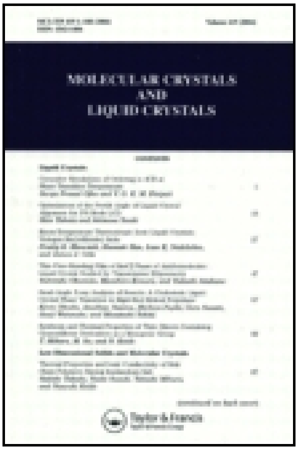

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Dielectric Properties of Polymer Thin Films for the Organic Gate Dielectric Layer

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Polymethylmethacrylate (PMMA)'s thermal and mechanical stability, high resistivity, and suitable dielectric constant make it an ideal candidate for the polymer thin film for the dielectric layer. PMMA thin films were fabricated on a glass substrate, using the spin coating process, at room temperature. The thermal-degradation temperature of PMMA was about 280°C, and the glass transition temperature (Tg) was about 110°C. To determine the effect of annealing, the coating films were annealed at 70–200°C for 60 m under argon atmosphere. The surfaces of the coating films were compact and uniform at all the annealing temperatures. The surface energies of the coating films were obtained by measuring the contact angles with deionized water and di-iodomethane. The coating films were found to have low surface energies. Up to below Tg, the dielectric constants of the coating films slightly increased owing to an increase of the total polarization arising from dipoles and trapped charge carriers. Above Tg, the coating films began to degrade; as such, their dielectric constants decreased. To ensure the reliability of the thermal endurance of the dielectric properties of the coating films, annealing was repeated three times, at 100°C. The coating films then showed no degraded dielectric properties.

Keywords: dielectric property; PMMA; spin coating process

1. INTRODUCTION

The most usual gate dielectric in organic semiconductor devices is silicon dioxide thermally grown on crystalline silicon. For large-area applications, however, the use of the inorganic dielectrics grown at high temperatures is not of particular interest. The use of organic or polymeric materials that can be spin-cast or dip-coated is more attractive [1]. Dielectric materials are used for organic thin-film transistors (OTFT) like polyimide (PI) [2,3], polyvinylphenol (PVP) [4], and

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polyvinylalcohol (PVA) [5], fabricated at low temperatures [6]. Polymethylmethacrylate (PMMA) is a good candidate for the dielectric layer in metal-insulator-semiconductor (MIS) structures. PMMA is a polymeric resist commonly used in high-resolution nanolithographic processes that use electron beams, deep UV (220–250 nm), or X-ray radiation. PMMA has also been used as a protective layer for wafer thinning. Its thermal and mechanical stability, high resistivity ($>2 \times 10^{15}\,\Omega\,\mathrm{cm}$), and suitable dielectric constant, which are similar to that of silicon dioxide ($\varepsilon = 2.6$ at 1 MHz, $\varepsilon = 3.9$ at 60 Hz), make it a good candidate for the dielectric layer in MIS structures. Besides, PMMA can be easily deposited on large areas through spin coating process and by baking at low temperatures ($<170^\circ$C) [7].

Spin coating is extensively used in microelectronics for depositing thin films of materials such as photoresists or spin-on glasses on semiconductors. It is accomplished by dispensing a solution onto a wafer, which is subsequently spun at a preset speed [8–10]. The equations governing spin coating are determined by the physical principles of mass and momentum conservation. They involve a complex combination of convection-diffusion with mass transfer. The convection is highly dominant in the earlier stages of spinning, unlike solvent diffusion-evaporation, which gains importance at the later stages of spin coating [11].

In this work, the dielectric properties of PMMA and the effect of the annealing temperatures and repeated cycles of annealing on the coating films were determined using the spin coating process. In particular, the changes in the surface energy and the dielectric constant at various annealing temperatures (70–200°C), the capacitance-voltage (C-V) behavior at various frequencies (20 kHz-1 MHz), and the effect of repeated annealing cycles at 100°C on the dielectric property were observed.

