Spin coated nano scale PMMA films for organic thin film transistors

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Abstract

Nano scale poly methyl methacrylate (PMMA) films are prepared by spin coating the solution of PMMA on to p-Si substrate. The thickness of the films coated is measured by Ellipsometry. The SA-XRD spectrum of the as grown and annealed films indicated the amorphous nature. The SEM analysis revealed no pinholes, pits and dendritic features on the surface. Both as grown and annealed films indicated smooth surface and amorphous structure. The capacitance-voltage (C-V) behaviour of the metal-insulator-semiconductor (MIS) structure with Al/PMMA/p-Si has been studied. The C-V behaviour carried out for various frequencies (f) ranging from 20 kHz to 1 MHz and for a bias voltage range of -20 V to +20 V. Both as grown and annealed films showed a small flat band voltage ($V_{FB}$) shift towards the negative voltage. The small shift in the $V_{FB}$ observed may be due to charge traps and de-traps. The obtained C-V behaviour for as grown and annealed films indicated that as grown PMMA nano scale thin films do not have many defects such as voids and inhomogeneity etc. The observed C-V behavior, a very low shift in the flat band voltage ($V_{FB} \approx 0$); reasonably higher dielectric constant values; thermal stability up to 280°C; amorphous and smooth surface implies that nano scale thin PMMA film coated by spin coating could be used as an efficient dielectric layer in field effect organic thin film transistors (OTFTs).

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1. Introduction

Poly(methyl methacrylate) (PMMA) is one of the important polymers and there are numerous proposals for its application as dielectric in organic thin film transistors (OTFTs) [1-4], as sensors [5,6], as optical lenses in cameras and optical fibers [7-11]. As a dielectric layer in OTFT structure along with high dielectric constant value, it need to satisfy various constraints concerning band offsets, limits on charge traps, processability, reproducibility, stability against degradation, small leakage current and high breakdown potential. PMMA’s thermal and mechanical stability, together with its high resistivity (>2x10^15 Ω cm), suitable dielectric constant and easy to deposit on large areas by spin coating make PMMA an ideal candidate as a dielectric layer in MIS (metal-insulator-semiconductor) structures. During the fabrication of OTFTs using solution process and vacuum coating methods, the coated dielectric layer has to withstand the high processing temperature. Secondary standard PMMA obtained from Sigma-Aldrich was chosen for our investigation mainly because of its reported high melting point (>300 °C) along with the above discussed general properties of PMMA. In resent years, owing to a number of practical applications in the field of micro and opto-electronics, a great deal of interest has been paid to the study of the dielectric and conduction behaviour of varies insulating materials. A considerable work has been reported on morphology, dielectric, conduction and ageing behaviour of PMMA films [12-18].

To our knowledge, there is no detailed report on the capacitance-voltage (C-V) behavior and the effect of annealing on the dielectric and C-V behavior of the nano scale thick PMMA films prepared by spin coating technique. The present work deals with the structure, morphology, variation of dielectric constant (ε) for various frequencies (f) ranging from 20 kHz to 1 MHz, capacitance-voltage (C-V) behavior for various frequencies (20 kHz-1MHz), the effect of annealing (70°C-200°C) on the morphology and the effect of annealing on the dielectric and C-V behavior of spin coated nano scale thin PMMA films.

2. Experimental

Conventional PMMA obtained from sigma-Aldrich was used without further purification to form the insulator layer. Anisole was used as a solvent to dissolve PMMA. The solution was spun on Si substrate (p-type Si) at room temperature to prepare PMMA thin films. Before depositing PMMA, the surface preparations of silicon wafers were done by degreasing it with organic solvents such as trichloroethylene (TCE), ethanol and then followed by a rinse in deionized (DI) water. After spin coating process, the samples were dried in the vacuum chamber to evaporate the solvent remained in the film and then the bottom metal contact was formed by evaporating aluminum (Al) on the back side of the Si substrate. Finally, the top metal contact was formed by evaporating Al over the PMMA film surface by using a suitable metal mask. The films were annealed at 100 °C for 60 minutes in argon (Ar) ambient. The PMMA films coated were identified by using a FTIR spectrometer. Thermo gravimetric analyzer (TGA) was used to identify the thermal stability of the films coated. The glass transition temperature (Tg) range of the above said films were identified by using Differential Scanning Calorimetry (DSC). Spectroscopic ellipsometry (SE, J.A. Woolam Co., Model WVASE32) was used to measure the thickness of the films coated on Si substrate. The surface morphologies of the as grown and annealed PMMA films were investigated by means of SEM (FEI company, XL-305). The capacitance-voltage (C-V) measurements were performed using HP 4284A. The C-V measurements were carried out for a voltage range of -20 V to 20 V for various frequencies from 20 kHz to 1 MHz. In each study, a number of samples were investigated and the results are discussed for a film of typical thickness 290 nm.

