{-7}$ torr using a cryogenic pump. A graphite disc was used as a sputtering target. Si (100) wafers that were not heated during deposition were used for substrates. A Kaufman ion gun was used to generate nitrogen ions that were accelerated to 600 eV.

TABLE I Film deposition conditions

| | Chamber pressure (torr) | Laser power density (W/cm$^2$) | Ion beam current (mA) | Remark |
|---|---|---|---|---|
| a-C | $2.5 \times 10^{-7}$ | $3.5 \times 10^9$ | 0 | Laser ablation |
| | | $1.7 \times 10^9$ | | |
| | $1 \times 10^{-3}$ | $3.5 \times 10^9$ | 0 | $N_2$ gas reactive |
| | $4 \times 10^{-3}$ | | | laser ablation |
| | $8 \times 10^{-3}$ | | | |
| a-CN | $2.8 \times 10^{-5}$ | $3.5 \times 10^9$ | 10 | Nitrogen ion |
| | | | 20 | beam assisted |
| | | | 30 | laser ablation |
| | | | 40 | |
| | | | 50 | |
| | | $1.7 \times 10^9$ | 10 | |
| | | | 20 | |
| | | | 30 | |
| | | | 40 | |
| | | | 50 | |

Thin films of about 0.4 $\mu$m in thickness were selected for investigations. Structural properties of the films were investigated by X-ray diffractometry (XRD) and Raman spectroscopy using a laser having wavelength of 514.5 nm in the scan range of 1000–2000 cm$^{-1}$. Optical band gaps of the films were determined from spectroscopic ellipsometry. Surface morphologies of the films were investigated by atomic force microscopy. Mechanical properties of the films were examined using a scratch tester, combined with acoustic emission (Revestest, CSEM, Switzerland) having Rockwell "C" diamond stylus of cone apex angle of 120 degree and tip radius of 200 $\mu$m. The loading rate, speed, and load range for the scratch test were 100 N/min, 100 mm/min, and 1–3 N, respectively. The hardness of the films were examined by a Vicker microhardness tester.

## 3. Results and discussion

### 3.1. Structural properties

All films prepared gave no diffraction lines in the XRD diagrams indicating that the films were amorphous. Fig. 1 shows Raman spectra of a-C and a-CN films prepared at laser energy density ($P_w$) of $3.5 \times 10^9$ W/cm$^2$ and with various ion beam current. Broad peaks at 1200–1400 cm$^{-1}$ and at 1400–1600 cm$^{-1}$ are observed for a-C film, which appear to be characteristic D (D means "disordered") and G (G means "graphitic") bands of a-C, respectively [9]. Similar Raman spectra are obtained for the a-CN films but the D and G bands slightly shift to lower and higher wavenumbers, respectively, as nitrogen ion beam current increases. Marton *et al.* [10] reported that Raman spectra of CN materials are qualitatively similar to those of similarly deposited a-C films, as observed in the present study. Marton *et al.* [10] also reported that the G band shifts to higher energy by 30–40 cm$^{-1}$ as the nitrogen content of the film varied from 0 to 20%. It is, therefore, considered that the a-CN films obtained in the present study are graphitic and the nitrogen content in the film increases as nitrogen ion beam current increases.

Fig. 2 shows optical band gaps of these films calculated from spectroscopic ellipsometry analyses. The

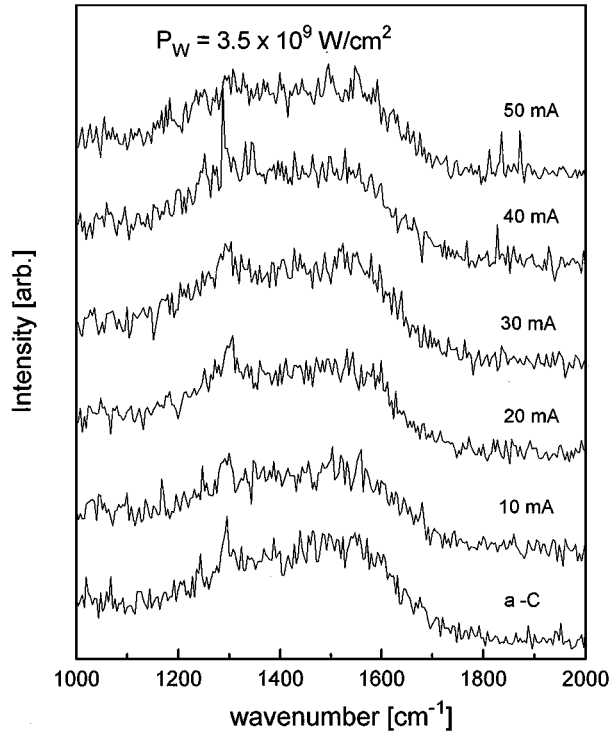


*Figure 1* Raman spectra of a-C and a-CN films deposited at laser power density ($P_w$) of $3.5 \times 10^9$ W/cm$^2$ with various ion beam current.