2. EXPERIMENTAL DETAILS

2.1. Preparation of the Coating Films

PMMA with a molecular weight of 90,000 was obtained from Sigma-Aldrich and was used without further purification to form the dielectric layer. Anisole was used as a solvent to dissolve PMMA. The solution concentration was between 5 and 10 wt.%. To prepare the coating films, the solution was spun on a boron-doped Si (100) substrate (p-type Si) at room temperature (RT). Before coating, the surfaces of the silicon wafers were prepared by degreasing them with organic solvents like trichloroethylene and ethanol and then rinsing them in deionized water. Uniform amounts of the solution (about $0.2 \sim 025$ ml) were introduced at the center of the substrate, and the solution was spun for about a minute. For the polymer dielectric characterization, 300-nm-thick polymer films were fabricated at the spin speed of 4,000 rpm, with 8.3 wt.% solution. After the completion of the spin coating process, the coating films were dried in a vacuum chamber for 60 m to evaporate the solvent residue in the coating film, and the coating films were then annealed at 70–200°C for 60 m, under argon atmosphere. After annealing, the coating films were exposed to the air for cooling, until it reached RT. To ensure the reliability of the thermal endurance of the dielectric properties of the coating films, annealing was repeated three times, at 100°C. A bottom metal contact was formed by evaporating aluminum (Al) on the back side of the Si substrate, and a top metal contact was formed by evaporating Al over the polymer film surface, using a suitable metal mask.

2.2. Characteristics of the Gate Dielectric

Thermogravimetric analysis (TGA) was used to determine the degree of thermal stability of PMMA. Samples were run from RT to 500°C, with a heating rate of $10^{\circ}C\,min^{-1}$ under nitrogen atmosphere. The glass transition temperature (Tg) range of PMMA was measured using differential scanning calorimetry (DSC). The heating rate was $0.4^{\circ}C\,min^{-1}$ under nitrogen atmosphere, and the temperature range was from 60°C to 180°C. Spectroscopic ellipsometry (SE, J. A. Woolam Co., Model WVASE32) was used to measure the thickness of the films that coated on the Si substrate. The surface energies of the coating films were obtained by measuring the contact angles with deionized water and di-iodomethane, through static contact angle goniometry. The C-V measurements were performed using an HP4284A multi-frequency LCR meter. The C-V measurements were carried out at a voltage range of -50 V to 0 V for various frequencies (from 20 kHz to 1 MHz).

3. RESULTS AND DISCUSSION

The thermogram of PMMA is shown in Figure 1. The spectrum shows that the degradation of PMMA began at 280°C with the evolution of monomeric methylmethacrylate and CO_2 from 280°C to 400°C. As shown in the DSC spectrum in Figure 2, the glass transition region of PMMA was around 110–120°C. The operating temperature of PMMA was below 110°C. Annealing is a process related with the stress relief and the local structural rearrangement of polymer chains.

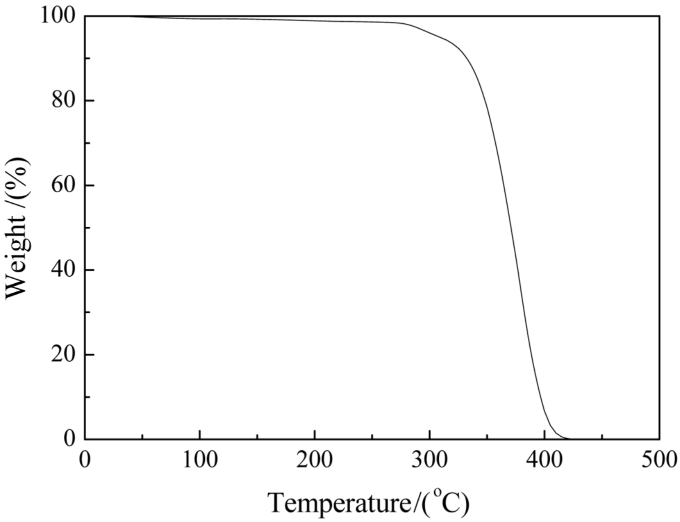

FIGURE 1 Thermal stability of PMMA shown through TGA (Thermogravimetric analysis) curve (heating rate: 10°C min^{-1}, under nitrogen atmosphere).

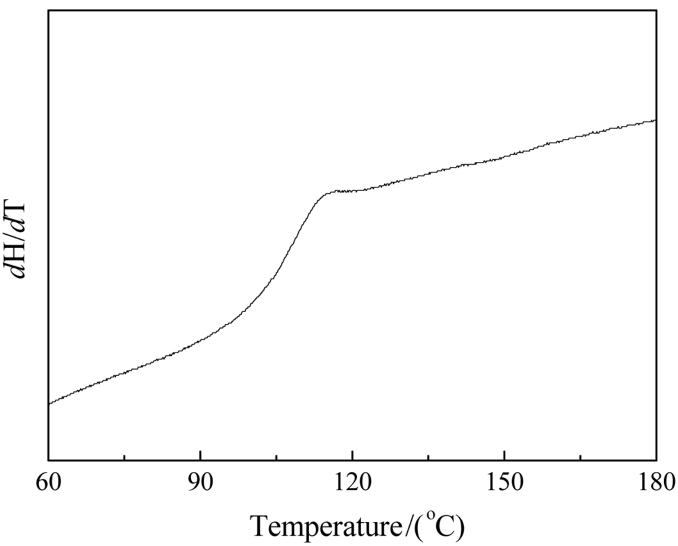

FIGURE 2 DSC (Differential Scanning Calorimerty) of PMMA (heating rate: 0.4°C min^{-1}, under nitrogen atmosphere).

