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Controlled evolution of surface patterns for ZnO coated on stretched PMMA upon thermal and solvent treatments

Haibao Lu [a,*], Yingzhi Liu [a], Wei Min Huang [b], Changchun Wang [c], David Hui [d], Yong Qing Fu [e,**]

[a] Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150080, China
[b] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore
[c] School of Materials Science and Engineering, Jiangsu Key Laboratory of Advanced Structural Materials and Application Technology, Nanjing Institute of Technology, Nanjing 211167, China
[d] Composite Material Research Laboratory, Department of Mechanical Engineering, University of New Orleans, LA 70148, USA
[e] Department of Physics and Electrical Engineering, Faculty of Engineering and Environment, University of Northumbria, Newcastle upon Tyne NE1 8ST, UK

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ABSTRACT

Poly (methyl methacrylate) (PMMA) possesses the excellent optical properties and thermal stabilities, its shape memory effect can be triggered by heating or solvent absorption. Zinc oxide (ZnO) films, the most common semiconductor materials, were usually deposited on polymer substrates as a transparent conductive element for applications to electro-optical devices. In this paper, ZnO films with different thicknesses were deposited on PMMA substrates with different pre-strains. The influences of the shape memory effect (SME), thermal expansion mismatch, and ethanol soaking on the evolutions of surface topographies were systematically investigated. Results revealed that the isotropic wrinkles without any preferential orientation were induced by the thermal expansion coefficient mismatch between ZnO film and PMMA substrate during annealing. The well-aligned wrinkles perpendicular to the direction of pre-strain resulted from the SME of PMMA triggered by heating. In addition, cracks appeared instead of wrinkles since the isotropic swelling of PMMA upon soaking in ethanol.

1. Introduction

Surface patterns induced by depositing a stiff film on the top of a compliant substrate have been extensively investigated for their potential applications in electronic devices, sensors, optical devices and actuators [1–5]. The mechanisms for producing surface patterns include wrinkling, creasing, cracking, and buckling [6–11]. Wrinkling is one of the surface buckling phenomena, which is conventionally generated in bi-layer structures consisted of a thin metallic layer and a polymer substrate. Wrinkle structures have a wide range of applications including switchable wettability, erasable systems and flexible electronics, because their significantly influences on the wettability, roughness and adhesion of the surface [3,12–15].

Shape memory polymers (SMPs), a kind of stimulus responsive materials, have been widely studied in the past decades due to their shape memory effect (SME) [16–21]. Such smart materials are capable of fixing the pre-deformed shape under appropriate conditions, and then return from the temporary shape to the original shape under a right stimulus, such as electricity, light, heat and solvent [22–30]. Specifically, a bi-layer structure, which is composed of a mental layer and a thermally-induced, pre-stretched SMP substrate, could form complex wrinkling patterns. When it is heated and then cool down, the SME-induced compressive stress field inside the film can result in wrinkle patterns [31–33].

Compared with other kinds of SMPs, poly (methyl methacrylate) (PMMA) as a kind of physically cross-linked polymers, provide the excellent optical properties and thermal stability. Such attractive features enable its applications in solar, sensor, battery electrolytes, optical, and conductive devices [34–37]. The SME of PMMA triggered by heating or solvent absorption in small strain condition has been previously reported [38–40]. Recently, various metal and oxide films have been deposited on the PMMA substrate to achieve different functional properties (for example, optical, and electrical),

* Corresponding author.
** Corresponding author.
E-mail addresses: luhb@hit.edu.cn (H. Lu), richard.fu@northumbria.ac.uk (Y.Q. Fu).

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and a variety of surface patterns are generated by using the SME or thermal expansion mismatch [41]. Zinc oxide (ZnO) is one of the most common semiconductor materials for applications to sensors and light emitting diodes (LEDs) [42–45]. ZnO films were usually deposited on polymer substrates as a transparent conductive element for applications such as electromagnetic shielding materials and electro-optical devices [46,47].

ZnO film (and aluminum doped ZnO) has been frequently deposited onto PMMA to form transparent electrode. In application, electro-thermal effect would be generated on these ZnO transparent electrodes, and could trigger shape memory effect in the PMMA. Deposition of ZnO films onto PMMA could easily generate wrinkle patterns on the surface. By adjusting the film thickness or film stress appropriately, such wrinkle patterns could be significantly changed. In that case, the properties of the ZnO devices could be adjustable. In this paper, various surface wrinkling patterns were generated by coating different thicknesses of ZnO films onto pre-stretched PMMA substrates. The influences of pre-strain, post-annealing and ethanol soaking on the evolutions of surface topographies of ZnO coated on PMMA were systematically investigated.

2. Experimental procedure

PMMA sheets obtained from Ying Kwang Acrylic, Singapore, with thickness of 1 mm and glass transition temperature (T_g) of about 110 °C, were used in this study. PMMA sheets were cut using a laser beam into the designed shape as shown in Fig. 1. The gauge length of the samples was set as 20 mm. The samples were uniformly pre-stretched by using the customized tensile vise into different predetermined strains (0%, 1%, 5%) at high temperature of 120 °C. And then, strain was kept until it cools down to the room temperature (about 22 °C), the cooling rate is 5 °C/min. Subsequently, ZnO films were deposited on one side of PMMA using a magnetron sputtering equipment. Zn (99.99%) target was used during sputtering, with a DC power of 200 W and an Ar/O2 flow ratio of 50/50 SCCM (standard cubic centimeter per minute) at a gas pressure of ~5 mTorr. In order to investigate the influence of film thicknesses on the surface morphologies, ZnO films with thicknesses varying from 5 nm to 65 nm were deposited on PMMA substrate. The thicknesses of ZnO films were tuned by changing the deposition time, and measured by a quartz crystal microbalance (QCM).