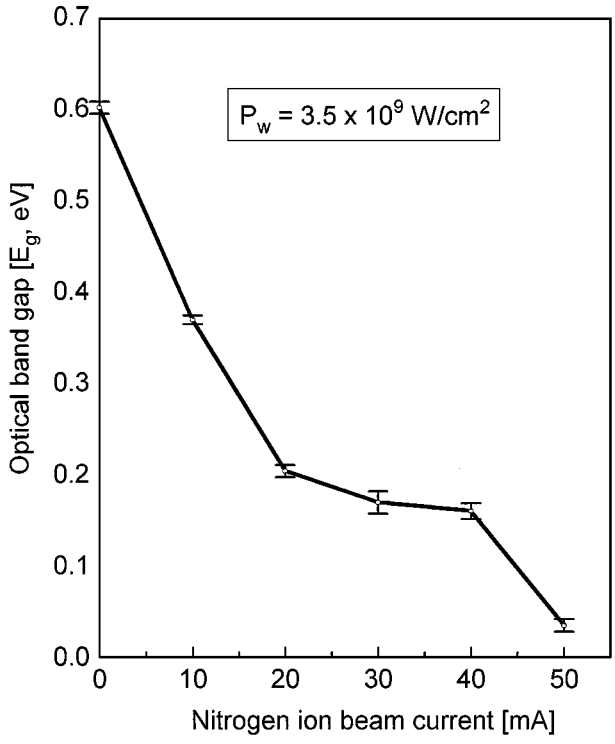


*Figure 2* Optical band gaps of a-C and a-CN films deposited at $P_w = 3.5 \times 10^9$ W/cm$^2$ with various ion beam current.

band gap of a-C film is about 0.6 eV that is comparable to 0.5 eV reported by Savvides [11]. The band gaps of a-CN films decrease as nitrogen ion beam current increases and reach almost zero at 50 mA. Xion *et al.* [7] reported the band gap of 0.25 eV for a-CN film, which is within the range obtained in the present study. From the fact that the band gap of graphite is zero, it is considered that the bonding nature in the a-CN films becomes

