Effect of annealing temperature on electrical properties of poly (methyl methacrylate): titanium dioxide nanocomposite films using spin coating deposition technique

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Abstract. Nanocomposite poly (methyl methacrylate) :titanium dioxide (PMMA :TiO₂) film were deposited on glass substrate. The effect of annealing temperature, especially on electrical, dielectric and the morphological properties of the thin films were investigated by current-voltage (I-V) measurement, impedance spectroscopy, and FESEM. The annealing temperature is varies from 120°C, 140°C, 160°C, 180°C and 200°C. The electrical properties results showing when nanocomposite film annealed at 120°C produce the lowest current. Meanwhile, when the annealing temperature increased, the current increased drastically and this indicates the PMMA:TiO₂ nanocomposite film are no longer having insulating properties. The dielectric properties also indicate that film annealed at 120°C has the best dielectric properties compared to other temperature. The FESEM results show that as the temperature increased, the PMMA:TiO₂ nanocomposite film started to create a phase separation between the PMMA matrix and TiO₂ nanoparticles.

1. Introduction

Presently, research to develop composite materials between polymers with inorganic materials has been steadily growing to improve the properties of polymer to be used in multiples field. The composition between two materials usually identifies as nanocomposite or hybrids materials. Nanocomposite material is defined a composite between two material which polymer with inorganic nanoparticles materials [1]. By combining these two materials, novel functions can be generated which leads to a wide range of interesting applications.

Basically, the properties of the nanocomposite materials solely depend on the preparation process. For examples the ratio of concentration between the polymers and inorganic material, the temperature use, and types of deposition techniques. There are two general approaches to prepare the nanocomposite materials. First, by using top-down technique, where the inorganic particles in nanometer (nm) sized were synthesized to form nanostructures then added into polymer. Second approached by using bottom up techniques, where the inorganic particles were directly dispersed into polymer matrix from a molecular
level [2]. This integration of polymer and inorganic components is achieved by the conventional sol-gel process. Meanwhile, spin coating technique are the most convenience method to obtain a good nanocomposite thin films [3].

Poly (methyl methacrylate) (PMMA) is one of the most versatile polymeric materials. It has been widely used for applications such as solar cells, optic [4, 5], and electro-optics [5] and as resist for photolithography. PMMA offer low-temperature process, it strong and lightweight and it was reported that PMMA can transmit up to 92% of visible light [6, 7]. PMMA also has been assessed as to be used as gate dielectric due to its high resistivity [3, 8]. Apart of then numerous advantages, PMMA also has disadvantage for example its low dielectric properties [9] and pinholes are formed when several thicknesses is reduced. Titanium dioxide (TiO₂) is one of the promising candidate materials in organic-inorganic applications. Due to its excellent dielectric and optical properties, it is extensively being used as thin film in optical devices [10] and also as a filler to enhance the polymer or organic capabilities. Some researchers have demonstrated by incorporation the TiO₂ into PMMA, they obtain an improvement in the optical properties for example capabilities in absorbing light in UV region [11-13].

To our knowledge, there is no report on the dielectric and electrical characterizations behavior of PMMA:TiO₂ nanocomposite film as dielectric layer. The study of electrical and dielectric properties of metal-insulator- metal (MIM) structure using PMMA:TiO₂ nanocomposite film as dielectric would gives useful information when to be fabricate organic capacitor or organic field effect transistor (OFET). In this work, the PMMA:TiO₂ nanocomposite thin film were prepared by spin coating method deposited on Al/Ti/glass substrates and annealed at temperature ranging from 120 to 200 °C. We report on the electrical, dielectric and surface morphology properties of the PMMA:TiO₂ nanocomposite films.

