ELSEVIER

Polymer 42 (2001) 4867–4872

polymer

www.elsevier.nl/locate/polymer

Effect of film thickness on the electrical properties of polyimide thin films

T. Liang, Y. Makita, S. Kimura*

Material Characterization and Analysis Laboratories, JSR Corporation, 100 Kawajiri, Yokkaichi, Mie 510-8552, Japan

Received 6 July 2000; received in revised form 7 November 2000; accepted 4 December 2000

Abstract

Dielectric constant and conduction current of thin/ultrathin films of polyimides on substrates with thicknesses of 80–2000 nm were measured by using a small electrode system. Polyimides used in this study were poly(diphenylmethane-2,3,5-tricarboxycyclopentyl aceticimide, TCA-DDM) and poly(pyromellitic dianhydride oxydianiline, PMDA-ODA). With decreasing film thickness, the dielectric constant decreased but the conduction current increased. Using IR reflection absorption spectroscopy, we found that the polyimide chains are oriented parallel to the electrodes. The dependence of the dielectric constants on film thickness was explained by the orientation of polymer chains. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide; Thin films; Dielectric constant

1. Introduction

Substrates coated with thin polymer films (thickness <1000 nm) or ultrathin films (thickness <100 nm) have been used widely in the field of microelectronic industry [1]. There is considerable interested in the electric properties of thin films and measurements of their properties become increasingly important and necessary. Particularly, polyimide thin films have been widely used owing to their excellent thermal and electrical properties. One of the most important applications of polyimides thin films is used as the inter-level dielectric insulators within LSI. In this case, the polyimides thin films must have low dielectric constant and high electric resistance, so the measurement of the electrical properties for polyimides thin films is a necessary technology. It is needed to attach electrodes on films during electrical measurements. For thin films, removed from substrates, attachment of electrodes becomes difficult due to the mechanical strength. Thus, measurements of electrical properties on thin films attached on substrates become often necessary.

It has been shown that the physical properties of polymer thin films such as the glass transition temperature are much different from those of bulk materials [2–5]. Experiment also shows that the electrical properties of polymer films vary with the film thickness when film thickness is less than 1000 nm [1,6]. Iida et al. [6] found that the dielectric constant of polyimide films drastically decreased when the film thickness was less than 0.3 μm. Since Iida et al. [6] used the vapor deposition polymerization method (which is much different from the actual process for making polymer thin films) to prepare the on-substrate films, their result seemed to be lack of universality.

At present, the electrical properties of the on-substrate thin films are still speculated from their bulk samples. It is necessary to have adequate measurements of the electrical properties for the on-substrate thin films.

In this study, we have attempted to directly measure the dielectric and conductive properties of the polyimide films on substrates with film thicknesses of 80–2000 nm. In order to examine the effect of orientation of the polyimide chains on the dielectric constant, we also carried out measurements of the IR reflection spectra.

2. Experimental

For the electrical measurements of the thin films with thickness <100 nm, some problems or difficulties should be solved.

The first problem is to find a suitable substrate for the electrical measurement of polymer thin films. The substrate should be flat, conductive, and easy for film coating. For the polished metal substrates, their surface roughness is about 20–50 nm. Therefore, they are not suitable to be used as the substrate of the thin film with thickness less than 100 nm. After testing for several kinds of substrate, we found the As-doped Si wafer was satisfied at the above-mentioned conditions. The roughness and the conductivity of the

---

* Corresponding author. Tel.: +81-593-45-8179; fax: +81-593-45-8112. *E-mail address:* shin-ichi_kimura@jsr.co.jp (S. Kimura).

0032-3861/01/$ - see front matter
PII: S0032-3861(00)00881-8

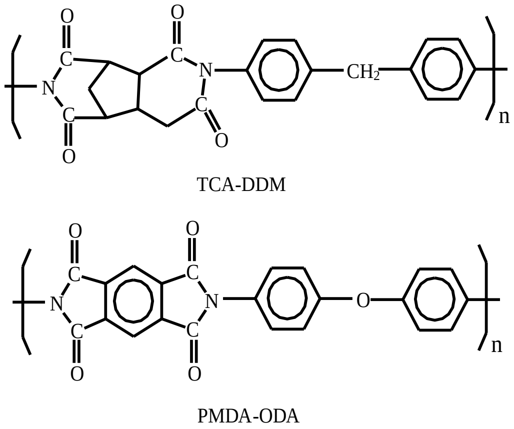

Fig. 1. Chemical structure of TCA-DDM and PMDA-ODA polyimides.

