

## Deposition of Polyimide Films by Ionized Cluster Beam

K. W. KIM<sup>1)</sup>, N. Y. KIM<sup>2)</sup>, C. E. HONG<sup>2)</sup>, S. Y. KIM, and C. N. WHANG

*Dept. of physics, Yonsei University, Seoul 120-749, Korea.*

<sup>1)</sup> *Dept. of physics, Sunmoon University, Asan, Chungnam 336-840, Korea.*

<sup>2)</sup> *Dept. of Physics, Soongsil University, Seoul 156-743, Korea.*

Pyromellitic dianhydride (PMDA) and oxydianiline (ODA) were co-deposited using dual ICB sources. The bulk and surface chemical properties of PI films were studied by using Fourier transform infrared spectroscopy (FT-IR) and X-ray photoemission spectroscopy (XPS). Capacitance-voltage (C-V) and current-voltage (I-V) measurements were carried out to study the interfacial and the electrical properties of PI films. Surface morphology of PI films deposited under various ICB conditions were studied using atomic force microscopy (AFM).

### 1. INTRODUCTION

Polyimides (PI) have received considerable attention due to their good thermal stability, low dielectric constant, and good mechanical properties<sup>1)</sup>. They have been used in applications ranging from aerospace to microelectronics. PI films are conventionally prepared by curing of spin-coated PAA solution or curing of vapor-deposited PAA films. Unfortunately, these methods revealed that the prepared PI films contained relatively high amount of isoimide. Moreover these techniques are difficult to control the precise film properties such as crystallinity or purity. Ionized cluster beam deposition (ICBD) technique is known<sup>2)</sup> to be a unique film formation technique that enables flexible control of film properties such as molecular orientation, film crystallinity, chemical purity, and film substrate interface. Thus we employed the ICBD technique to fabricate highly purified PI films. We investigate the chemical properties, interfacial properties, the surface morphology, and the electrical properties of PI films deposited by ICB.

### 2. EXPERIMENTAL PROCEDURES

The detailed description of our ICBD system was presented elsewhere<sup>3)</sup>. Here we briefly describe the deposition process of PI films. Two ICB sources were used to deposit PI films. The PMDA and ODA molecules ejected from the heated crucibles through the narrow nozzles form clusters due to the adiabatic expansion process. To have 1:1 stoichiometric ratio of PMDA and ODA clusters, the crucible temperature were held at 210°C and 180°C, respectively. After the clusters were ionized by electron beam irradiation, they were accelerated by high voltage applied between the ionizer and the substrate holder. We held the substrate temperature at 60°C to form a PAA film, and cured this film at 250°C for 30 min, in a dry nitrogen atmosphere to imidize the deposited films. Films of 100 nm thickness were deposited onto Si(100) substrates under various ICBD conditions.

The bulk and surface chemical properties of PI films were studied by using Fourier transform infrared spectroscopy (FT-IR) and X-ray photoemission spectroscopy (XPS). Capacitance-voltage (C-V) and current-voltage (I-V) measurements were carried out to study the interfacial and the electrical properties of PI films. Surface morphology of PI films deposited under various ICB conditions were studied using atomic force microscopy (AFM).

### 3. RESULTS AND DISCUSSION

The bulk chemical properties of cured and uncured films were investigated using FT-IR. Figure 1 shows the FT-IR spectra from (a) the uncured film deposited with neutral cluster beam (NCB,  $V_a = 0$  V,  $V_e = 0$  V), (b) the cured film deposited with NCB (c) the cured film deposited with ionized cluster beam (ICB,  $V_a = 800$  V,  $V_e = 200$  V), where  $V_a$  and  $V_e$  indicate the acceleration voltage and the ionization voltage of the clusters, respectively. The ionization current was held at 15 mA. As shown in Fig. 1(a), the uncured film appears to have a fraction of unreacted material as indicated by the anhydride carbonyl peaks (1775 and 1850  $\text{cm}^{-1}$ ) and the amide coupling peak (1650  $\text{cm}^{-1}$ ). These peaks indicate that the uncured film is the admixed state of