3. Results and discussion

The FTIR spectrum of as grown and annealed PMMA of 90nm thin film is shown in the Fig.1. The peak observed at 1150 cm⁻¹ is assigned to C-O stretching (ester) where as the peaks observed at 1450
cm\(^{-1}\) and at 1740 cm\(^{-1}\) are assigned to O - CH\(_3\) bending and C = O stretching respectively. Broad and multibanded small peaks observed near 3000 cm\(^{-1}\) may be due to symmetrical and asymmetrical C-H stretching. Films subjected to annealing shows no changes in the spectrum except a small decrease in the intensity of the peaks observed near 2400 cm\(^{-1}\) at above 100 °C. The observed spectrum eliminated the possibility of solvent (anisole) molecules in the deposited film.

Fig. 1. FTIR spectrum of (a) as grown (b) annealed at 100 °C of PMMA thin film.
The TGA spectrum of the above said film is given in the Fig 2. The spectrum shows that the degradation of PMMA begins at 270 °C with the evolution of monomeric methyl methacrylate and CO₂ from 270 °C to 400 °C [19, 20]. From the DSC spectrum (Fig.3), the glass transition region of PMMA film is found to be around 95 °C to 145 °C. Surface morphology of dielectric layer is very important because it affects the property of the semiconductor layer coated over it.

Fig.2. TGA spectrum of PMMA thin film.

Fig. 3. DSC spectrum of PMMA thin film.
Fig. 4. SEM image of (a) as grown (b) annealed at 100 °C (c) 1st cycle of annealing at 100 °C (d) 2nd cycle of annealing at 100 °C (e) 3rd cycle of annealing at 100 °C.
Fig. 4a, b shows the SEM image of the as grown and annealed PMMA films. The film surface of as grown and films annealed at 100 °C is compact. No pits, pinholes and dendritic features are found in the surface. Macroscopic granular chains appear at the surface in the stretching direction of PMMA film. The granular structures (grooves) vary in size from few nanometers to hundreds of nanometers. Improved surface smoothness and greater grooves are found for films annealed at 100°C. Figure 4c-e shows the SEM images of PMMA films subjected to repeated annealing cycles at 100°C. It is observed that the surface smoothness improved with the repeated annealing cycles studied. The surface morphology of both as grown and annealed films is quite homogeneous and amorphous nature.

3.1 Annealing and dielectric behaviour

Annealing is a process related with stress relief and local structural rearrangement of polymer chains. To know the annealing effect on the dielectric and capacitance-voltage behavior of PMMA films, investigations were carried out for various annealing temperatures ranging from 70°C to 200°C and identified that films subjected to annealing at 100°C showed better dielectric and capacitance-voltage characteristics. It is also observed from the SEM analysis that films annealed at 100°C showed very smooth surface, which is one of the most important requirement of a dielectric layer in thin film transistors. Therefore, investigation of variation of dielectric constant ($\varepsilon$) with frequency ($f$) and variation of capacitance ($C$) with voltage ($V$) for various frequencies were done at 100°C for three annealing cycles to see the effect of repeated annealing.

Fig. 5 shows the variation of dielectric constant with different annealing temperature for a frequency of 1 MHz. As grown films shows a relative dielectric constant value of 2.64.

![Graph](image_url)

**Fig. 5.** Variation of dielectric constant with annealing temperature.

Films annealed at 70°C showed a little increase in the dielectric constant value where as films subjected to annealing above 70°C showed a decrease in dielectric constant value with the increase of annealing temperature. As the annealing temperature increases, the rate of decrease of the dielectric constant increases. The observed dielectric behavior indicates the weak polar nature of the PMMA film.
studied [21]. The increase in the value of the dielectric constant obtained for temperature up to 70°C is due to an increase of total polarization arising from dipoles and trapped charge carriers [22, 23].

The observed decrease of dielectric constant with increase of annealing temperature above 100°C may be assigned to the reasons such as intensified thermal oscillations of molecules at higher temperatures leading to the diminished order of their orientation, the improved stoichiometry, reduction of defects and faster structural relaxation leading to a decrease in the effective thickness of the PMMA film with increase in annealing temperature. Fig.6a-d shows the variation of capacitance with bias voltage for various frequencies (20 kHz - 500 kHz). Accumulation, depletion and inversion regions are observed for both as grown and annealed films.
Fig. 6. Variation of capacitance with bias voltage for (a) as grown film (b) 1\textsuperscript{st} cycle of annealing at 100 °C (c) 2\textsuperscript{nd} cycle of annealing at 100 °C and (d) 3\textsuperscript{rd} cycle of annealing at 100 °C.