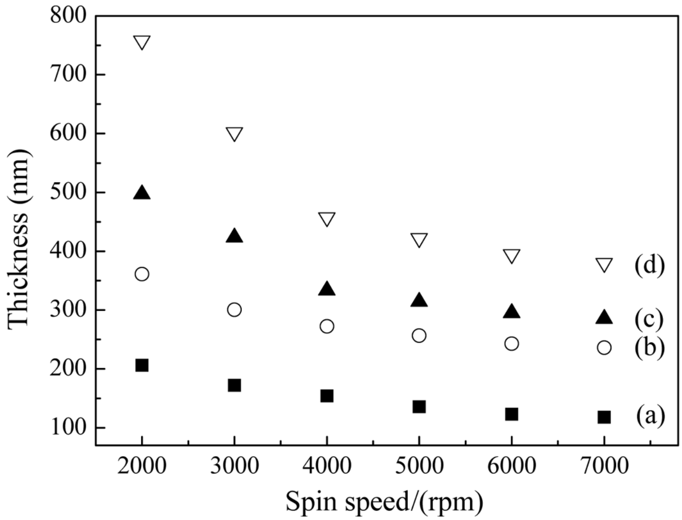

FIGURE 3 Thickness variation of the coating films at different spin speeds and solution concentrations: (a) 5.0 wt.%, (b) 6.7 wt.%, (c) 8.3 wt.%, and (d) 10.0 wt.%.

To determine the effect of annealing on the dielectric property of a coating film as a polymer gate dielectric, investigations were carried out at various annealing temperatures (70, 100, 150, and 200°C) for 60 m.

Figure 3 shows the thickness of the coating films with various spin speeds and solution concentrations. The thickness decreased with increasing the spin speed and increased along with the solution concentration. The thicknesses of the coating films did not change much at the spin speed above 4,000 rpm. The observed trend suggests that the spin coating process is controlled by two separate mechanisms: pure, centrifugally driven fluid flow and solvent evaporation.

Table 1 shows the surface energy of the coating films (43 mJ m^{-2}), which rarely changed with the change in the annealing temperature.

TABLE 1 Surface Energies of the Coating Films at Different Annealing Temperatures

Annealing temperature (°C)	Surface energy (mJ/m^2)
25	43.32
70	45.95
100	43.01
150	43.59
200	43.54

Annealing hardly affected the surface energy, which indicates that although annealing changed the bulk properties owing to the rotation and twisting of the polymer chain, it hardly affected the states of the surfaces.

The dielectric constant (ε) value can be calculated (ignoring the quantum mechanical and depletion effects on the Si substrate and gate) using the following equation:

$$C = \frac{\varepsilon\varepsilon_0 A}{d} \tag{1}$$

where A is the device area, d is the thickness of the dielectric layer, ε_0 is the permittivity of the free space ($8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}}$), and C is the measured accumulation capacitance. Figure 4 shows the dielectric constant calculated from the C-V characteristics at 1 MHz. The as-coated films showed a dielectric constant value of 3.15. The coating films annealed at 70°C showed a slight increase in their dielectric constant values, whereas the coating films that had been subjected to annealing above 70°C showed a decrease in their dielectric constant values with the increase in the annealing temperature. As the annealing temperature increased, the rate of decrease of the dielectric constant increased. The observed dielectric behavior indicated the

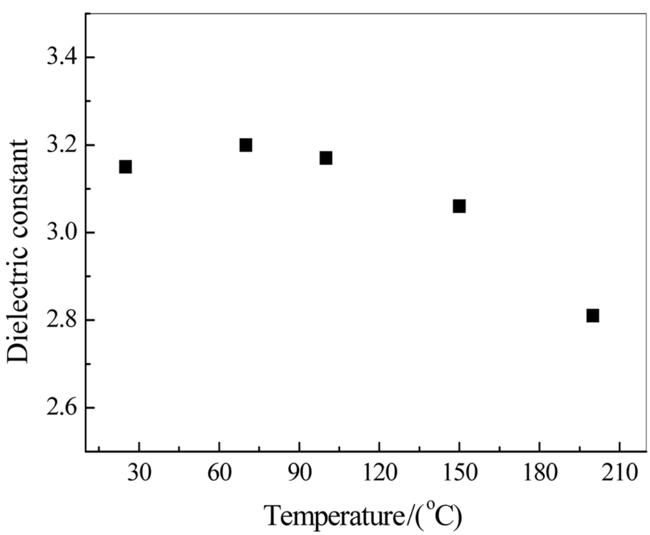

FIGURE 4 Dielectric constant of the coating films at various annealing temperatures (70°C, 100°C, 150°C, and 200°C), at 1 MHz.

weak polar nature of the coating film studied. The increase in the value of the dielectric constant obtained for temperatures up to 70°C can be attributed to the increase in the total polarization arising from dipoles and trapped charge carriers.

