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Synthesis of crystalline polyimide film by ionized cluster-beam deposition

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Polyimide thin films were deposited by the ionized cluster-beam deposition technique. Imidization and crystallization of polyimide films were investigated using transmission electron microscopy and Fourier transform infrared spectroscopy. Polyimide films deposited under optimum conditions showed a maximum imidization and good crystal structure, which is superior to that of films fabricated by other techniques.

1. Introduction

Polyimide (PI) is becoming an important polymer in the microelectronic application because of its good thermal stability, low dielectric constant, and inertness to chemical attack [1]. For example, PI is used as an interlevel dielectric insulator coupled with highly conducting materials such as copper to achieve improved signal-propagation speed and reduced cross-talk level in a high-density multilevel interconnection scheme [2]. In this case, the crystallinity and chemical purity of PI films play an important role in the electrical properties of the multilevel interconnection scheme.

PI film is conventionally prepared by two-step synthesis; first, two monomers, such as pyromellitic dianhydride (PMDA) and oxydianiline (ODA), are mixed in a highly polar solvent to form polyamic acid (PAA) solution, the precursor of PI. The PAA solution is coated on a substrate surface and then the solvent is removed by heating at the appropriate temperature ($\sim 300\,^{\circ}$C). Then the PAA film transforms to the PI film through thermal and/or chemical dehydration. Unfortunately, this solution method has several problems inherent in the processes; PAA is hydrolytically unstable, solvent is retained within the film, and environmental and health problems are connected with the use of the toxic solvent. This method also experiences some difficulties in film thickness and uniformity control.

The vapour-deposition polymerization or sputtering techniques offer alternative processes for the fabrication of PI films. However, the results of the sputtering method with a PI target [3] revealed that the structure of the prepared film did not include the imide coupling, and the results of co-evaporation of PMDA and ODA [4] revealed that the prepared PI films contained relatively high amounts of isoimide, $> 20\%$. Moreover, the polymer films fabricated by the solution method, sputtering technique or vapour deposition are amorphous and the molecular structure of the film is very complicated [5]. Thus precise control of film properties using these techniques is very difficult.

Ionized cluster-beam deposition (ICBD) is known [6] 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, in this study, we employed the ICBD technique to fabricate crystalline PI film. We investigated the crystallinity and the chemical properties of the PI films deposited by ICBD. To our knowledge, this is the first study reporting the formation of crystalline PI film by the physical vapour-deposition technique.

2. Experimental procedure

Fig. 1 shows a schematic drawing of the ICBD system. It consists of a vacuum system, two ICB sources, ionizer, substrate holder, and electrical power supplies. The whole equipment is mounted on a conventional pumping system using an oil diffusion pump equipped with a liquid-nitrogen cold trap (base pressure in the low 10^{-7} Torr range). A liquid-nitrogen cooling jacket is installed around the sample holder to improve the vacuum condition and condense unwanted residual impurities, and the residual gas of clusters around the substrate.

Two ICB sources, as shown in Fig. 2, were used to deposit PI films, PMDA and ODA powder were charged in each stainless-steel crucible, and they were heated separately by tungsten wire heaters. The molecules ejected from the heated crucible through the

