Neutron reflectivity studies on polystyrene thin films

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It is well known that physical properties of polymer thin films are quite different from those of bulk. One of the most interesting topics is the thickness dependence of glass transition temperature (T_g). In the case of polystyrene (PS) on Si substrate, the decrease of T_g was observed by ellipsometry, X-ray/neutron reflectivity and so on. On the other hand, the increase of T_g was also observed for poly(methyl methacrylate) (PMMA) thin film with decreasing film thickness. Such a singular behavior of polymer thin film is now understood in terms of surface mobile layer, bulk-like layer and interfacial layer, implying that film is constructed of multi-layer structure. In order to reveal the unresolved mechanism of glass transition of polymer thin film, the distribution of T_g in polymer thin films must be studied experimentally, not aiming at the determination of only one T_g value. One big advantage of neutron scattering is that it can discern hydrogen and deuterium due to the difference of neutron scattering length. In this report, we studied the distribution of T in a multi-layered PS thin film by stacking hydrogenated PS (h-PS) and deuterated PS (d-PS) alternatively with neutron reflectivity.

Figure 1 shows neutron reflectivity profiles from 5-layered thin film at 313K, 358K and 393K. The observed reflectivity profiles were analyzed by a program, which is based on the formula derived by Parratt and results of fit were also included in Figure 1 as solid lines. The results of fit were quite nice and we evaluated thickness and roughness for each layer, separately. Temperature dependence of total film thickness is shown in Figure 2 and T_g, which was indicated by solid arrow was almost same as bulk T_g (=376K), certificating the validity of our method. Decomposing into each layer from top to bottom, each layer seemed to have different T_g though total film exhibited almost bulk behavior. Further discussion especially on depth dependence of T_g will be given at poster session.

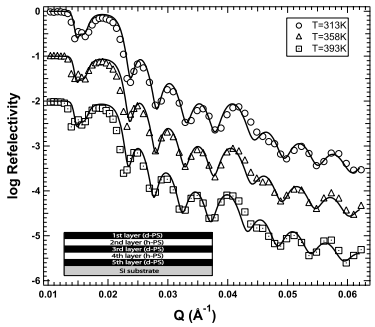

Figure 1 Neutron reflectivity profiles from 5-layered thin film and reflectivity profiles are shifted vertically for clarity.

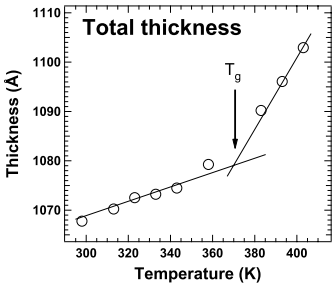

Figure 2 Temperature dependence of total film thickness and solid arrow corresponds to T_g of this thickness.