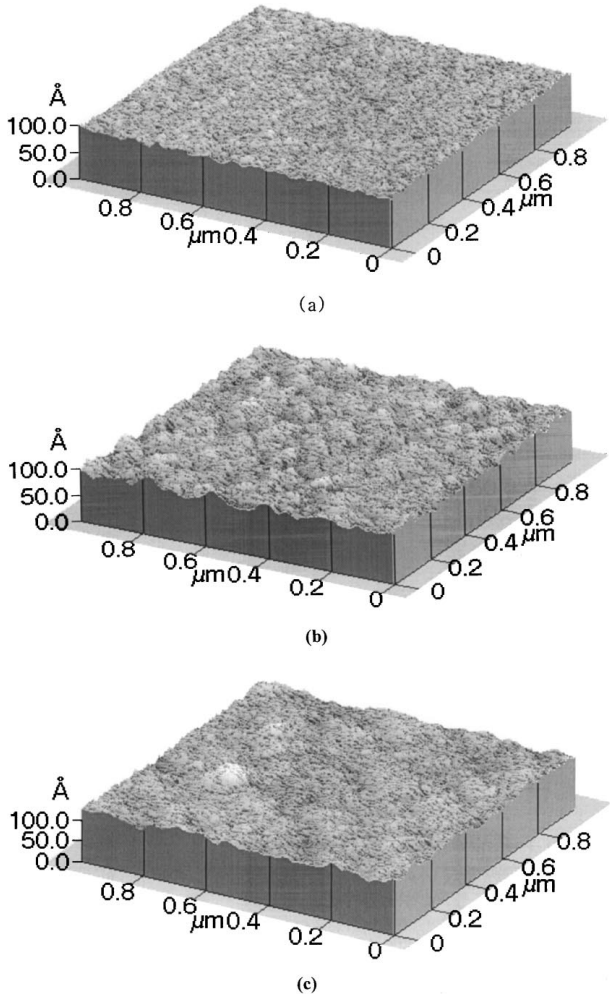


*Figure 3* Atomic force micrographs of surfaces of a-C (a) and a-CN (b) and (c) films deposited at $P_w = 3.5 \times 10^9$ W/cm$^2$. The a-CN films showed in (b) and (c) were deposited at the ion beam current of 10 mA and 30 mA, respectively.

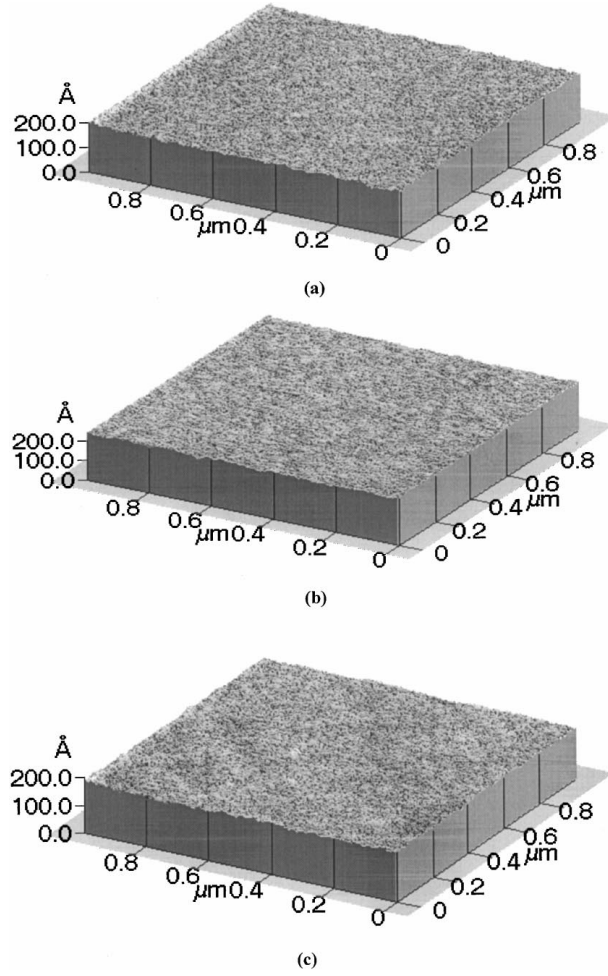


*Figure 4* Atomic force micrographs of surfaces of a-C (a) and a-CN (b) and (c) films deposited at $P_w = 1.7 \times 10^9$ W/cm$^2$. The a-CN films showed in (b) and (c) were deposited at the ion beam current of 10 mA and 30 mA, respectively.

more similar to that of graphite as the ion beam current increases.

## 3.2. Surface morphologies

Figs 3 and 4 show atomic force micrographs of the surfaces of a-CN films prepared by ion beam assisted laser ablation at $P_w = 3.5 \times 10^9$ W/cm$^2$ and $1.7 \times 10^9$ W/cm$^2$, respectively, and with various ion beam currents. Also shown are atomic force micrographs of a-C films for comparison. As shown in Fig. 3, the surfaces of a-CN films (b–c) prepared at $P_w = 3.5 \times 10^9$ W/cm$^2$ are generally rougher than that of a-C film (a). However, the surfaces of a-CN films (Fig. 4b–c) prepared at $P_w = 1.7 \times 10^9$ W/cm$^2$ are as smooth as that of a-C films (Fig. 4a). Fig. 5 shows atomic force micrographs of the surfaces of a-CN films prepared by reactive laser ablation. The surfaces of these films become rougher as $N_2$ gas pressure increases. Similar trend was reported by Zhen *et al.* [12] for the CN films prepared by reactive sputtering. Fig. 6 summarizes root mean square (rms) surface roughness calculated from the atomic force micrographs of the above films. As shown, the smoothest a-CN films with rms roughness in the range of 0.31–0.38 nm are obtained at $P_w = 1.7 \times 10^9$ W/cm$^2$. The rms roughness obtained in the present study is comparable to those (0.2–0.3 nm) reported by Zheng *et al.* [12] for the CN films prepared by reactive sputtering.