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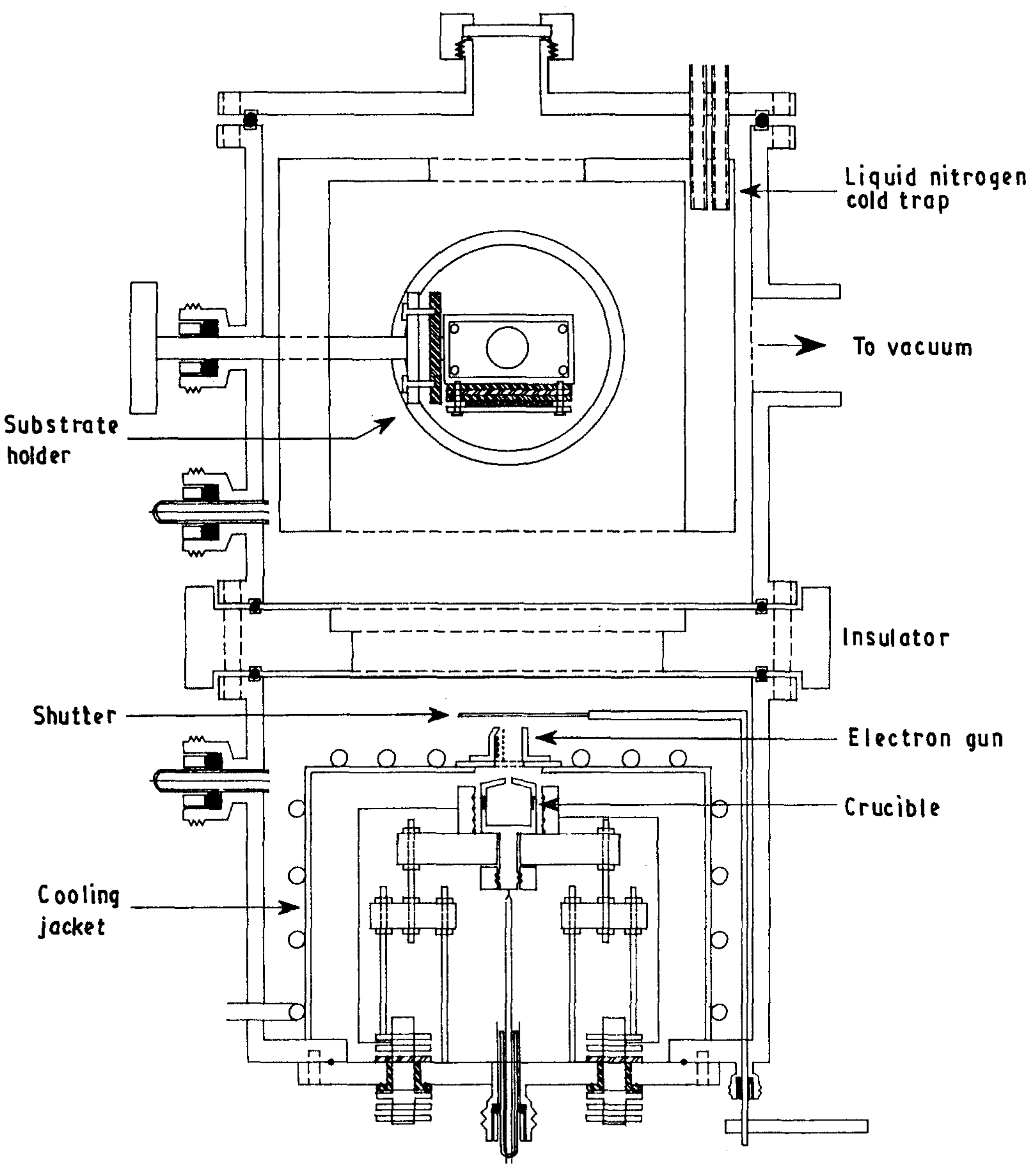

Figure 1 Schematic diagram of the ICBD system.

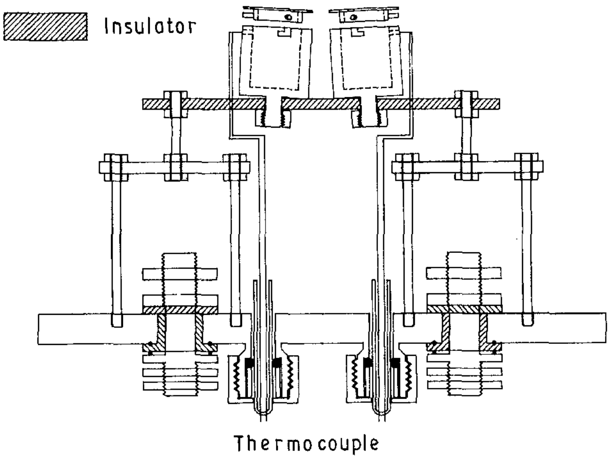

Figure 2 Schematic diagram of the source assembly used to deposit PI film. PMDA and ODA powders are filled in each crucible, which is heated by the tungsten-wire heaters.

narrow nozzle form clusters due to the adiabatic expansion process. After the clusters were ionized by the electron beam, they were accelerated by the high voltage applied between the crucibles and the substrate holder. The crucible temperatures for forming PMDA and ODA clusters were held at 210 and 180 °C, respectively, to have 1:1 stoichiometric ratio of PMDA and ODA. The acceleration voltage, V_a, was varied from zero to 1200 V, and the ionization voltage, V_e, and current for the ionization were varied up to 200 V and 20 mA, respectively.

