

The effect of film thickness on the depth-wise chain orientation of rigid rod-like polyimide

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1. Introduction

Polyimide (PI) attracts more attention as an insulating material in many microelectronic devices such as flexible printed circuit boards (FPCBs), aligning films in LCD, and photoresists or dielectric interlayer in integrated circuits (ICs) due to its outstanding thermal, mechanical and electrical properties [1,2]. Recently, demands on highly reliable dielectric properties of PI films are increased as they are applied to smart devices which requires high frequency signal transmission. One possible approach to meet the needs is to increase the thickness of the insulating film. However, the increase of film thickness can ruin the film uniformity in the film thickness direction, which may cause many problems such as film curling, low peel strength or delamination with substrates, and so on. Thus, it is important to understand the variation of depth-wise microstructure of rod-shaped PI when the film thickness increases, in order to precisely control the process when manufacturing the thick PI films.

2. Theory

Polymer solution cast on a substrate preferentially align to the direction of the film plane. It is because the biaxial tensile stress is exerted on the polymer chains during the solvent evaporation under the confinement of substrate [3,4]. It means that the larger the amount of solvent evaporation, the stronger the tensile stress on the polymer chains, which finally affects the degree of in-plane chain orientation at the dried state.

PI film is made by casting the precursor solution, poly(amic acid) (PAA), onto a substrate, and drying and curing the coated PAA. Drying process solidifies the PAA first, and the

subsequent curing process makes the PAA imidized to PI that has more rigid chain backbones [5,6]. The chain orientation of PAA after drying is affected by the amount of solvent evaporation, in other words, the amount of residual solvent after drying. Therefore, it is possible to estimate the depth-wise microstructure of PAA which is represented by the degree of in-plane chain orientation by measuring the residual solvent concentration in the film depth direction. Tracking the amount of residual solvent is also important because the remaining solvent acts as a plasticizer during the curing process [7,8]. Solvent molecules enhance the chain mobility, and results in the rapid imidization during the curing process. If most PAA chains are converted to rigid PIs before they have enough time to make a well-ordered structure, the cured PI film cannot have a high degree of in-plane chain orientation. Thus, chain orientation of fully imidized PIs may hardly deviate from that of the dried PAA [9].

3. Experimental

To make a PAA solution, 3,3',4,4'-biphenyltetracarboxylic acid (BPDA, Ube Industries) is added to the solution in which p-phenylene diamine (PDA, DuPont) is dissolved beforehand. The prepared PAA is cast on clean glass substrates and two different thick films having wet thickness of 80 μ m, 250 μ m, respectively are made. The films are dried at 120°C in a convection oven for 4 different drying times, 3, 5, 7, and 10 minutes. The depth-wise residual solvent concentration is measured at each drying time by using confocal Raman spectrometer (LabRAM HR800, Horiba Jobin Yvon). The PAA films dried at 120°C for 10 minutes are then cured in a heating chamber attached to a rheometer (RMS 800, Rheometrics). The starting temperature is set 120°C and is increased with the ramp speed of 5°C/min. The depth-wise degree of imidization (DOI) is measured at different temperatures, 150°C, 170°C, 200°C, and 350°C during the curing process using the same confocal Raman spectrometer. The fully imidized PI film is cut by focused ion-beam (Helios650, FEI), and the cross-section of the film is exposed to the polarized Raman spectrometer to examine the depth-wise chain orientation.

4. Results and Discussion

During the drying process, the variation of residual solvent concentration is investigated. For thick PI (30 μ m thick), the average amount of residual solvent is much larger than the thin PI (10 μ m thick) after 10 minutes of drying, and a depth-wise inhomogeneous distribution of solvent concentration is observed. It is because the solvent near the substrate is difficult to diffuse out to the surface when the film thickness increases. The larger amount of residual solvent implies that less tensile stress is exerted on the thick film, and makes PAA chains having lower degree of in-plane orientation at the dried state.

The dried PAA film is cured and the DOI is measured at different temperatures during the curing process. For thick PI, DOI increases at low temperature with non-uniform distribution along the film depth direction. This is ascribed to the fact that thick film has more solvent

after drying which enhances the imidization reaction. As a result, PAA chains having lower degree of in-plane orientation after drying are imidized faster to rigid PI in the case of thick PI. As the polymer chains cannot be packed densely after it becomes rigid, the degree of in-plane chain orientation of fully cured PI can be strongly affected by the chain orientation of the dried PAA.

To quantify the degree of in-plane chain orientation of fully imidized PI, the Fraser fraction [10], f , which represents a fraction of perfectly oriented polymer chains to the direction of film plane, is employed. When the fraction f is close to 1, PI chains more likely align to the in-plane direction. As can be seen in Figure 1, the thick PI film shows less degree of in-plane chain orientation throughout the film thickness and the side-to-side difference of f is observed. The result is similar to the estimated chain orientation of the dried PAA, which proves that a considerable part of final chain orientation of PI is determined by the microstructure developed during the drying process.

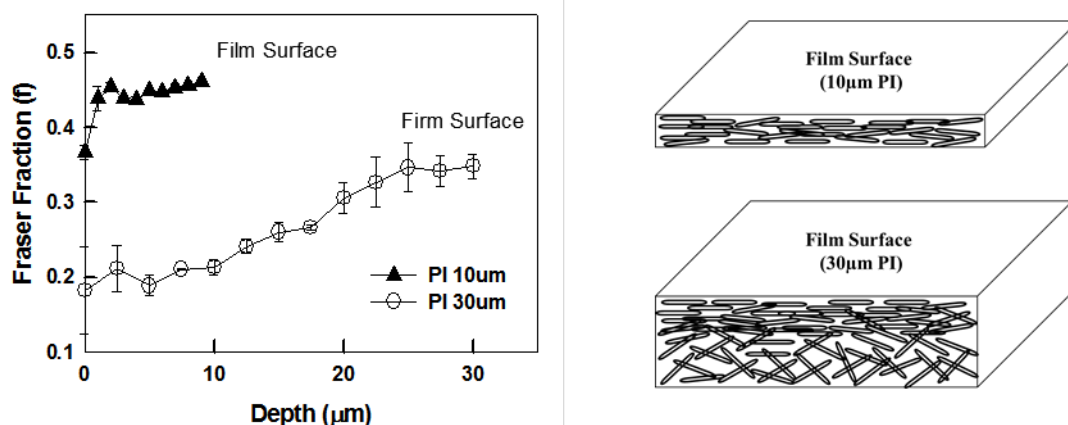


Figure 1. Depth-wise profile of Fraser fraction (f) of two different thick PIs (10 μm , 30 μm), and the inferred diagrams of chain orientation [9].

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