## 3.3. Mechanical properties

Fig. 7 shows friction coefficients obtained from scratch test for a-CN films. Fig. 7a and b are for a-CN films deposited with ion beam at $P_w = 3.5 \times 10^9$ W/cm$^2$ and $1.7 \times 10^9$ W/cm$^2$, respectively, and Fig. 7c is for a-CN films deposited in $N_2$ gas. It is noted that the friction coefficients of a-CN films deposited with ion beam at $P_w = 1.7 \times 10^9$ W/cm$^2$ (Fig. 7b) have the lowest values of about 0.05, which is lower than that (0.1) reported by Li *et al.* [3].

Fig. 8 shows a typical acoustic emission diagram obtained during scratch test. The first crack load and critical load were determined from the diagram as shown in the figure. Fig. 9 shows the first crack load and critical load for the above films. It is noteworthy that first crack load and critical load of a-CN films deposited with ion beam of 10 mA at $P_w = 1.7 \times 10^9$ W/cm$^2$ (Fig. 9b) are 11.5 and 19.3 N, respectively, which are the highest values obtained.

Fig. 10 shows typical optical micrographs taken after the scratch test for (a) a-C film, (b) a-CN film deposited with ion beam, and (c) a-CN film deposited in $N_2$ gas.

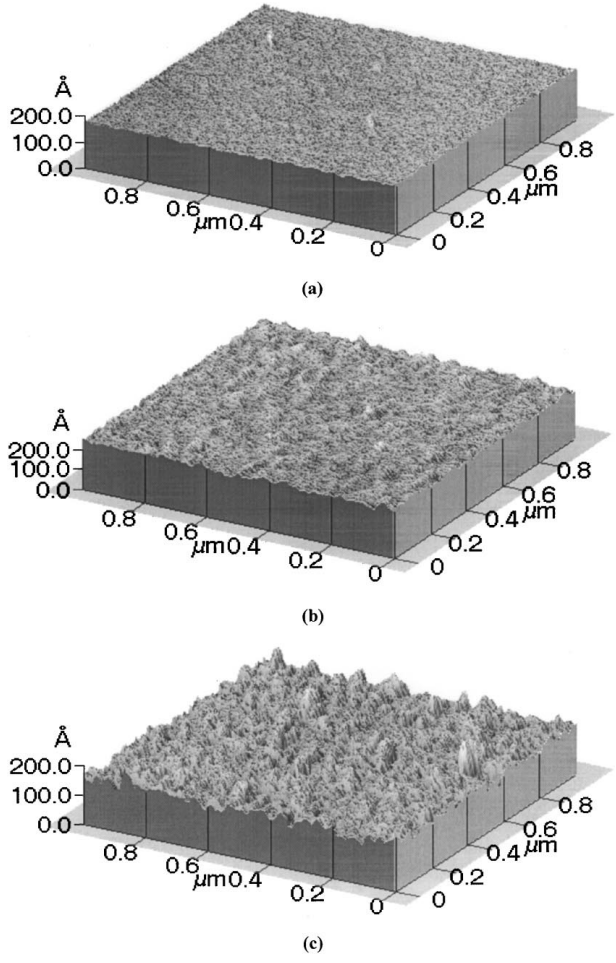


*Figure 5* Atomic force micrographs of surfaces of a a-CN films deposited at $P_w = 1.7 \times 10^9$ W/cm$^2$ by reactive laser ablation with varied $N_2$ gas pressure: (a) 1 mTorr (b) 4 mTorr (c) 8 mTorr.