As-doped Si wafer are less than 1 nm and higher than 10^3 S, respectively.

The second problem is to avoid the formation of pinholes throughout the film since they will result in an electrical short circuit between the measurement electrodes. Rhodes [7] showed that the pinhole density increased dramatically with decreasing film thickness. One of the most effective methods to avoid the pinholes is to reduce the area of measurement electrode. The other effective method is to prepare the thin film using the double coating technique (we did not use the double coating technique in this paper). In this paper, we used the dot electrode (with area less than 0.2 mm^2) to measure the electrical properties of polymer thin/ultrathin films successfully.

The third problem is to measure the thickness of film and the area of electrode precisely since the precision of the electrical parameters such as dielectric constant depends on the precision of the values of film thickness and electrode area. However, it is not easy to measure the film thickness accurately when the film is thinner than 1000 nm. Having compared several methods of thickness measurement, we found that ellipsometry was the most suitable one because of its precision and non-destructive measurement. In order to obtain the correct area of the electrode less than 0.2 mm^2, we used a computer image analysis system to measure the electrode area.

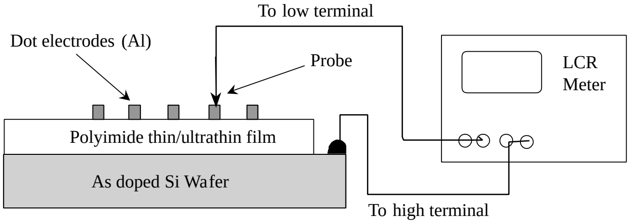

Fig. 2. Diagram of the system for dielectric constant measurements of polymer thin films.

2.1. Sample preparation

Poly(diphenylmethane-2,3,5-tricarboxycyclopentyl aceticimide) (TCA-DDM) was used in this study and its chemical structure is shown in Fig. 1. This polyimide is a pre-imidized one that can be dissolved in γ-butyrolactone. The weight average molecular weight for this polymer was measured by a light scattering instrument (DAWN-EOS, Wyatt Technology Corporation) to be 62,000.

In order to compare the dielectric constants of the free-standing film with those of the on-substrate film, poly(pyromellitic dianhydride oxydianiline) (PMDA-ODA) was also used since its free-standing film was easily obtained. The chemical structure of PMDA-ODA is also shown in Fig. 1.

Polymer thin films can be prepared by many methods. The most popular one in industrial application is the spin-coat method. Here, we used the spin-coat technique to prepare the polyimide thin films. Before spin-coating, As-doped Si wafer was washed with 1% hydrofluoric acid solution to remove the silicon oxide on the wafer surface. The γ-butyrolactone solution was spun onto As-doped Si wafer, and heated at 180°C for 1 h to remove the solvent. The film thickness was controlled by the concentration of the PI solution and the rotation rate of the spin-coater. Aluminum was vacuum evaporated through a special mask on the surface of the polyimide films to form dot electrodes (Al)–polyimide film–As-doped Si wafer sandwich samples as shown in Fig. 2. The mask has holes of diameter of 0.2–0.4 mm (thicker films using that of 0.4 mm, thinner films using that of 0.2 mm), and the area of electrode was measured by computer image analysis system within 1% error. The film thickness was measured by an ellipsometer (DVA-36LH, Mizojiri Co. Ltd).

Infrared (IR) reflection absorption spectroscopy (RAS) was applied to evaluate the orientation of molecular chains for TCA-DDM. IR spectra were obtained by using a Nicolet Fourier transform IR spectrometer with resolution of 4 cm^{-1}. A gold substrate and p-polarized radiation were used for RAS measurement. The polarized incident beam was reflected off on the sample surface at a glancing angle of incidence of 76° and the detector using a liquid nitrogen cooled mercury cadmium telluride detector with sensitive between 700 and 3000 cm^{-1}.