These samples of PMMA coated with ZnO film were heated to 120 °C (above T_g of PMMA substrate) at a heating rate of 5 °C/min and kept for 5 min, followed by cooling down to room temperature. Therefore, the PMMA could recovery to its original shape completely and formed surface patterns. Surface morphologies of ZnO coated on PMMA substrate were characterized using an optical microscope. The heated samples were further soaked in ethanol for different durations to study the effects of solvent-induced relaxation on the surface morphology of ZnO coated on PMMA. The pre-strains of PMMA substrates and the thicknesses of ZnO films for the samples are summarized in Table 1.

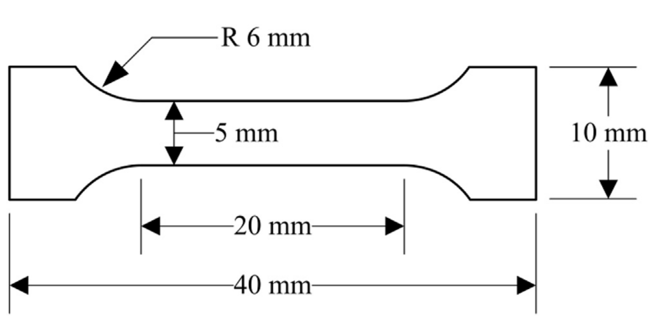

Fig. 1. Dimensions of sample of PMMA substrate.

3. Results and discussion

3.1. Surface morphologies

Figs. 2–5 show the surface morphologies of the samples with different pre-strains (0%, 1% and 5%) and various thicknesses of ZnO film (5 nm, 15 nm, 30 nm and 45 nm), respectively. It can be found that the surface morphologies of ZnO film deposited on PMMA substrate are dependent on the thickness of ZnO film, pre-strain and heating.

Before annealing, when the film thickness is small (5 nm), no apparent wrinkles can be seen in the surface of the sample 3 (Fig. 2(a)). Similarly, same weak surface features could also be found on the surface of sample 1 and sample 2. The film stress in the ZnO thin layer during deposition causes the formation of these weak patterns. If the thickness of ZnO film is increased to 15 nm, sample 4 forms irregular and weak wrinkles on the surface (as shown in Fig. 3(a)). Similarly, sample 5 and sample 6 show the same shallow wrinkles, and no significant differences appear on their surfaces, which indicate that small pre-strain has little effect on the surface topographies after film deposition at room temperature. For the samples with the film thickness of 45 nm, as illustrated in Fig. 5(a1), it shows a large number of irregular cracks before annealing. These cracks divide the surface into several closed domains. For sample 11 (Fig. 5(b1)), there are considerable cracks that slightly elongate along the pre-stretched direction. As shown in Fig. 5(c1), for sample 12, there are a majority of cracks aligned along the direction of pre-strain. In these samples, pre-strain significantly influences the surface morphologies.

After annealing, many weak wrinkles perpendicular to the direction of pre-strain can be observed on the surface of sample 3 (Fig. 2(b), thickness of ZnO film is 5 nm). For sample 1 and sample 2, the surface morphologies have very weak wrinkles after annealing. It indicated that the pre-strain has little effect on the surface pattern when the film thickness is small. From Fig. 3(b), we can see that the disordered (isotropic) wrinkles emerge on the surface of sample 4 with the film thickness of 15 nm. The surfaces of sample 5 and sample 6 are occupied by wrinkles which are well-aligned to the perpendicular direction of the pre-strain, as shown in Fig. 3(c) and 3(d). Comparing Fig. 3(b), 3(c) and 3(d), it can be found that wrinkles become increasingly directional with the increase of pre-strains.

When the film thickness is increased to 30 nm, the disordered cracks emerge on the surface of sample 7 after annealing (Fig. 4(a)), and some wrinkles scatter around the cracks. In comparison to Figs. 2(b) and 3(b), it can be inferred that there is a critical value (the thickness of 30 nm) at which the cracks begin to generate. For sample 8 and sample 9 after annealing (Fig. 4(b) and 4(c)), wrinkles are gradually disappearing, leaving only cracks along the pre-strain direction and perpendicular to the direction of the pre-strain in the surfaces.

Fig. 5(a2)-(c2) represent the evolution of surface cracks as the pre-strain increased. As illustrated in Fig. 5(a2), after annealing, sample 10 no longer shows clear wrinkles and only a large number of irregular cracks can be seen. Compared with Figs. 3(b) and 4(a), plenty of irregular cracks divide the surface into several closed domains when the thickness of ZnO film is beyond the critical value, 30 nm (mentioned above). With the pre-strain increased to 5%, the cracks are aligned along the direction of pre-strain increasingly. It can be concluded that initiation and evolution of