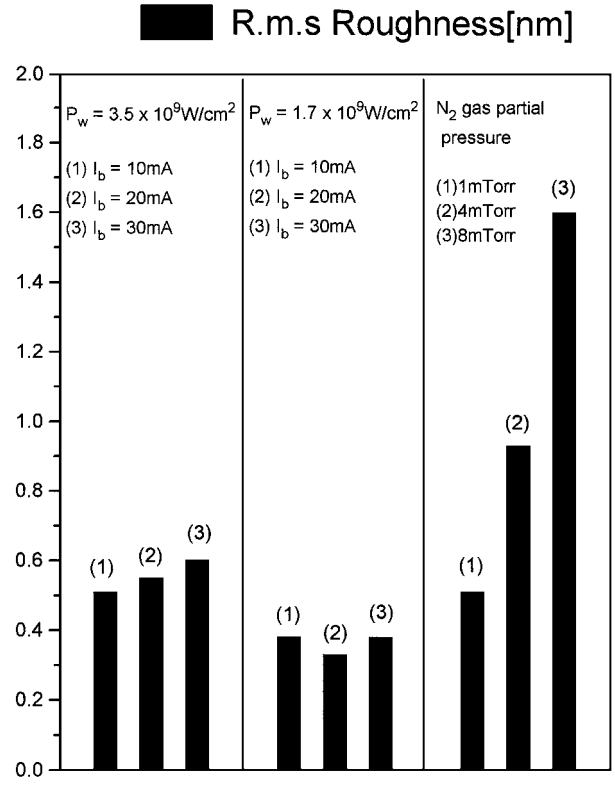


*Figure 6* Root mean square roughness of a-C and a-CN films deposited with ion beam at $P_w = 3.5 \times 10^9$ W/cm$^2$ and $P_w = 1.7 \times 10^9$ W/cm$^2$ and deposited in $N_2$ gas atmosphere.

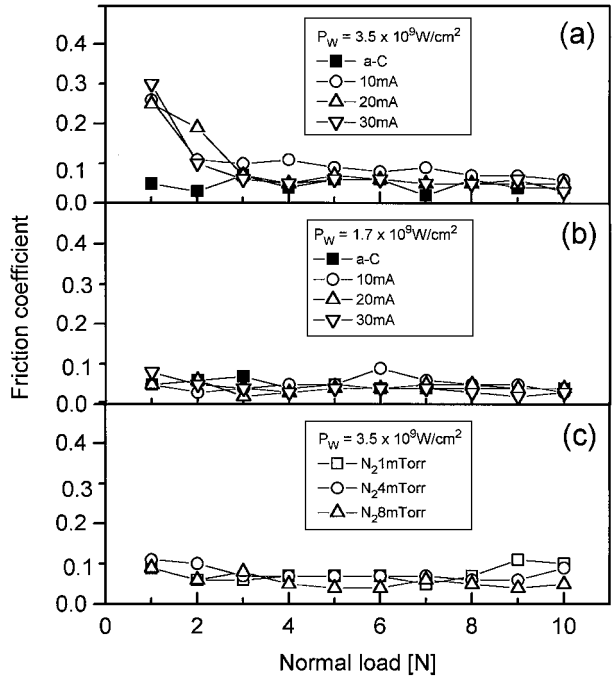


*Figure 7* Friction coefficient obtained from scratch test for a-C films and a-CN films deposited with ion beam at (a) $P_w = 3.5 \times 10^9$ W/cm$^2$ and (b) $P_w = 1.7 \times 10^9$ W/cm$^2$ and (c) deposited in $N_2$ gas atmosphere.

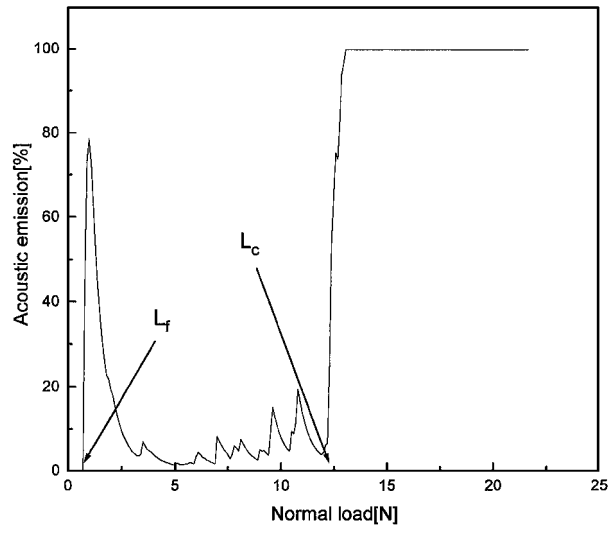


*Figure 8* Typical acoustic emission diagram obtained during scratch test shows the definition of the first crack load ($L_f$) and critical load ($L_c$).

Obvious transverse crack and flakes are observed for the a-C film and the a-CN film deposited in $N_2$ gas even at low applied load. Cracks, however, are barely seen for the a-CN film deposited with ion beam until relatively high applied load (see magnified micrographs on the right).

