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Surface glass transition temperature characterized by metal-atom deposition/desorption on organic films

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ABSTRACT

Surfaces and interfaces play an important role in obtaining high-performance organic devices. An essential property of organic films is the surface glass transition temperature (surface-Tg) and many methods for characterizing surface-Tg have been studied. We propose a novel method for characterizing surface-Tg based on metal-vapor atom deposition and desorption. We monitored metal-vapor deposition and desorption on organic surfaces using double quartz crystal microbalances. Mg vapor is not deposited on organic surfaces with a low bulk-Tg such as a colorless photochromic diarylethene (DAE) film. This deposition phenomenon is caused by Mg-atom desorption from the surface based on active surface molecular motion. However, Mg deposition began after a certain time of continuous evaporation (deposition threshold time). The threshold time elongated with increased substrate temperature and elongated dramatically at a substrate temperature several degrees below the bulk-Tg for DAE. The surface molecular motion becomes active and the metal-atom desorption accelerates as the temperature neared the surface-Tg. Thus a temperature with a dramatic elongation of the threshold time indicates the surface-Tg. This method can be applied to a variety of organic films.

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1. Introduction

The surfaces and interfaces of organic films affect the performance of organic devices [1–3]. The surface glass-transition temperature (surface-Tg) of a polymer gate insulator modulates the performance of thin-film transistors [4] and, therefore, is an essential property for obtaining high-performance devices. Several methods have been proposed to characterize surface-Tg: the atomic force microscopy (AFM)-based method [5–7] and observation of surface nanodeformation generated by nanoparticle embedding [8]. It has been reported that surface-Tg is lower than bulk-Tg, which is determined by conventional methods such as differential scanning calorimetry (DSC) [9–11]. For example, the surface-Tg of polystyrene is lower than the bulk-Tg by around 20 K depending on its molecular weight [12].

Photochromism is reversible color change upon light irradiation and various properties of molecules, crystals and/or films also change based on photoisomerization [13,14]. Some of photochromic diarylethenes (DAEs) exhibit a selective metal-vapor deposition phenomenon; metal deposition during vacuum evap-

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http://dx.doi.org/10.1016/j.apsusc.2017.07.079 0169-4332/© 2017 Elsevier B.V. All rights reserved. oration on the DAE surface is modulated by the isomerization state [15–17]. The origin of selective metal-vapor deposition is a high-rate desorption of metal atoms from the photo-generated low-Tg colorless surface of an amorphous DAE film; a low-Tg surface generates an active surface molecular motion and accelerates the desorption. From a different point of view, metal-atom deposition/desorption characteristics sensitively reflect the surface-Tg state. In this paper, we propose a novel method to characterize surface-Tg (or surface molecular motion state) based on observation of the metal-vapor atom deposition/desorption.

2. Results and discussion

Fig. 1 is a model depicting that the surface molecular motion or surface-Tg effects on metal-vapor atom desorption. In general, surface-Tg is lower than bulk-Tg [9–12]. When the substrate temperature (Tsub) is lower than the surface-Tg (left illustration in Fig. 1), at which the organic surface is in a glassy state, incident metal-vapor atoms on the surface are easily adsorbed, diffuse, nucleate by collision between atoms on the surface, and create a film. Even in this state, metal atoms with low interaction with organic molecules, such as magnesium (Mg), are easily desorbed. When surface-Tg <Tsub < bulk-Tg, molecules in the inner film are in a glassy state, but the surface-molecular motion becomes very







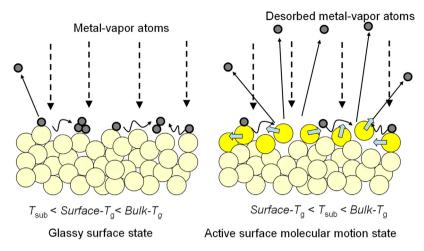


Fig. 1. Model of metal-vapor atom deposition and desorption depending on surface molecular motion (surface-Tg).

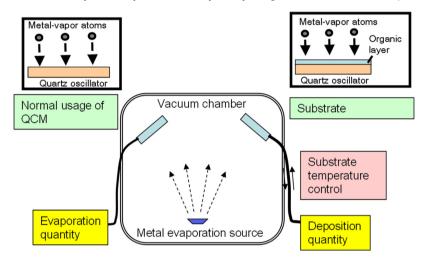


Fig. 2. Experimental setup with double QCM for characterizing metal-vapor deposition property on organic surfaces.

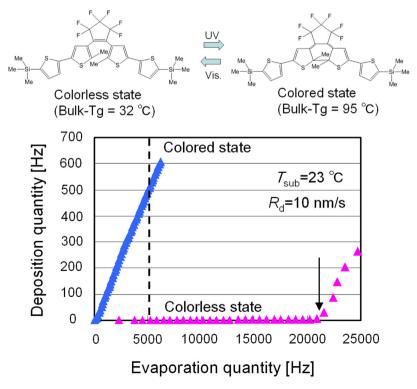


Fig. 3. Molecular structures of photochromic DAE and Mg-deposition properties on the colored and colorless DAE surfaces.

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