Figure 5 shows the variation of the C-V curve at various frequencies for the as-coated and the three-time-annealed times (at 100°C) films. The observed decrease in the capacitance with increasing frequency may be due to the tendency of the induced dipoles in the PMMA to orient themselves towards the direction of the applied field. The dielectric behavior that was observed in the annealing cycles may be attributed to the local structural rearrangement of the PMMA chains.

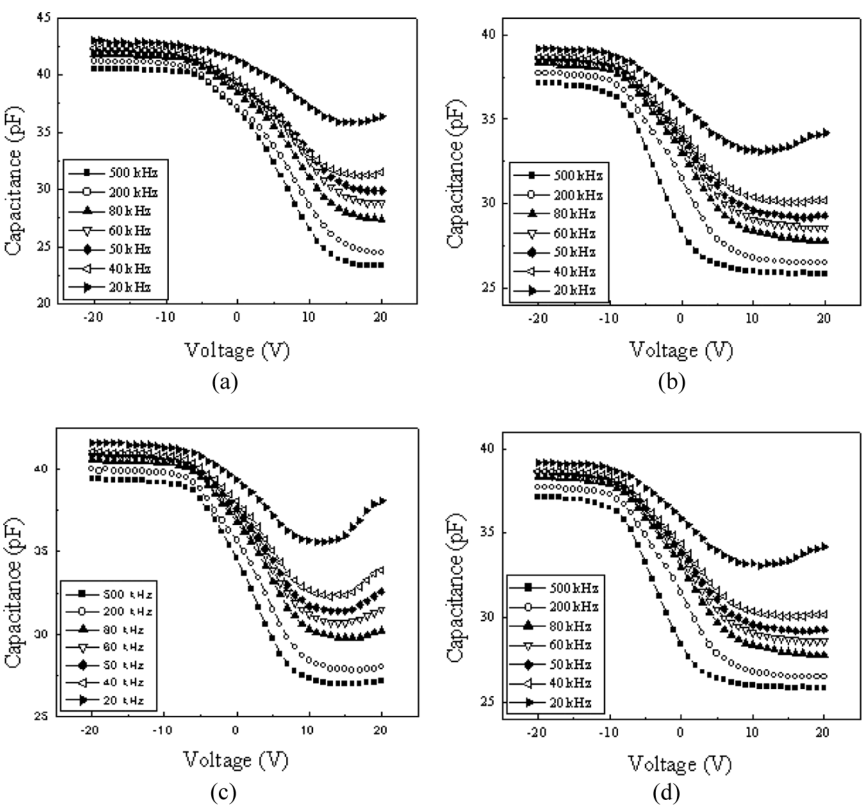

FIGURE 5 Variation of capacitance with voltage for the (a) as-coated film, (b) first annealing cycle, (c) second annealing cycle, and (d) third annealing cycle, at 100°C.

Minimal change in the capacitance values was observed when the coating films were subjected to annealing. After the third annealing cycle at 100°C, a similar capacitance value at the frequency range was found. After repeated annealing, the PMMA coating film was shown to be a reliable polymer gate dielectric layer.

4. CONCLUSION

The thermal-degradation temperature of PMMA was about 280°C. The T_g of PMMA was found to be about 110°C through DSC. The surface energy was low both in the as-coated and the annealed films. Up to below T_g, the dielectric constant of the coating films slightly increased owing to the increased total polarization arising from dipoles and trapped charge carriers. Above T_g, the coating films began to degrade; as such, their dielectric constants decreased. To ensure the reliability of the thermal endurance of the dielectric properties of the coating films, annealing was repeated three times, at 100°C. The C-V characteristics of the Al/PMMA/p-Si structure showed very good depletion behavior. The observed C-V behavior of the as-coated film indicated that such coating films have minimal defects, such as voids, stresses, and homogeneity. Minimal change was observed in the capacitance value when the coating film was subjected to annealing. After the third annealing cycle at 100°C, a similar the C-V behavior at the frequency range was observed. Below T_g, the coating films did not show degraded dielectric properties. The observed thermal stability, low surface energy, and the dielectric constant implied that PMMA formed through spin coating can be used as an efficient gate dielectric layer in OTFTs.

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