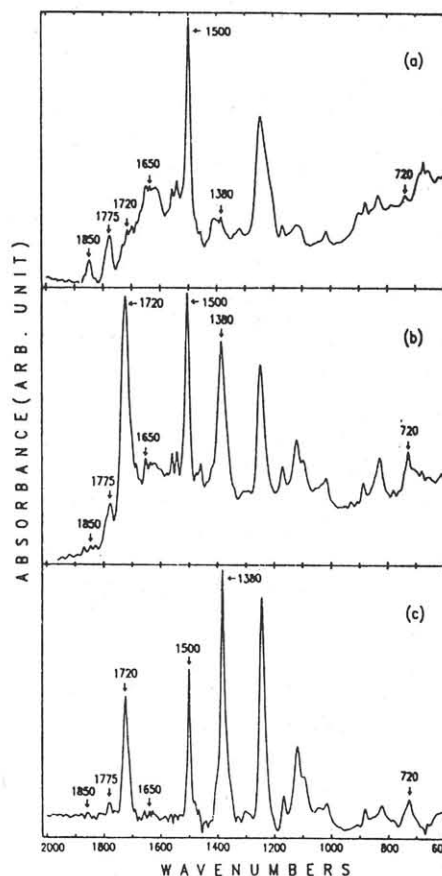


Fig. 1. FT-IR spectra from (a) the uncured film deposited by NCB ( $V_a = 0$  V,  $V_e = 0$  V) and the cured films deposited by (b) NCB and (c) ICB ( $V_a = 800$  V,  $V_e = 200$  V). Ionization current is 15 mA.

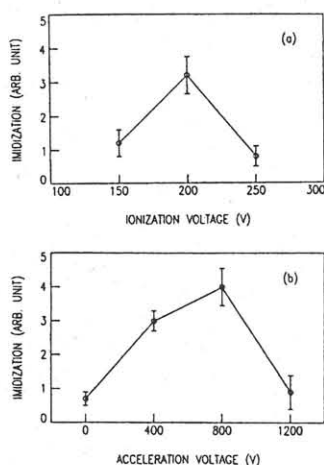


Fig. 2. Imidization ratio as a function of (a) ionization voltage ( $V_e$ ) and (b) acceleration voltage ( $V_a$ ). The electron current for ionization was around 15 mA.

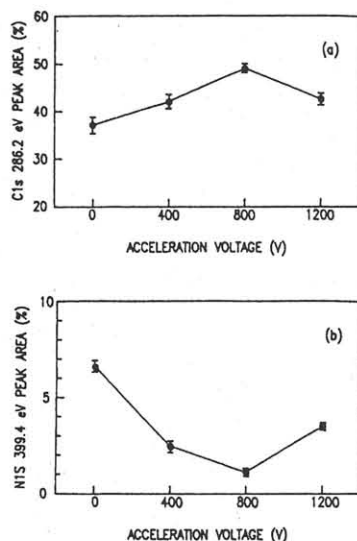


Fig. 3. Variations of (a) 286.2 eV C 1s peak area and (b) 399.4 eV N 1s peak area as a function of cluster acceleration voltage. The ionization voltage and the ionization current were fixed at 200 V and 15 mA, respectively.