2. Experimental method

2.1 Metal-Insulator-Metal (MIM) Fabrication

The preparation of nanocomposite PMMA:TiO₂ thin film were prepared as reported in previous publication [14]. Before coating, the glass substrate was clean by sonication method in acetone, methanol and de-ionized (DI) water for 10 minute respectively. Titanium (Ti) and aluminium (Al) with the thickness of 60 and 40 nm were deposited on glass substrate acting as bottom electrode. Nanocomposite PMMA:TiO₂ were formed on Al/Ti/glass by spin coating and dry at 50 °C for 5 min. These steps were repeated several times to obtain a certain thickness. The final films were annealed only at once at temperature ranging from 120 to 200 °C for 30 min. For measurements of electrical and dielectric properties, Al electrodes were evaporated on the surface of the film through a mask as top electrodes to form metal-insulator-metal (MIM) configuration. The device structure in this work was then, Al/PMMA:TiO₂/Al/Ti/glass.

2.2 Device Characterization

The current-voltage (I-V) and measurement was performed at room temperature by the two point probe method using Keithley 4200 semiconductor characterization system connected to a probe station. Meanwhile, the dielectric properties were measured using impedance spectroscopy (Solatron S1260). To test the electrical properties, the bias voltage is swept from 0V to 5. The surface morphology and cross-section image of the thin film was measured using Field Emission Scanning Electron Microscope (FESEM, JEOL JSM 7600F).
3. Result and discussion

3.1 Surface Morphology

In order to study the annealing process, the FESEM images of the samples were measured, before and after annealing. The FESEM images of the samples before and after annealing at 120 and 180°C, are shown in Fig. 1 (a, b, c) respectively. The thickness of the thin films was found to be in the 987, 890, 793, 150 and 36 nm for 120°, 140°, 160°, 180° and 200°C respectively. Although, the film thickness for samples that being anneal at temperature 120° to 140° C is greater than 500 nm, the optimization during the deposition process on the spin speed and time can be varied in order to have film thickness below than 500 nm. Drastic changes in the film thickness for the sample anneal at 180° and 200°C is because PMMA can withstand the maximum temperature is 160°C before it melt which is consistent with the temperature that is being reported by other researchers [15, 16]. The confirmation of existing of TiO₂ nanoparticles on the surface of the PMMA:TiO₂ nanocomposite films have been published in our previous work [17]. The density of TiO₂ nanoparticles on the surface increased noticeably and porous surface occur after annealed the PMMA:TiO₂ nanocomposite film above 120°C for 30 min. When anneal the nanocomposite film at 180°C and above cause the phase separation between the PMMA and TiO₂ nanoparticles. This is because the PMMA start to degrade at temperature of 160°C [15].

![Figure 1. FESEM images of the nanocomposite PMMA:TiO₂ (a) anneal at 120°C (b) anneal at 180°C](image)

3.2 Dielectric Properties

In order to investigate the effect of annealing temperature on the dielectric properties of nanocomposite PMMA:TiO₂ thin films, the dielectric studies were performed using impedance spectrometer. Fig. 2 shows the real permittivity, $\varepsilon_r$, of PMMA:TiO₂ nanocomposite film with five different annealing temperatures. All PMMA:TiO₂ nanocomposite thin films reveal that the real permittivity, $\varepsilon_r$, are dependent to the annealing temperature. The values of real permittivity, $\varepsilon_r$, at frequency of 1 kHz and 1 MHz are reducing when the annealing temperature is increased. The nanocomposite film anneal at 120°C gives the highest real permittivity, $\varepsilon_r$ (12 at 1kHz and 10 at 1MHz) is due to an increased of total polarization arising from dipoles and trapped charge carriers. Films annealed at 180°C and 200°C give the lowest real permittivity, $\varepsilon_r \approx 0$ at same frequency. This indicates that weak polar nature of the PMMA as the matrix in the nanocomposite films. Hence, from the view point of dielectric constant, only three temperatures are suitable for obtaining a good insulation for metal-insulator-semiconductor (MIS) capacitor and organic field effect transistor (OFET) fabrication. Fig. 2 also indicates that the variation of real permittivity, $\varepsilon_r$, with frequency from 10Hz to 10 MHz for nanocomposite PMMA:TiO₂ films. The observed decreased of
dielectric constant with increasing frequency is because the induced dipoles in the film tried to rearrange themselves in the direction of applied field.