The accelerated PMDA and ODA clusters broke into small fragments on the substrate surface to form PAA film. These PAA films were cured at 200 °C for 30 min *in situ* in a nitrogen atmosphere to imidize the PAA film. This curing temperature is somewhat lower than that of the other methods (> 300 °C) such as solution synthesis, the sputtering technique or the vapour deposition method. The base pressure of the system was maintained in the low 10^{-6} Torr range during film deposition. The crystallinity and chemical properties of the resulting PI films were investigated with selective-area diffraction of a transmission electron microscope (TEM) and Fourier transform infrared spectroscopy (FT–IR), respectively. The thickness of the cured PI films was determined by ellipsometry. Films 100 nm thick were deposited on an NaCl substrate.

3. Results and discussion

It has been reported [7] that, for polymer materials, each cluster contains several tens to a few hundred molecules. The clusters generated by the ICBD process are ionized by electron bombardment. The ionized clusters are assumed to be singly charged [7]. These singly charged clusters are accelerated by the applied voltage, V_a, to reach the substrate. When a cluster collides with the substrate, weakly coupled molecules in a cluster break up into single molecules which migrate on the substrate until they reach an appropriate position or vacancy on the substrate. By repetition of this process, a uniform and defect-free polymer film might be grown. We deposited PI films using ICBD equipment as shown in Figs 1 and 2. The chemical properties of cured and uncured films were investigated using FT–IR.

Fig. 3 shows the FT–IR spectra from the uncured sample deposited with a neutral cluster beam ($V_a = 0$ and $V_e = 0$, Fig. 3a), the cured sample deposited with a neutral cluster beam (Fig. 3b), and the cured sample deposited with an ionized cluster beam ($V_a = 800$ V, and $V_e = 200$ V, Fig. 3c). As shown in Fig. 3a, the uncured film appears to contain a considerable fraction of unreacted material, as indicated by the anhydride carbonyl peaks (1775 and 1850 cm^{-1}) and amide coupling peak (about 1650 cm^{-1}) [8]. These peaks indicate that the uncured film is the admixed state of unreacted monomers and PAA. On curing the films, there is a marked decrease in the anhydride carbonyl and amide coupling peaks; and imide peaks (1720, 1380 and 725 cm^{-1}) appear or increase remarkably, which indicate reaction and subsequent imide formation. The aromatic stretch peak at 1500 cm^{-1} remains unchanged or changes only a little, indicating that the decreased intensity in the anhydride carbonyl and amide coupling peaks is not caused by the loss of diamine due to sublimation. Because this peak is relatively unaffected by the degree of polymerization or conversion to imide, it is used as a standard reference peak of PI films [9]. In the case of the cured PI film deposited with ICB, the area of the 1380 cm^{-1} peak becomes larger than that of the cured film deposited with the neutral cluster beam.

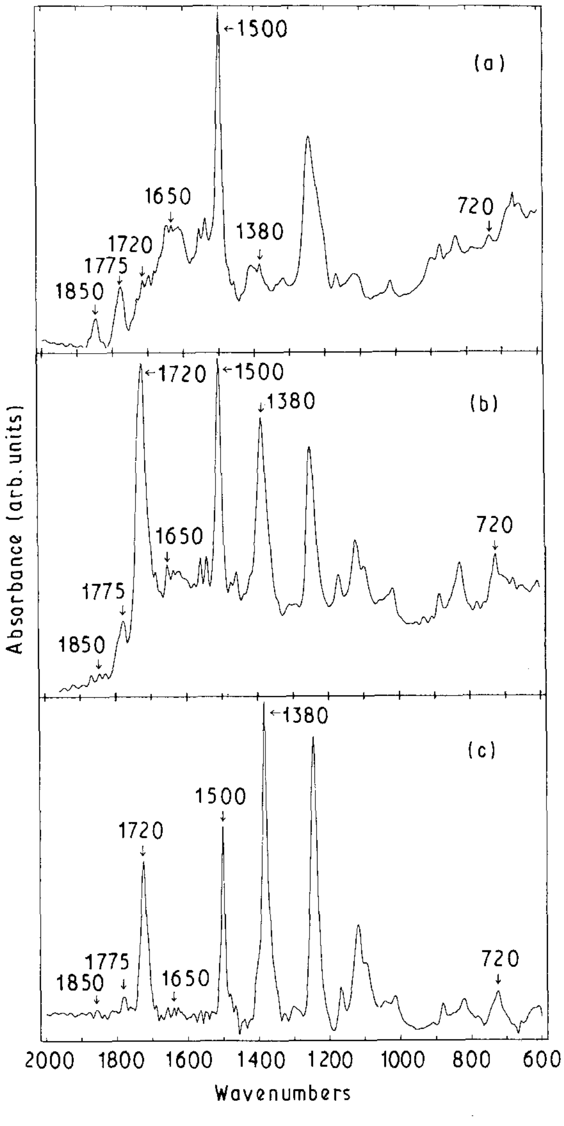

Figure 3 The FT–IR spectra from (a) the uncured sample deposited with a neutral cluster beam ($V_a = 0$ and $V_e = 0$), (b) the cured sample deposited with a neutral cluster beam, and (c) the cured sample deposited with an ionized cluster beam ($V_a = 800$ V, and $V_e = 200$ V). The electron current for ionization was around 15 mA under optimum conditions.

