Effects of Zinc Oxide Nanoparticles on Polystyrene Thin Films

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Abstract

Polymer thin film is the base material of various electronic devices. The organic films need to be stable on metal oxide substrates while processing application to preserve their properties. However, increasing temperature by operation of an electronic device causes polymer thin films lost their stability. Some researchers have discovered that a thermal stability of polymer thin films is enhanced by adding small amount of nano-fillers. The phenomena is different from classical knowledge which the existence of impurity in polymer thin film usually induces dewetting behavior. The effects of addition of zinc oxide nanoparticles on thermal stability of polystyrene thin film are investigated in this research. The films thickness studied in this work are about 30 nm. The concentrations of zinc oxide nanoparticles are vary from 0.05 – 0.20 wt.%. After annealing all thin films for various times, film topographies are studied by using optical microscope. Dewetting area are observed and calculated to compare the percentages of each samples. Surface energies of each film are studies by contact angle measurement.

Keywords: Polymer thin film: Dewetting: Nanoparticles

Introduction

Polymer film are a well-known material used in various technological applications like dielectric coatings, optical coatings, lithography resisting, electronic packaging, and surfaces lubricating because of a remarkable insulation property of polymer. Electronic technology concept nowadays is smaller and faster. Therefore polymer film becomes thinner. Producing a stable and defect-free polymer films on metal oxide substrates is difficult because of the differences of chemical composition between two materials.

Many researches have been investigated how to retardation dewetting behavior of polymer thin films, for example, modification of polymeric structure and/or substrate surface [1-3] addition of polymer additive [4-6], and addition of nanoparticles [7-8].

In this research, the stability of polystyrene thin films added by zinc oxide nanoparticles is investigated. All films with the thickness less than 30 nm are annealed under various heat treatment conditions. The thermal stability of all films is investigated. Topography is examined by optical microscopy (OM). The dewetting areas were measured by using commercial graphical analysis software. Contact angles are measured using a contact angle meter.

Materials and Methods

Polystyrene with narrow size distribution (PS52K, Mn = 12,000 g/mol, Mw/Mn = 1.07) was purchased from Polymer Source Inc. (Canada). Zinc oxide with diameter size less than 20 nm was purchased from Sigma-aldrich. Suspension of the nanoparticles in toluene was prepared by using ethanol as a dispersant. Nanoparticle suspensions were mixed with polystyrene at the concentrations of 0.05, 0.10 and 0.20 wt.%. These solutions were clear and stable, indicating the miscibility of the two materials.

Silicon wafer substrates were cleaned by soaking in a 7:3 v/v solution of conc. H_2SO_4 and 30% H_2O_2 at about 80 °C for 1 h. The substrates were rinsed with deionized water for several times and dried by pressurized nitrogen gas. All substrates were freshly cleaned for the preparation of polymer films. Thin films of polystyrene on silicon wafer were prepared by spin casting from 0.5 wt.% solutions, yielding thicknesses of about 30 nm. The spinning rate was kept constant at 1000 rpm for about 10 s. All samples were left at room temperature for a night. Then, the dewetting processes of all films were accelerated by annealing the samples in a vacuum oven at 180 °C. Surface structure of the films at different annealing times was investigated using optical microscopy. The dewetting areas were measured by using commercial graphical analysis software.

The film thickness was measured by atomic force microscopy (AFM). Surface energies of polystyrene and composite film were measured following the Owens–Wendt–Kaelble approach [5]. Water and diiodomethane were used as solvents.

Results and Discussion

After spin coating, all films were clear and continuously spread cover silicon wafer substrates. Effects of zinc oxide nanoparticles on thermal stability of polystyrene thin films were investigated. Rising the temperature, higher than glass temperature of polystyrene, induces dewetting behavior of polymer thin film. As a result, annealing all films at 180 °C for 5 min, dewetting process was initiated. Dewetting behavior of composite films between polystyrene and zinc oxide nanoparticle was followed by optical microscope, as shown in Figure 1.