Fig. 3 shows the imaginary permittivity, $\varepsilon''$ for PMMA:TiO$_2$ nanocomposite film anneal at various temperature in the range of 120 to 200°C as a function of measuring frequency. The dependence of imaginary permittivity, $\varepsilon''$ on temperature measured at two selected frequencies (1 kHz and 1 MHz) shows that, as temperature increased, the imaginary permittivity, $\varepsilon''$ is decreased. Large imaginary permittivity, $\varepsilon''$ at low frequencies for all samples indicate that the films showing that the nanocomposite film severe high leakage current problem [18]. The imaginary permittivity, $\varepsilon''$ are nearly 0 when the nanocomposite PMMA:TiO$_2$ films were anneal at temperature above 180°C. Table 1 show the dielectric properties measurement results for the nanocomposite PMMA:TiO$_2$ at different annealing temperature.

Figure 2. Real permittivity of PMMA:TiO$_2$ nanocomposite film anneal at different temperature.

Figure 3. Imaginary permittivity of PMMA:TiO$_2$ nanocomposite film anneal at different temperature.
Table 1. Summary of dielectric properties of PMMA:TiO$_2$ nanocomposite films

| Temperature (°C) | Film thickness (nm) | Real Permittivity, $\varepsilon_r$ | Imaginary Permittivity at 1 kHz, $\varepsilon''$ |
|------------------|---------------------|----------------------------------|---------------------------------|
|                  |                     | 1 kHz  | 1 MHz  |                     |                     |
| 120              | 520                 | 12     | 10     | 2.84               |                     |
| 140              | 490                 | 6      | 4.3    | 1.88               |                     |
| 160              | 390                 | 5.6    | 3.7    | 2.56               |                     |
| 180              | 150                 | 0.2    | 0.7    | 0                  |                     |
| 200              | 36                  | 0.1    | 0.1    | 0                  |                     |

3.3 Electrical properties

I-V of the nanocomposite film annealed at 120, 140 and 160°C has the lowest current in the range of nanoampere (nA). On the contrary, the film annealed at 180 and 200°C has the highest current which is in the milliampere (mA). I-V characteristics for film annealed at 200°C showing the high rectifying curve because the film thicknesses are approximately 36 nm compare to other samples. Film thickness of the insulator are responsible in determine the device performance because a variation in film thickness will cause a large fluctuation in its electrical behaviour of the dielectric layer [19-21].

The leakage current density-voltage characteristics were also examined because the insulating property is critical design consideration for the insulator to be used as insulator or dielectric in metal-insulator – semiconductor (MIS) capacitor or organic field effect transistor (OFET). Fig. 4 shows the I-V properties of MIM structure nanocomposite film with different anneal temperature. The leakage current density for nanocomposite film annealed at 120°C is $3.14 \times 10^{-9}$ A/cm$^2$ at 5V, while it increased to $4.26 \times 10^{-9}$ and $7.41 \times 10^{-9}$ A/cm$^2$ at the same voltage applied as the annealing temperature increased to 140 and 160°C respectively. The insulating properties are reduced when the annealing temperature is increased from 160 to 200°C. The nanocomposite film annealed at 200°C ($3.3 \times 10^{-6}$ A/cm$^2$) has larger leakage current that anneal at 180°C ($1.02 \times 10^{-6}$ A/cm$^2$), is due to the perforated surface morphology of the nanocomposite film that cause the Al top contact is diffuse into nanocomposite film.

Figure 4. Leakage current density characteristics of PMMA:TiO$_2$ nanocomposite film anneal at different temperature
4. Conclusion

In conclusion, we have successfully prepared good nanocomposite PMMA:TiO$_2$ films on glass substrates by using the simple deposition technique that is spin coating. The effect of annealing temperature on the dielectric, electrical and morphology of the nanocomposite PMMA:TiO$_2$ are examined. The current-voltage and dielectric characteristics indicate that the optimum annealing temperature for nanocomposite film to be used as insulator in OFET or organic capacitor 120°C. Anneal at 180°C and above, makes the interaction between polymer chains and TiO$_2$ nanoparticles become weakened and at the same time the mobility of TiO$_2$ nanoparticles is augmented. Under these conditions, the nanocomposites films are no longer having insulation properties.

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