The above films had similar Vicker microhardness of about 2300 [Hv], which is comparable to those reported by other studies [4, 10].

## 4. Conclusions

Amorphous carbon nitride thin films have been prepared on Si (100) wafers by nitrogen ion beam assisted Nd:YAG laser ablation techniques. Amorphous carbon and carbon nitride films have also been prepared by the conventional laser ablation techniques for

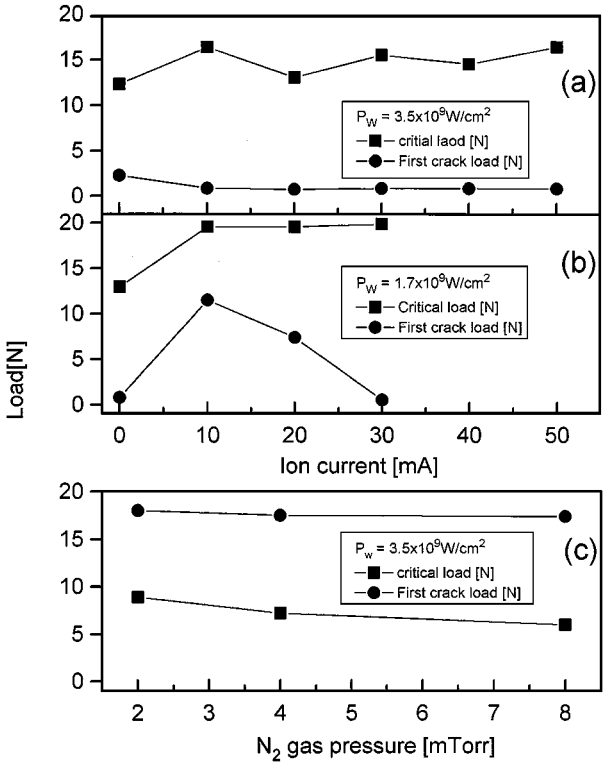


*Figure 9* First crack and critical loads determined from scratch test for a-C films and a-CN films deposited with ion beam at (a) $P_w = 3.5 \times 10^9$ W/cm$^2$ and (b) $P_w = 1.7 \times 10^9$ W/cm$^2$ and (c) deposited in $N_2$ gas atmosphere.

comparison. Surface morphological, structural and mechanical properties of the films have been investigated. The amorphous carbon nitride films deposited by the ion beam assisted laser ablation techniques had generally better mechanical properties compared to the amorphous carbon films and amorphous carbon nitride films deposited in $N_2$ atmosphere. The amorphous carbon nitride films deposited at optimum ion beam current of 10 mA and laser power density of $1.7 \times 10^9$ W/cm$^2$ showed excellent mechanical properties: root mean square surface roughness of 0.33 nm, friction coefficient of 0.02–0.08, the first crack and critical load of 11.5 and 19.3 N respectively, and Vicker hardness of 2300 [Hv]. It is considered that the films have high potential for protective coatings for microelectronic devices such as magnetic data storage media and heads.

## References


1. E. C. CUTIONGCO, D. LI, Y.-W. CHENG and C. B. BHATIA, *J. Tribology* **118** (1996) 543.
2. C. J. TORNG and SIVERSTEN, *J. Mater. Res.* **5** (1990) 2490.
3. D. LI and Y.-W. CHUNG, *Tribology Trans.* **37** (1995) 479.
4. H. X. HAN and B. J. FELDMAN, *Solid State Commun.* **65** (1988) 921.
5. F. FUJIMOTO and K. OGATA, *Jpn. J. Appl. Phys.* **32** (1993) L420.
6. X. WANG and P. J. MARTIN, *Thin Solid Films* **256** (1995) 148.
7. F. XION and R. P. H. CHANG, *MRS Proc.* **280** (1993) 587.