2.2. Measurement of dielectric constant

In order to make contact with the dot electrode that was less than 0.2 mm^2, we prepared a special probe system that can be adapted to an LCR meter (HP 4284A LCR meter). The probe was supported by a spring bearing to keep the stylus force to the sample constant. Fig. 2 shows the diagram for measurements of the dielectric constant of polyimide thin/ultrathin films. This probe system showed a flat frequency response within the frequency range of 1 kHz–1 MHz and the AC level was 10–100 mV according to the film thickness. All measurements were performed in air and at room temperature. The dielectric constant ϵ was calculated by the following equation:

$$\epsilon = \frac{(C_x - C_r)t}{\epsilon_0 \pi d^2/4} \tag{1}$$

where C_x is the measured capacitance, C_r the calibration capacitance, t the thickness of the sample, and d the diameter of the electrode; $\epsilon_0 = 8.85 \times 10^{14}$ C/m. C_r was calculated according to ASTM D150.

2.3. Measurement of current–time and current–voltage behaviors

We also applied the same type of probe system as Keithley 6517 electrometer. Using this probe system, the current–time and current–voltage behaviors of polyimide thin/ultrathin films were measured. The applied field was 0.2 MV/m (applied voltage was changed with film thickness according to voltage ($V = 0.2 \times$ thickness (in μm)). For Keithley 6517 electrometer, the response time is 8 ms to related accuracy for voltage source, and the reading rate is 115 readings/s for current measurement. All measurements were performed in air and at room temperature.

3. Results and discussion

3.1. Effect of substrates on dielectric constant measurement

The surface roughness of Si wafer is less than 1 nm, so it is an ideal substrate for polymer thin films. However, the conductivity of normal Si wafer is not good enough (about 10^{-3} S), so this led to the capacity of sample to decrease abnormally in the high frequency range, due to the dielectric dispersion for the series combination of capacitance C and resistance R. In the present system, the relaxation time is of the order of 10^{-8} s since $R \sim 100\ \Omega$ and $C \sim 100$ pF. Fig. 3 shows the frequency dependence of apparent dielectric constant ϵ for PMDA-ODA film on a normal Si wafer and that on an As-doped Si wafer. The thicknesses of the free standing film, the film on normal Si wafer and the film on As-doped Si wafer are 51, 2.3 and 2.3 μm, respectively. In the case of As-doped Si wafer, the conductivity (about 10^3 S) is high enough for the measurement of electrical properties of polymer thin films since its result was consistent with the result on the films of ordinary shape.

3.2. Effect of film thickness on dielectric constant

Fig. 4 shows the frequency dependency of dielectric constant for TCA-DDM films with thickness of 78, 158, 441, 1098, 1826 and 2710 nm. The dielectric constant decreased with increasing frequency could be attributed to the orientation polarization of molecular chains. When the film thickness was larger than 1000 nm, the dielectric constant of films did not vary with film thickness. On the other hand, when the film thickness was less than 1000 nm, the dielectric constant of films decreased with decreasing film thickness drastically. The extent of the decrease of dielectric constant was more remarkable in the high-frequency range than in the low-frequency ranges.

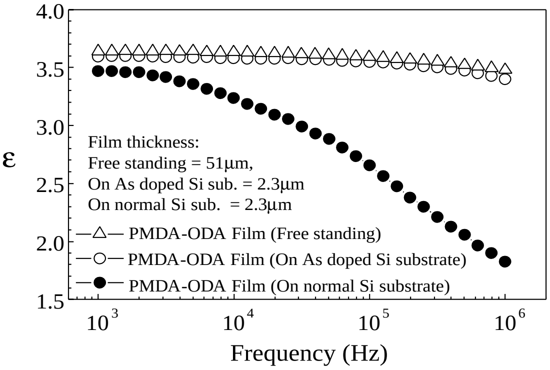

Fig. 3. Dielectric constants of PMDA-ODA film on wafers and that of the free-standing film.

The behavior that dielectric constant of polymer thin films varies with film thickness has been reported by several authors [6–11]. Two factors were considered to cause the electrical properties of polymer thin films to be much different from those of bulk materials: (1) the orientation of polymer chains along the substrate [8–11]; and (2) the interaction of polymer chains with the substrate or the electrode [2].

Many studies [8–11] have shown that the molecular chains of polyimides is oriented parallel to the substrate surface remarkably when the film thickness is less than 100 nm. Computer simulations also pointed out that the polymer chains in the proximity of the solid wall are oriented parallel to the surface [8,9]. The structure of polymer chains in the interfacial region could be described as a gradual evolution from two-dimensional-like structure at the surface to a three-dimensional Guassian conformation in the bulk [8]. From fluorescence study, it was found that the polyimide chain might be oriented in the direction of the film plane when the film was prepared by spin-coat method at high spinning speed [8].