The peaks at 1720, 1380 and 725 cm^{-1} are known to be imide peaks. Recently, it has been found that both the 1720 and 725 cm^{-1} peaks overlap the anhydride absorbance band [10]. Therefore, we have chosen the 1380 cm^{-1} peak as a measure of the degree of imidization. The degree of imidization was determined in this study by comparing the 1380 cm^{-1} peak area normalized to the 1500 cm^{-1} peak area. Fig. 4

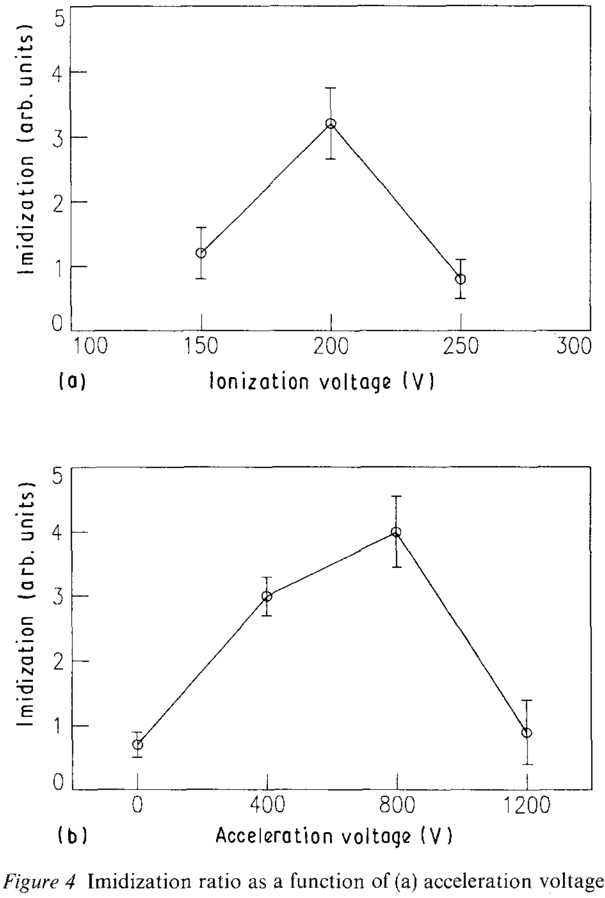

Figure 4 Imidization ratio as a function of (a) acceleration voltage, V_a, and (b) ionization voltage, V_e.

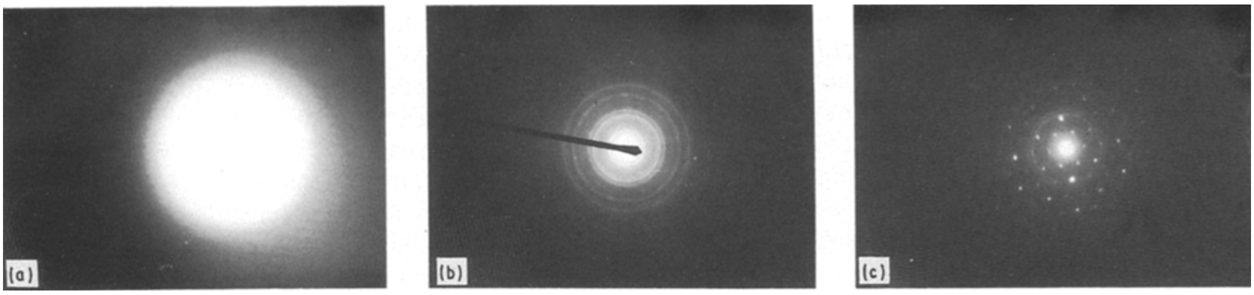

Figure 5 TEM diffraction patterns of PI films (a) deposited with a neutral cluster beam, (b) deposited with ICB at $I_e = 15$ mA, $V_e = 200$ V, and $V_a = 400$ V, (c) deposited with ICB at $I_e = 15$ mA, $V_e = 200$ V, and $V_a = 800$ V.

shows the imidization ratio as a function of accelerating voltage, V_a, and ionization voltage, V_e. As shown in Fig. 4a and b, the imidization increases in the initial stage of acceleration and ionization, and then decreases. Fig. 4 reveals that the imidization has a maximum value at $V_e = 200$ V and $V_a = 800$ V. At the optimum deposition condition, the ionization current was around 15 mA.