After annealing all films at 180 ˚C for 5 min, small holes were detected in pure polystyrene film and all mix films. Hole diameter in polystyrene was about 20 µm and decrease to about 5 µm in mix films with 0.20 wt.% concentration of zinc oxide in the same condition. Increasing anneal time to 15 min, small holes grew up and hole diameters were about 50 and 30 µm in pure polystyrene film and mix films, respectively. Subsequently, anneal for 50 min, pure polystyrene film showed that detected holes were expanded and came close together to form ribbon structure. Conversely, hole diameters of 0.10 and 0.20 wt.% zinc oxide composite film were remain about 30 µm. Process of dewetting behavior became to a final step when annealing pure polystyrene film at 180 °C for 70 min. The droplets of polymer in hexagonal arrangement were revealed in the film. This recognized pattern referred to the final state of dewetting process called completely dewet. However, all mix films were in intermediate state at the same condition. None of composite films exhibited the completely dewet unless an annealing time was increased to 90 min (not shown). Additionally, at the final state of dewetting process of pure polystyrene film, annealing time is 70 min, percent dewetting area of composite films with 0.05, 0.10 and 0.20 wt.% were about 75%, 70% and 65%, respectively.

Consequently, optical micrographs exhibit that addition small amount of zinc oxide nanoparticles, at least 0.05 wt.%, can retard dewetting behavior of polystyrene films. Moreover, increasing concentration of zinc oxide nanoparticles increases thermal stability of polymeric films. After annealing for 70 min. the polystyrene film with 0.20 wt.% concentration of zinc oxide nanoparticles indicates that the holes detected in the film are not enlarged by increasing heating time. It looks as though the nanoparticles discontinue hole's enlargement.

For that reason, zinc oxide nanoparticles are expected to present pinning contact line effect in polystyrene films. The nanoparticles may be fitted in the polystyrene chain segment, because of their tiny size [9]. Then the mobility of polymeric films is decreased and holes cannot expand. The viscosity of the films increases and finally the velocity of dewetting behavior are slower. Finally, addition of zinc oxide nanoparticle retards dewetting behavior of polystyrene film. Thermal stability of composite films is improved. Moreover, the surface energy, calculate by using contact angle value, of pure polystyrene film and composite films have no significant difference. The results support to pinning contact line effect.

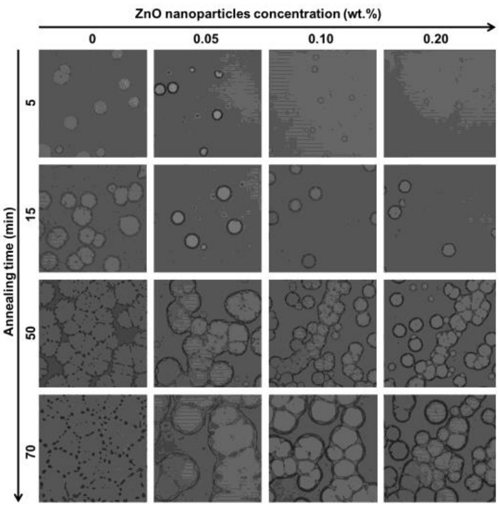

Figure 1 Optical micrograph illustrate dewetting pattern of polystyrene films added with zinc oxide nanoparticles from 0 – 0.20 wt.% Film thickness is about 30 nm. All films are annealed at 180 °C. Image size is 300 μm x 300 μm.

Conclusions

Addition small amount of zinc oxide nanoparticles can retard dewetting behavior of polystyrene films. Increasing concentration of zinc oxide nanoparticles increases thermal stability of composites films. Moreover, optical micrographs reveal that the pining nanoparticles break holes growing in polymer layer. Percent dewetting area of 0.20 wt.% mixed film is constant at about 65% after annealing for 70 min while percent dewetting area of pure polystyrene film becomes 100%, or completely dewet, at the same condition. Existing of zinc oxide nanoparticles discontinue hole's enlargement. This nanoparticles may be fitted in the polystyrene chain segment and reduce polymeric mobility. Dewetting process of this system is inhibited and also thermal stability of all composite films is improved. Likewise, The mechanism controlling the retardation of dewetting behavior should be pining contact line effect.

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