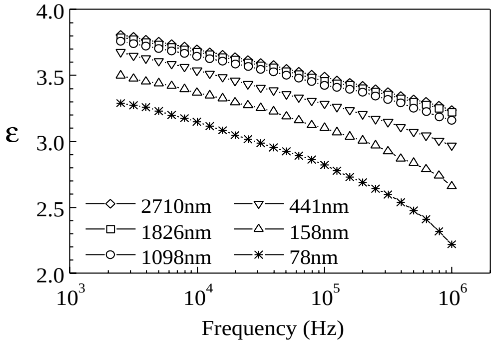

Fig. 4. Dependence of dielectric constant on frequency for TCA-DDM films with thicknesses of 78, 158, 441, 1098, 1826 and 2710 nm at room temperature.

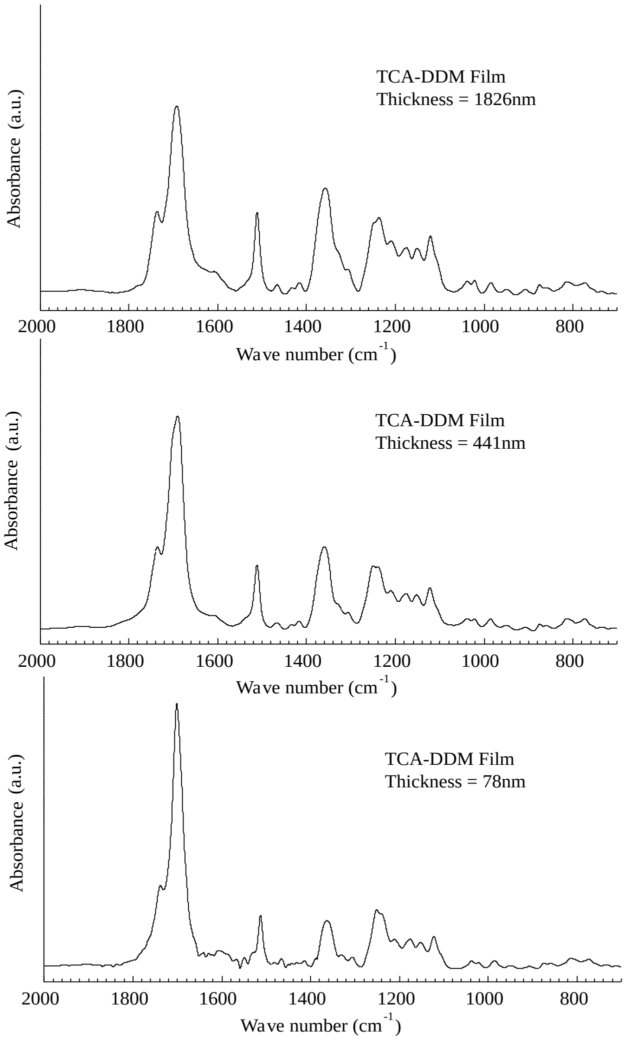

Fig. 5. Infrared-absorption spectra (RAS) for TCA-DDM films with thicknesses of 78, 441 and 1826 nm.

Fig. 5 shows the IR spectra (RAS) for TCA-DDM films with different thickness. The bands of TCA-DDM at 1690, 1510, and 1360 cm^{-1} can be assigned to the asymmetric C=O vibration, a C–C skeleton vibration of the *para*-substituted benzene rings, and the C–N stretching vibration, respectively [12]. Since the direction of electric field of polarized light is perpendicular to the film surface for RAS measurement, its IR intensity will become weaker if a molecular group turns parallel to the film surface, and vice versa. Here, the C–N stretching vibration (1360 cm^{-1}) and the skeletal vibration (1510 cm^{-1}) become weaker with decreasing film thickness indicating that the C–N and phenyl groups tend to be oriented parallel to the film surface for the thinner film. On the other hand, the C=O vibration (1690 cm^{-1}) becomes stronger with decreasing film thickness, so it indicates that the C=O group is oriented perpendicular to the film surface for the thinner film.

Fig. 6 shows the structure of the TCA-DDM chain. It is seen that the phenyl ring and the C–N bond are oriented in the direction of the chain backbone, while some C=O groups are oriented perpendicular to the chain backbone. From this structure and the IR data, we consider that the polymer chains are mostly oriented along the substrate surface for the thinner films.