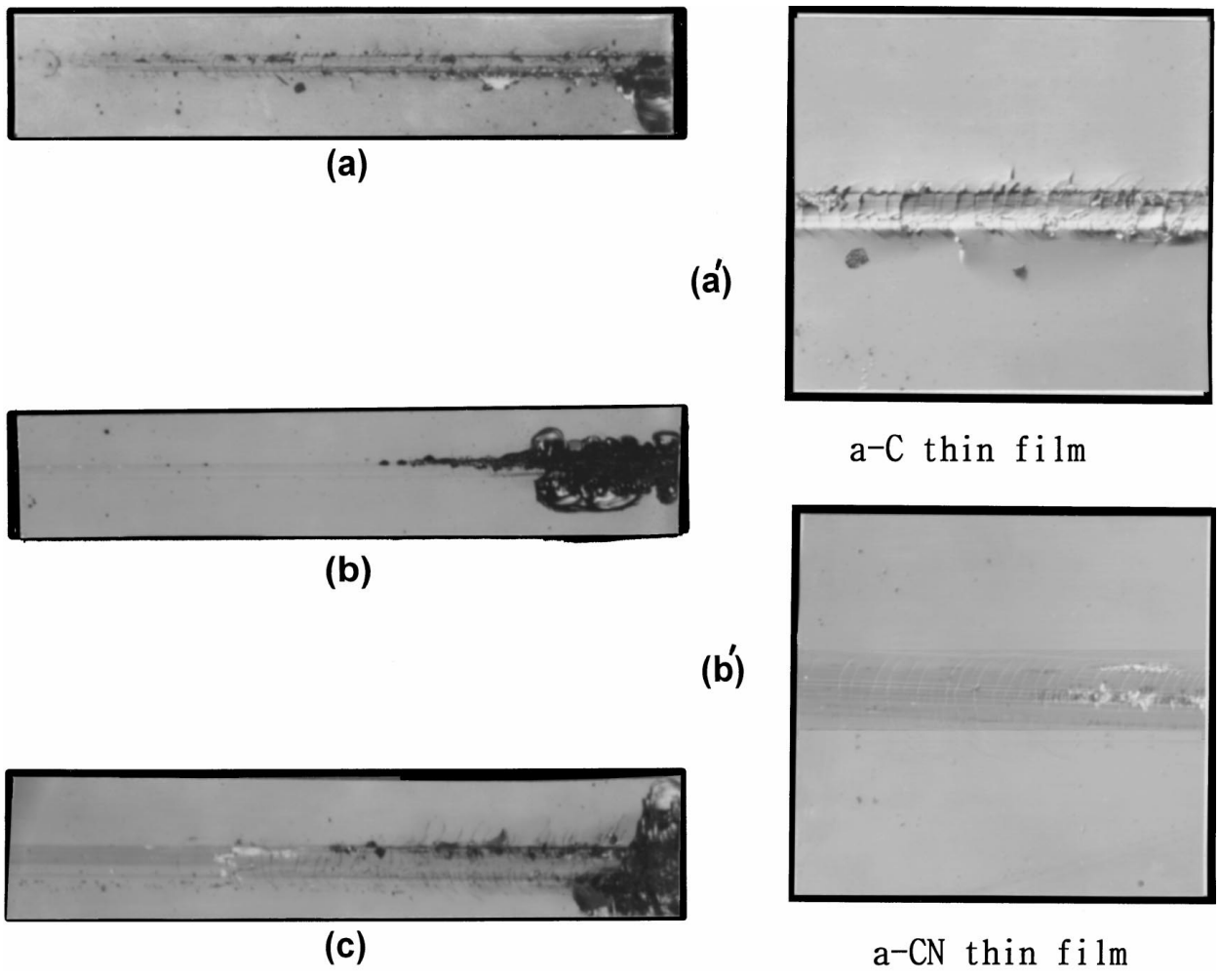


*Figure 10* Typical optical micrographs taken after scratch test for (a) a-C film, (b) a-CN film deposited with ion beam, and (c) a-CN film deposited in $N_2$ gas atmosphere. Also shown (a′) and (b′) are magnified micrographs of the middle parts of (a) and (b), respectively.

8. J. L. VOSSEN and W. KERN, "Thin Film Processes" (Academic Press, New York, 1978) pp. 175–204.
9. A. LETTINGTON and J. W. STEEDS, "Thin Film Diamond" (Chapman & Hall, London, 1994).
10. D. MARTON, K. J. BOYD and J.W. RABALIS, *Int. J. Modern Phys. B* **9** (1995) 3526.
11. N. SAVVIDES, *J. Appl. Phys.* **59** (1986) 413.
12. W. T. ZHENG, N. HELLGREN, H. SJOSTROM and J. E. SUNDGREN, *Surface & Coatings Technol.* **98** (1998).

*Received 15 April 1997*
*and accepted 14 October 1998*