The effects of solvents on the properties of ultra-thin poly (methyl methacrylate) films prepared by spin coating

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A B S T R A C T

Poly (methyl methacrylate) (PMMA) is extensively used as an insulating layer in organic electronic devices. In this study, spin coating method was used to cast thin layers of PMMA for dielectric application from solutions in three different solvents, namely dimethylformamide (DMF), n-butyl acetate and toluene. The solvent's vapor pressure causes the solvent to vaporize at different rates leading to layer's distortion and different surface roughnesses. Preparation of suitable surface morphologies, for example, pinhole-free and crack-free was studied. A step profilometer was used to measure the film thicknesses. Alternatively an equation correlating final film thickness to spin speed and solution concentration was proposed. A metal/insulator/metal parallel plate capacitor structure was fabricated and the current density dependence on the applied electric field was measured. The resulting low surface roughness, low leakage currents, high breakdown voltage, and high dielectric constant were obtained for the 100 nm-thick PMMA film prepared with DMF.

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1. Introduction

Poly (methyl methacrylate) (PMMA) is a thermoplastic polymer containing hydrophobic methyl radical groups, which can play a role as a moisture inhibitor, as well as encourage good ordering of the active organic over layer as it is deposited on the surface with high resistivity of 2×10^{15} Ω/cm, similar to that of silicon dioxide [1]. In electronic device applications, PMMA was used as an insulating layer in photolithography and organic thin film transistors (OTFTs). For example, PMMA acted as a positive resist for electron and ultraviolet photolithography, as an imprintable material for hot-embossing soft lithography and as a matrix for nonlinear optical composite materials because of its excellent transparency in the visible spectrum and as a good dielectric layer in OTFTs.

Effect of solvent dissolution on mechanical and physical properties of PMMA casted film has been extensively studied by many researchers while solvent effect on electrical properties of PMMA is rarely reported. Influence of solvent on mechanical and physical properties of PMMA was also shown in the literature reviews. For examples, Briscoe et al. [2] investigated the stiffness and hardness of PMMA films cast from chloroform, toluene, and carbon tetrachloride, finding lower values for the latter solvent. Patra et al. [3] investigated the thermal, mechanical,

and structural properties of PMMA samples cast from solutions of chloroform, toluene, and dimethylformamide (DMF). Hydrogen bonding was found to be responsible for an increased glass transition temperature when prepared using DMF and toluene. Zhou et al. [4] found that the strong interaction between PMMA and acetone resulted in the formation of porous particles while the weak interaction between tetrahydrofuran and PMMA produced honeycomb structure particles. Semaltianos [5] spin coated PMMA films using chlorobenzene and found formation of surface pinholes and large-sized circular pits. Noh et al. [6] demonstrated that the 100 nm-thick PMMA films could be prepared using n-butyl acetate (nBA) for top-gate polymer field-effect transistors. The best root-mean-square roughness values of nBA and toluene are 0.52 and 0.32 nm, respectively [7]. From the previous reports mentioned above, the type of solvent selected plays an important role on uniformity and thickness of the PMMA films. A solvent with a lower vaporizability results in a better uniformity and a lower thickness. Therefore, the solvent should be selected on the basis of the desirable thickness and uniformity [8–10]. DMF, nBA, and toluene are promising candidates as suitable solvents that this study chooses to prepare PMMA ultrathin film. Furthermore, effect of PMMA dissolution by selected solvent is still also investigated along with PMMA thin film fabrication by spin coating. For thin film fabrication by spin coating, many parameters occur during the spin process such as spin speed, spin time including dissolution of PMMA in various selected solvents which are related to concentration, viscosity, and solvent evaporation which are optimized to give good film quality such as good thickness and surface roughness. For electrical property, in order to increase

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insulator capacitance to achieve the lowest leakage current corresponding to the highest breakdown strength, the film thickness must be minimized without the presence of pinholes, pits, or any other types of defects. In electronic applications, when a semiconductor thin film is deposited on the dielectric layer, a low surface roughness is also crucial in order to achieve reliability and stability of threshold voltages and other related electrical properties [11].

The aim of the present study is to investigate the influence of spin speed and concentration of PMMA dissolved in selected solvent, DMF, nBA, and toluene, on the film thickness, surface roughness, surface morphology, and the electrical property on of PMMA thin films spin-cast.

2. Experimental details

2.1. Material and device preparation

PMMA having an average molecular weight of ~996,000 as measured by gel permeation chromatography was purchased from Sigma-Aldrich. Analytical reagent grade DMF, nBA, and toluene were purchased from LAB-Scan Analytical Sciences.

Glass substrates were cleaned with a soft brush in detergent and dried with a nitrogen gas, then cleaned again with piranha solution at 60 °C for 1 h, then rinsed with deionized water and finally dried with the nitrogen jet.

A metal/insulator/metal (MIM) parallel plate capacitor structure was fabricated step by step on 2 cm × 2 cm cleaned glass substrates following below procedure. Firstly, bottom-metal aluminum electrodes were fabricated by a thermal evaporator through a metallic mask on glass substrate. For an insulating layer, PMMA was dissolved in each solvent, DMF, nBA, and toluene. The samples were spun in nitrogen glove-box on the patterned aluminum on glass substrate for 180 s at a spin speed of 2000 rpm. Films were allowed to dry in an argon atmosphere for 1 h at 60 °C, then for another 1 h at 120 °C in order to remove residual solvents and to anneal the polymer films. The last step for MIM parallel capacitor is thermal evaporation of aluminum metal again on an insulating layer to obtain parallel plate capacitor structure for further characterization.