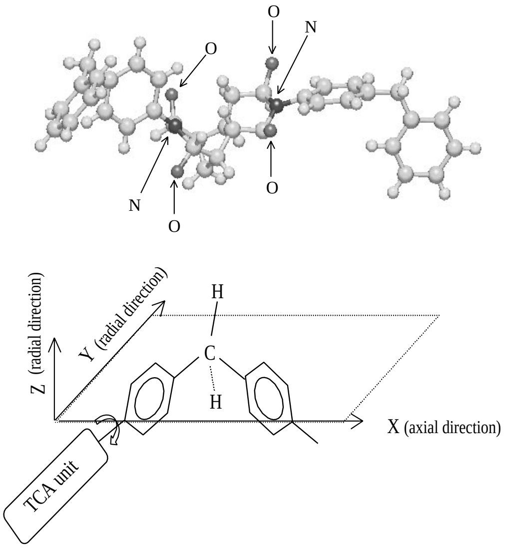

Fig. 6. Chemical structure and definition of direction of TCA-DDM chain. The average configuration of TCA unit was used when calculating the electronic polarizability of the TCA-DDM unit.

For polymers possessing a rigid main chain and having no side chain such as TCA-DDM used in this paper, the value of P_{axial} (electronic polarizability in the axial direction) is different from that of P_{radial} (polarizability in the radial direction). In order to calculate the electronic polarizability of TCA-DDM in a monomer unit, we define the axial direction and the radial direction as shown in Fig. 6. We obtained $P_{\mathrm{axial}} = 251$ and $P_{\mathrm{radial}} = 181$ (in arbitrary units) by MOPAC calculation of electronic polarizability. Thus it is reasonable to assume the $P_{\mathrm{axial}} > P_{\mathrm{radial}}$ in the TCA-DDM polymer. When dielectric constant is due to the electron polarization as in the present polyimide, dielectric constant is proportional to P. Since dielectric measurements were carried out in the thickness direction, it will be small when polymer chains are oriented parallel to the substrate because P_{radial} is the direction of measurement. The lower dielectric constant for the thinner film results in an increase in the fraction of the oriented chains in the near-interface region. According to these results, we could conclude that the orientation of polymer chains should be an important factor that leads to the decrease of dielectric constant for thin polymer films, especially for the polymer with rigid molecule chains.

According to the model of polymer thin films suggested by Beaucage [13] and Keddie et al. [14], the physical properties in the near-interface layer or region are much different from that in the bulk. Experiments have shown that the glass transition temperature and density in the near-interface layer are much lower than in the bulk for polystyrene thin film

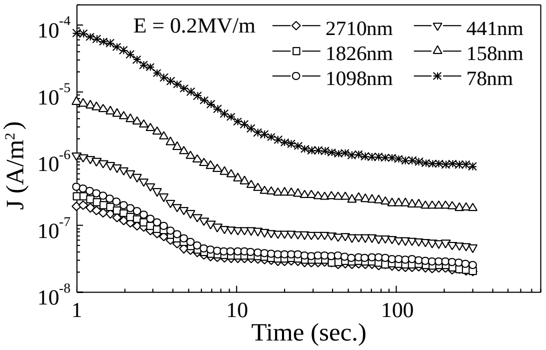

Fig. 7. Conduction current–time relaxation for TCA-DDM films with thicknesses of 78, 158, 441, 1098, 1826 and 2710 nm at room temperature.

on Si wafer [13,14]. In our case, we speculated that the dielectric constant in the near-interface layer was much lower than that in the bulk. Iida et al. [6] also reported a decrease of dielectric constant with decreasing film thickness for PMDA-ODA polyimide. They considered that the polymer chains were restricted by the solid wall of the substrate or electrode in the interfacial region between the polymer film and the substrate or electrode, and it leaded to the decrease of dielectric constant with decreasing film thickness.

3.3. Effect of film thickness on leakage current

Fig. 7 shows the leakage current–time relaxation of TCA-DDM films with thicknesses of 78, 158, 441, 1098, 1826 and 2710 nm. The current–time relaxation could be described by the following equation:

$$I(t) = \frac{V}{R_s} \exp\left(-\frac{t}{C_x R_s}\right) \tag{2}$$

where C_x is the capacity of the sample, and R_s the resistance of the measurement circuit. In our experiment, the time constant of the measurement circuit (C_xR_s) was about 10 s. The translational current before 10 s as shown in Fig. 7 could be attributed to the large time constant of the measurement circuit. When the film thickness was larger than 1000 nm, the current–time curve did not show significant changes. When the film thickness was less than 1000 nm, the time dependence is similar to that of thick films but the magnitude of the leakage current increased with decreasing film thickness drastically.