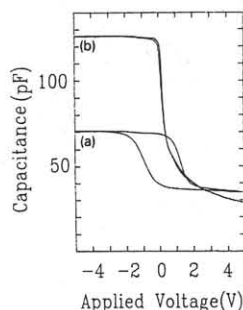


Fig. 4. C-V characteristic of PI films deposited by (a) NCB ( $V_a = 0$  V,  $V_e = 0$  V) and (b) ICB ( $V_a = 800$  V,  $V_e = 200$  V)

nonreacted monomers and PAA. On curing the films, anhydride carbonyl and amide coupling peaks are considerably decreased, while the imide peaks (1720, 1380, and 720  $\text{cm}^{-1}$ )

increase remarkably, which indicate subsequent reaction and imidization. The absorption spectra shown in Fig. 1(c) is consistent with the previously reported result for spin-coated PI film<sup>4)</sup>. Since the aromatic stretch peak at 1500  $\text{cm}^{-1}$  is relatively unaffected by the degree of polymerization or conversion to imide, it is used as a standard peak for PI characterization. We have chosen the 1380  $\text{cm}^{-1}$  peak as a measure of degree of imidization because it has been reported that both the 1720 and 720  $\text{cm}^{-1}$  peaks overlap with anhydride absorption bands. The degree of imidization is determined by comparing the 1380  $\text{cm}^{-1}$  peak areas normalized to 1500  $\text{cm}^{-1}$  peak area. Figure 2 shows the degree of imidization as a function of (a) ionization voltage ( $V_e$ ) and (b) acceleration voltage ( $V_a$ ). As shown in Figs. 2(a) and 2(b), the imidization increases at the low voltage region of acceleration and imidization, and then decreases. Figure 2 reveals that the imidization has a maximum value at  $V_e = 200$  V and  $V_a = 800$  V. Surface and interface properties of PI films play an important role in many applications, and XPS is preferred as a powerful diagnostic technique in surface and interface characterization. Thus we used XPS as a tool in the surface characterization of PI films. The XPS results were described in detail elsewhere<sup>5)</sup>. Here, we briefly describe XPS result. Figure 3 shows the variation of (a) 286.2 eV C 1s peak area which is assigned to imide coupling, and (b) 399.3 eV N 1s peak area which is assigned to isoimide. The ionization voltage and ionization current were fixed at 200 V and 15 mA, respectively. Figure 3(a) reveals that the PI films deposited at  $V_a = 800$  V have a maximum imidization, which is consistent with FT-IR analysis. Figure 3(b) shows that PI films deposited at  $V_a = 800$  V have negligible amount of impurity ( $\sim 1\%$  isoimide) which is significantly lower than that of PI films prepared by NCB ( $\sim 7\%$ ) or vapor deposition ( $\sim 20\%$ )<sup>6)</sup>. From Fig. 2 and Fig. 3, we found that the PI films having high quality bulk and surface chemical properties can be fabricated at ICB conditions of  $V_e = 200$  V and  $V_a = 800$  V.

The ICB PI is found to have a very high purity and high imidization, which can lead to improve the electrical properties such as C-V or I-V characteristics. Figure 4 shows typical C-V characteristics for (a) NCB PI and (b) ICB PI. The C-V characteristics for NCB PI shows a large flat band voltage shift ( $\Delta V_F$ ) and hysteresis which imply the existence of defects and trapped charges in the films, whereas the ICB PI reveals negligible amount of  $\Delta V_F$  ( $\sim 0.1$  V) and hysteresis. The interface trap density ( $D_{it}$ ) was calculated by the Terman's method using both measured and theoretical C-V curves. The minimum values of  $D_{it}$  for the ICB PI and the NCB PI are found to be  $6 \times 10^{10}$  and  $2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  at midgap energy, respectively. The value for the ICB PI is quite low presumably due to the sputtering of weakly adsorbed impurity at the initial stage of ICB. The I-V characteristics of ICB PI at room temperature reveals that the breakdown strength is better than 2.0 MV/cm and the electrical conduction current density of  $3.39 \times 10^{-8} \text{ A/cm}^2$  at  $E = 2.0$  MV/cm. These results clearly show that ICB PI films retain good dielectrical properties in spite of ionic irradiation.

The surface morphology is also important in practical applications. Figure 5 shows the AFM images of (a) NCB

PI film and (b) ICB PI film deposited at  $V_a = 800$  V,  $V_e = 200$  V. The rms roughness of ICB PI film is found to be 6.7 Å whereas 23 Å for NCB PI. It is thought that the ionization and acceleration of clusters lead to flat surface morphology presumably due to the enhanced adatom migration.