2.2. Characterization

For accuracy and reliable result, each characterization of the sample was conducted on 3 positions on the sample with 3 samples to analyze and average data values. The thickness measurement was measured using a step profilometer (Dektak 8000). Surface roughness of the polymer layer was scanned using tapping mode (Dynamic force mode) using a SPA400 atomic force microscope made by Seiko Instruments. Etched silicon tips were used with resonant frequency of 140 kHz and force constant of 3.5 N/m. Roughness measurements were calculated using SPIWin version 4.08F from scan sizes of 3 μm × 3 μm. The leakage current versus the electric field for the 100 nm-thick PMMA layers of the MIM parallel plate capacitor structure was measured by using a high-accuracy current–voltage measurement (Keithley 2612). A DC voltage, sweeping from 0 V to 40 V, is applied across the electrodes and the corresponding currents are measured. The data were analyzed according to ASTM D3755. Dielectric constant versus frequency and loss factor were measured by using an impedance analyzer (Agilent 4294a) with a fixed 10-mV AC voltage.

3. Results and discussions

To investigate the effect of spin speed on the thickness of PMMA, the solutions having 3 wt.% PMMA in DMF, nBA, and toluene were coated at different spin speeds. The thickness of each sample was then measured and plotted versus spin speed as shown in Fig. 1a. At all spin speeds, DMF resulted in the lowest thicknesses among the three solvents
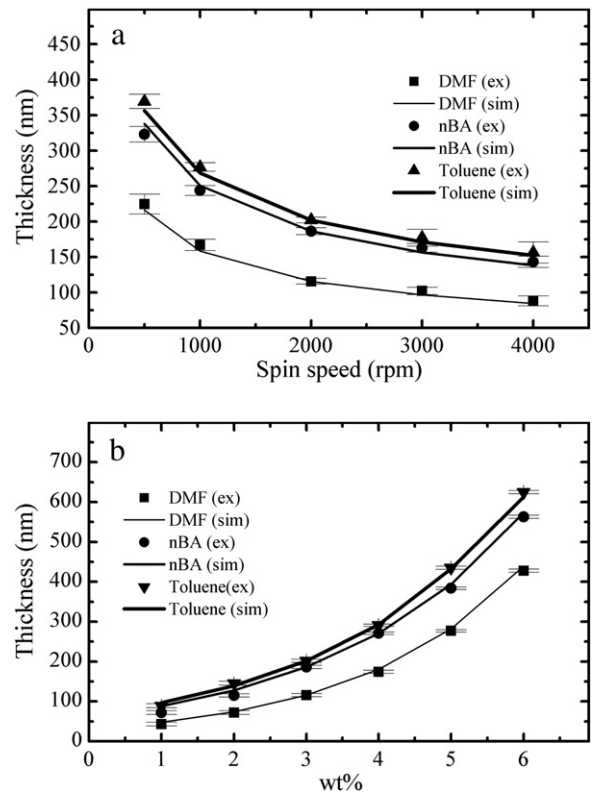

Fig. 1. (a) Thickness of PMMA films as a function of spin speed at 3 wt.% and (b) thickness of spin-coated PMMA films as a function of PMMA concentration in DMF, nBA, and toluene at a spin speed of 2000 rpm (where "ex" and "sim" represent experimental and simulation results, respectively).

used. This suggests that DMF enables uniform extended and interconnected PMMA chain network [2]. Moreover, hydrogen bonding in the PMMA chains formed by replacement of the methoxy groups of PMMA by amide groups of DMF is proposed to be responsible for the superior performance of the DMF over other solvents used to prepare PMMA [3]. Among all spin speeds experimented, 2000 rpm was found to give the least thickness fluctuation. Increasing the spin speed over 4000 rpm decreases the thickness further, however significant thickness fluctuation occurs at different locations of the samples as shown by the deviation in Fig. 1a. Although sub-100 nm-thick PMMA films are desirable in nanoelectronics, as published elsewhere [1,5], data obtained beyond 4000 rpm were not reliably recorded to draw a conclusion on their behavior. Keeping the spin speed at 2000 rpm, the PMMA thicknesses were plotted against concentration of PMMA in DMF, nBA and toluene as shown in Fig. 1b. The thicknesses of 100 nm were obtained using DMF, nBA and toluene at the projected PMMA concentrations of 2.7, 1.7 and 1.2 wt.%, respectively.

To find an optimal condition to achieve the desirable thickness (of around 100 nm to minimize leakage current, maximize breakdown field, and avoid pin-holes and cracks), simulation of the film thickness variation with concentration and spin speed was conducted and found to fit well with experimental results (shown as lines in Fig. 1a and b). Apart from concentration and spin speed, for example, rate of evaporation, substrate surface energy, viscosity, and polymer molecular weight are known to affect the thickness of the spin-coated PMMA films. Lima and de Andrade [12] proposed that thickness h depended on the concentration of the PMMA solution, c, and spin speed, ω, as indicated in Eq. (1):

$$h = Ac\omega^{-\alpha} \qquad (1)$$