Two types of reverse bias dependence (i.e., positive voltage supply to the top metal contact) are observed for as grown and annealed (1\textsuperscript{st} and 2\textsuperscript{nd} cycle) films for the frequency range studied. The C-V spectrum shows that there is an apparent onset of inversion and some flatness in the depletion regime. A small hump is observed between depletion and inversion regimes at lower frequencies. This is the usual
behavior of the non-tunnel MIS capacitors because of a delayed response of minority carrier density to the modulation of applied bias. For frequency below 80 kHz, the possibility of formation of the inversion layer is more pronounced where as for frequency above 200 kHz, the capacitances decreases with increase of bias voltage indicating the deep-depletion mode. Films subjected to the 3rd cycle of annealing shows the possibility of formation of the inversion layer for frequency less than 50 kHz. At low frequency, recombination-generation rates of minority carriers keep up with small-signal variation resulting in an inversion layer. It may be seen from the figure that frequency dispersion of capacitance is observed in the C-V characteristics indicating the presence of interface states (Dit) or traps [24-26]. The observed frequency dependence of accumulation capacitance may be attributed to the effect of series resistance (r_s) present in the device structure [27, 28]. The frequency dispersion observed in the depletion indicates the presence of higher density of interface states [28].

The observed decrease of capacitance with increase of frequency for the bias voltage range studied may be attributed to the reasons such as trapping-detrapping of charge carriers due to gap state density, increasing inability of the dipoles to orient themselves in a rapidly varying electric field and slow release of charge carriers from relatively deep traps in the amorphous PMMA film. As grown film shows a flat band voltage (V_{FB}) shifts towards the positive voltage value. Annealed films show a decrease in V_{FB} shift and it moves towards the zero flat band voltage value indicate the lower value of fixed charge density (Q_f) in the PMMA film. The observed V_{FB} shifts for as grown films corresponds to the electron trap and detrap [29]. Annealing improved the C-V behavior. The annealing behavior observed for PMMA film indicates that as deposited PMMA films do not have many defects such as voids, stresses, in homogeneity etc. The observed increase in the capacitance value may be due to the local structural rearrangement of polymer chains [30]. It is also observed that the thickness of the film was found to be decreased with the annealing cycle studied. The decrease in the effective thickness of the PMMA film in the MIS structure is also responsible for the observed increase of the capacitance value. It is expected that as deposited films are very much stressed by strain brought about during the spin coating, producing unrelaxed structures. The structure of the films gradually relaxes on heating during the measurements to decrease the film thickness [31].
The flat band voltage shift ($V_{FB}$) of ideal MOS capacitor is zero, based on the assumption that there is no work function difference between metal and semiconductor nor any charges (fixed or mobile) in the silicon and dielectric interfaces. In the present work with the Al/PMMA/p-Si capacitor structure, the $V_{FB}$ shift observed for both as grown and annealed films are very low. Almost similar C-V behavior with higher $V_{FB}$ shift value (-8V to -12V) was reported by LEE and Muraka [29] for Cu/fluorinated polyimide/ SiO$_2$/Si capacitor structure and by Musa and Eccleston [32] for Al/P3OT/p-Si structure. However, Folani [33] reported almost zero $V_{FB}$ shift for ITO/a-c:H in graphitic island/a-c:H/Al structure showing very low capacitance value in the range $10^{-11}$F. But PMMA used in our work using Al/PMMA(290nm)/p-Si structure subjected to 3rd cycle annealing shows almost zero $V_{FB}$ shift with higher range of capacitance value ($10^{-9}$F) for all the frequency ranges investigated, which is expected for a very good dielectric layer in OTFTs.

Fig. 7a-d shows the variation of dielectric constant with frequency for as grown film (a) 1st cycle of annealing at 100°C (c) 2nd cycle of annealing at 100 °C and (d) 3rd cycle of annealing at 100 °C.

The observed decrease of dielectric constant with increasing frequency may be due to the tendency of induced dipoles in the PMMA to orient themselves in the direction of the applied field. A little change in the dielectric constant value is observed when the film is subjected to annealing. Films subjected to the 3rd cycle of annealing at 100°C shows a higher dielectric constant value for the frequency range investigated. The dielectric behavior observed for annealing cycles may be attributed to the local structural rearrangement of PMMA chains.
4. Conclusions

Smooth and compact PMMA nano thin films were prepared by spin coating. SEM studies revealed that no pits and pin holes found on the surface. Both as grown and annealed films showed smooth surface. The observed topographical features of the as grown and annealed films indicated the amorphous nature of the films studied. The peaks observed in the FTIR spectrum eliminated the possibility of solvent (anisole) molecules in the deposited film. The TGA spectrum showed that the nano PMMA films started degrading only above 273°C. From DSC spectrum the glass transition temperature (Tg) range of nano PMMA film was found to be 97°C to 145°C. C-V characteristics of the Al/PMMA/p-Si structure showed very good depletion behaviour. However, frequency dependence of accumulation and inversion capacitance observed indicated the presence of series resistance in the device. C-V behavior observed for the as grown film indicating that as grown PMMA films do not have many defects such as voids, stresses, in homogeneity etc. The small shift in the VFB for as grown film may be due to the electron traps and de-traps. Films subjected to 3rd cycle of annealing showed a very low flat band voltage shift value (VFB ≈ 0). The observed C-V behavior, a very low shift in the flat band voltage (VFB ≈ 0), reasonably higher dielectric constant values, thermal stability up to 280°C, amorphous and smooth surface implies that nano scale thin PMMA film coated by spin coating could be used as an efficient dielectric layer in field effect organic thin film transistors (OTFTs).

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