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Surface Dynamics of Glassy Polymer Films and Its Effect on Glass Transition Temperature ZAHRA FAKHRAAI, JAMES A. FORREST, Department of Physics and Astronomy and Guelph-Waterloo Physics Institut, University of Waterloo, Waterloo, ON N2L 3G1 Canada — The surface dynamics of thin polymer films is believed to be different from that of bulk and is cited to be the source of Tg anomalies in thin films. In this study ellipsometry is used to measure the cooling rate dependence of Tg in thin polystyrene films. It is shown that as the temperature decreases below bulk Tg, the relaxation time behavior changes from Vogel-Fulcher to Arrhenius, with an activation energy that decreases linearly with film thickness, indicating that the relaxation time of the surface (limit of zero thickness) is also Arrhenius. To measure the relaxation time of the surface directly, a novel technique is used to produce nanometer size holes with well defined shapes and driving forces on the film surface. AFM is used to monitor the depth of the holes as a function of time at different temperatures. The relaxation times are obtained from the exponential decay of the depths. It is shown that at the low temperature limit the behaviour is Arrhenius with an activation energy similar to the one predicted from ellipsometry measurements. By combining these results the Tg of the surface can be estimated. These results can explain various contradictions in the literature and can provide a framework for a new theory to explain Tg reductions in thin polymer films.

Zahra Fakhraai
Department of Physics and Astronomy and Guelph-Waterloo
Physics Institut, University of Waterloo, Waterloo, ON N2L 3G1 Canada

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