In the case of thin/ultrathin films, the distance of two electrodes is so close that the electrons emitted by metal electrodes cannot be neglected. In addition, a study [15] has shown that Schottky emission becomes remarkable for the thin film samples (the electrons emitted from metal electrode at high electric field is called Schottky emision). We suggested that Schottky emission could be attributed to the thinner film exhibiting a higher conductivity than the thicker one.

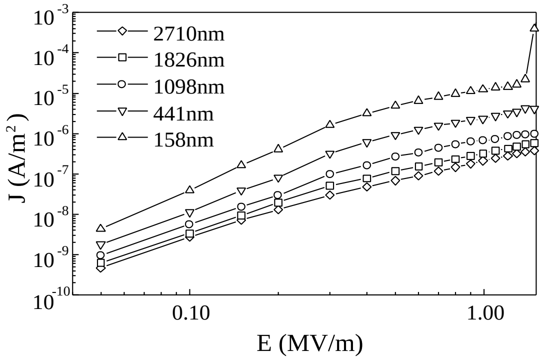

Fig. 8. Current–electric field characteristics for TCA-DDM films with thicknesses of 158, 441, 1098, 1826 and 2710 nm.

3.4. Effect of film thickness on I–E characteristics and dielectric breakdown

Fig. 8 shows the current–electric field characteristics for TCA-DDM films with thicknesses of 158, 441, 1098, 1826 and 2710 nm. The current–electric field characteristic for the sample with thickness of 78 nm cannot be measured due to electric short circuit between the electrodes. The *I–E* characteristics for all samples (except that of 78 nm sample) showed nonlinear behaviors and the current increased slowly with increasing voltage. This phenomenon is observed for many polymers, especially with higher moisture absorption [16].

4. Conclusions

We measured dielectric constant and conduction current of polyimide thin films on substrates with thickness of 80–2000 nm. The dielectric constant decreased but the conduction current increased with decreasing film thickness. The polymer chains were found to be oriented parallel on the substrates, according to IR reflection spectroscopy. The dependence of the dielectric constants on film thickness was explained by the orientation of polymer chains.

Acknowledgements

We thank Prof. K. Adachi (Osaka University) for advice and comments.

References

[1] David SS, Martynenko Z. Polymers in microelectronics. Amsterdam: Elsevier, 1989 (p. 158).

[2] Despotopoulou AM, Miller RD, Rabolt JF, Frank CW. J Polym Sci Part B 1996;34:2335.

[3] Zanten JH, Wallace WE, Wu W. Phys Rev E 1996;53:2053.

[4] Prucker O, Christian S, Bock H, Ruhe J, Frank CW, Knoll W. Macromol Chem Phys 1998;199:1435.

[5] Benecke C, Schmitt K, Schadt M. Liq Cryst 1996;21:575.

[6] Iida K, Liao C, Huang J, Makamura S, Sawa G. IEE Jpn Trans Electr Insul 1995;DEI-80:1.

[7] Rhodes SJ. Semicond Int 1981;24:65.

[8] Kumar SK, Vacatello M, Hadziioannou G. J Chem Phys 1988;89:4374.

[9] Vacatello M, Yoon DY, Laskowoki BC. J Chem Phys 1990;93:779.

[10] Lin L, Bidsrup SA. J Appl Polym Sci 1993;49:1277.

[11] Matsunobe T, Nagai N, Kamoto R, Nakagawa Y, Ishida H. J Photopolym Sci Technol 1995;8:263.

[12] Aerle NAJM, Barmentlo M, Hollering RWJ. J Appl Phys 1993;74:3111.

[13] Beaucage G, Composto R, Stein RS. J Polym Sci Part B 1993;31:319.

[14] Keddie JL, Jones RAL, Cory RA. Europhys Lett 1994;27:59.

[15] Miyoshi Y, Chino K, Jpn. J Appl Phys 1967;6:181.

[16] Nasa S. Proceedings of the Conference on Polymers for Microelectronics, 1993. p. 274.