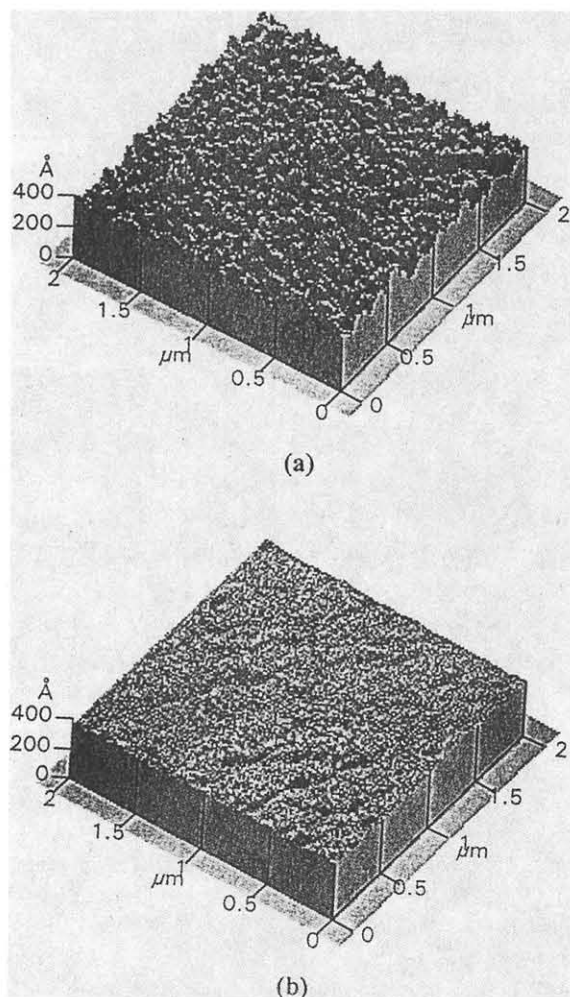


Fig. 5. AFM images of the PI films deposited by (a) NCB and (b) ICB  $V_e = 200$  V,  $V_a = 800$  V

#### 4. CONCLUSION

The electrical and chemical properties of PI films deposited by ICB are investigated in this study. It is found that this technique has the capability of growing PI film to have good chemical and electrical properties. The optimization of the deposition condition is found to improve these properties. The deposition parameters of the ICB system, such as ionization voltage and cluster acceleration voltage, play an important role in determining the chemical and electrical properties of PI film. We conclude that the ICB technique is very effective for the polymerization and has a wider range of application to organic materials.

#### Acknowledgements

This work was supported by the Electronics and Telecommunications Research Institute (ETRI) and in part by the Korea Science and Engineering Foundation (KOSEF)

through the Atomic-scale Surface Science Research Center (ASSRC).

#### References

- 1) C. E. Sroog, J. Polym Sci. Macromol. Rev. **11** (1976) 161.
- 2) H. Usui, I. Yamada, and T. Takagi, J. Vac. Sci. Technol. A **4** (1986) 52.
- 3) K. W. Kim, S. C. Choi, S. S. Kim, S. J. Cho, C. N. Whang, H. S. Choe, H. J. Jung, D. H. Lee, and J. K. Lee, J. Mater. Sci. **28** (1993) 1537.
- 4) M. C. Buncick and D. D. Denton, J. Vac. Sci. Technol. A **9** (1991) 350.
- 5) K. W. Kim, C. E. Hong, S. C. Choi, S. J. Cho, and C. N. Whang, J. Vac. Sci. Technol. A **12** (1994) 3180.
- 6) J. R. Salem, F. O. Sequeda, J. Duran, and W. Y. Lee, J. Vac. Sci. Technol. A **4** (1986) 369.