The optimum value of acceleration voltage for PI deposition is around 800 V. This value is considerably lower than that used for inorganic film deposition. For example, in the case of epitaxial silicon and high-quality metal depositions, the optimum acceleration voltage is around 3 kV [11]. This difference reflects the difference of cluster size between organic materials and metals. The size of the cluster of organic materials is known [7] to be about 10–100 molecules per cluster, while that of a metal cluster is distributed from several hundreds to several thousands of atoms [12]. Because the optimum kinetic energy of incident particles for high-quality film formation is known [13] to be in the range of a few electronvolts to a few tens of electronvolts, the optimum value of V_a for PI deposition is consistent with the above suggestion.

The ionization conditions for PI deposition are also different from metals, where V_e of 500 V and I_e of 100–300 mA are typical [11]. It is suggested that ionization energy for PI deposition higher than 200 eV might cause decomposition of molecules so as to enhance unwanted chemical reaction during deposition. In fact, the FT–IR spectra showed complicated small peaks in the range 1500–1700 cm^{-1} at higher values of V_a and V_e, indicating the formation of unsaturated bonds and some other impurities. At lower values of V_e, < 200 V, it is assumed that the ionization probability is not sufficient to form PMDA and ODA cluster ions and it decreases as the value of V_e decreases. The optimum value of V_e identified for PI deposition probably reflects these factors.

The electron current for ionization, I_e, is also lower than that used for metallic-film deposition. The ionization cross-section of an organic molecule is much larger than that of a metal atom. In addition, a cluster beam of smaller size has a higher ionization efficiency per unit mass-flux density because, as the cluster size increases, a larger fraction of the molecules are hidden inside the cluster and ionization probability per molecule becomes smaller [6]. Therefore, the PMDA and ODA cluster beam are considered to have a sufficient charge content to enhance PI film growth even at $I_e = 15$ mA. A higher value of I_e would not be desirable, especially for clusters which have weak intermolecular force, because clusters could break up due to charge repulsion upon multiple ionization [14].

The unique property of the ICBD technique [15] is that, when the clusters collide with the substrate, the cluster atoms are more easily scattered on the surface with high surface-migration energy. This effect results in the deposition of high-quality and/or crystalline thin-film formation at a substrate temperature significantly below that of conventional evaporation techniques. Thus we investigated the crystallinity of PI films deposited with neutral cluster and ionized cluster beams. Fig. 5 shows TEM diffraction patterns of PI films deposited on an NaCl crystal substrate using a neutral cluster beam (a), ICB at $V_a = 400$ V (b), and $V_a = 800$ V (c). A thin gold film ($\sim$ 5 nm) was deposited on the top of the PI film to avoid the charging effect during TEM observation. The PI film deposited with a neutral cluster beam shows an amorphous pattern. The film deposited at $V_a = 400$ V shows a ring pattern. The film deposited with ICB at $V_a = 800$ V shows a spot pattern, which is characteristic of single-crystalline orientation. The ring pattern in Fig. 5c is due to the gold film on PI. This crystalline PI film cannot be formed by other methods, such as the solution method and vapour-deposition polymerization.

In order to elucidate the reason why the crystalline PI film can be formed by the ICBD technique, we preheated the substrate at 120° C for 1 h in vacuum to remove adsorbed impurity, and then deposited PI film with ICB at $V_a = 400$ V. In this case, the PI films showed a very fine spot pattern indicating higher crystal orientation. Thus we suggest that surface migration and surface-cleaning effects, due to the sputtering of weakly absorbed impurities, result in crystalline PI film formation by ICBD.

4. Conclusion

The chemical and crystalline properties of PI film deposited by ICBD were investigated in this study. This technique is found to be capable of growing crystalline PI film. The parameters of the ICBD system play an important role in determining the chemical and crystalline properties of the PI film; the optimization of deposition parameters is found to improve the imidization and crystallographic property due to the high surface-migration energy, surface-cleaning effect and creation of activated centres for nuclear formation induced by ICBD. Thus we conclude that this technique is very effective in epitaxial polymerization and has a wider range of application to organic materials because of the flexibility in controlling the deposition.

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