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Annealing Temperature Dependence of the Nanosized Pits on Poly(methyl methacrylate) Surface

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We report the annealing-temperature-dependent evolution of nanosized pits on a poly(methyl methacrylate) film spin-coated on a glass substrate. The pits are formed on the polymer surface as the toluene solvent evaporates rapidly. The depth and width of the pits are measured by atomic force microscopy after the film is annealed at ambient temperature, below and above the glass transition temperature (105 °C) of the polymer, respectively. Compared with the statistical results obtained at ambient temperature, the pits are shallow and narrow on the film annealed at 75 °C as molecular vibration expands the film. However, it is found that the pits are deeper and wider on the film annealed at 120 °C than on the films annealed at the other two temperatures, which results from the evaporation of the inner residual toluene in the polymer film.

1. Introduction

Over the past decades, porous polymer films have been applied in the fields of physics, chemical engineering, and biology, and in organic electronic devices.[1,2] In particular, in chemistry, porous polymer films have been widely used in catalysis[3] and separation.[4] Biological researchers use porous polymer films for magnetic resonance imaging and directed cell growth.[5] Exploiting the porosity of the polymer film itself, organic quantum devices such as thin-film transistors[6] and sensors[7] are also nearing commercialization.

There are some methods that have been proposed to produce and manipulate nanosized pits in a polymer film.[8–12] Firstly, with the charged ions bombarding the polymer film, the electrons from the target are transferred to the highly excited states of the projectile, which leaves nanosized pits on the surface.[8] It has been found that the pit volume and shape could be tuned by varying the potential and kinetic energies of incident ions.[9] Secondly, nanosized pits on the polymer surface can be formed by polymer-solvent interaction.[10] Ton-That et al. manipulated the pit size on a poly(methyl methacrylate)/polystyrene (PMMA/PS) blend by controlling the solution concentration and weight ratio of PMMA/PS blend.[11] They also found that the pits on the PMMA/PS blend film became smaller as the annealing time increased.[12]

In this study, we modified the nanosized pits by changing the annealing temperature. The pits are formed on the polymer surface as the toluene solvent evaporates rapidly. The annealing temperature could affect the movement of the polymer chain; thus the evolution of the nanosized pits would occur subsequently.

2. Experimental Methods

The samples were fabricated as follows: Cover glass substrates were cleaned by sonication successively in acetone, potassium hydroxide solution, milliQ water, and then irradiated using an ultraviolet lamp. PMMA (Sigma-Aldrich 200 336, $M_w = 15000$) solutions with mass concentration of 10.35, 2.26, and 0.41% in toluene were prepared sequentially. PMMA films were prepared by spin-coating 20 μL solution under ambient conditions on glass substrates with rotation at a rate of 3000 rpm for 1 min, and then annealed at ambient temperature, 75 °C, and 120 °C for 30 min in an electrothermal vacuum drying oven (pressure <10 kPa). Finally, the samples are cooled to room temperature under vacuum.

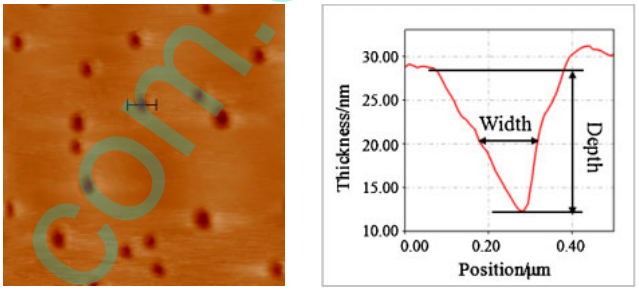

Fig. 1. (Color online) (a) 2D image of the surface topography of PMMA film prepared using 10.35% solution and annealed at ambient temperature, measured by AFM. (b) The profile of the pit in (a) indicated by the black bar. The depth and width of the pit are 15.9 and 147.9 nm, respectively.

Toluene is a strong solvent of PMMA and it evaporates rapidly during the spin-coating process, which leaves nanosized pits on the PMMA surface.[10] The polymer chains are generally frozen in the thin film before attaining a thermodynamically stable state, which prevents the chains from moving into the position of evaporated toluene.[11,12]

The surface topography of each film was characterized by atomic force microscopy (AFM; Being Nano-Instruments CSPM5500) performed in the tapping mode with a resonance frequency of 300 kHz and a scanning frequency of 1 Hz for each line. Figure 1(a) shows a typical two-dimension (2D) image of the surface topography of the PMMA film prepared using 10.35% solution and annealed at ambient temperature. The scanning range of the image was $5 \times 5\,\mu m^2$. Note that the pits appeared randomly on the PMMA surface. Figure 1(b) shows a depth profile of the pit indicated by a black bar in Fig. 1(a), with its depth and width at half depth being 15.9 and 147.9 nm, respectively.

3. Results and Discussion

To investigate the temperature-dependent evolution of nanosized pits on the PMMA surface, we analyzed statistically the

Table I. Probable values and distributions of depth and width of the nanosized pits on PMMA films prepared under different conditions. Data outside the parentheses demonstrate the most probable values of the depth and width of the pits, while those inside the parentheses show the linewidth of Gaussian fitting for their distribution.

Concentration (%)	Depth (linewidth) (nm)			Width (linewidth) (nm)		
	25 °C	75 °C	120 °C	25 °C	75 °C	120 °C
10.35	16.7 (5.9)	11.0 (3.7)	12.3 (14.0)	148.2 (64.0)	137.7 (31.4)	240.9 (201.7)
2.26	7.0 (5.0)	5.4 (3.2)	13.2 (11.9)	144.6 (76.1)	129.6 (69.8)	229.2 (323.1)
0.41	9.9 (3.2)	6.6 (3.6)	12.4 (9.6)	111.0 (41.8)	90.2 (24.2)	195.7 (80.9)

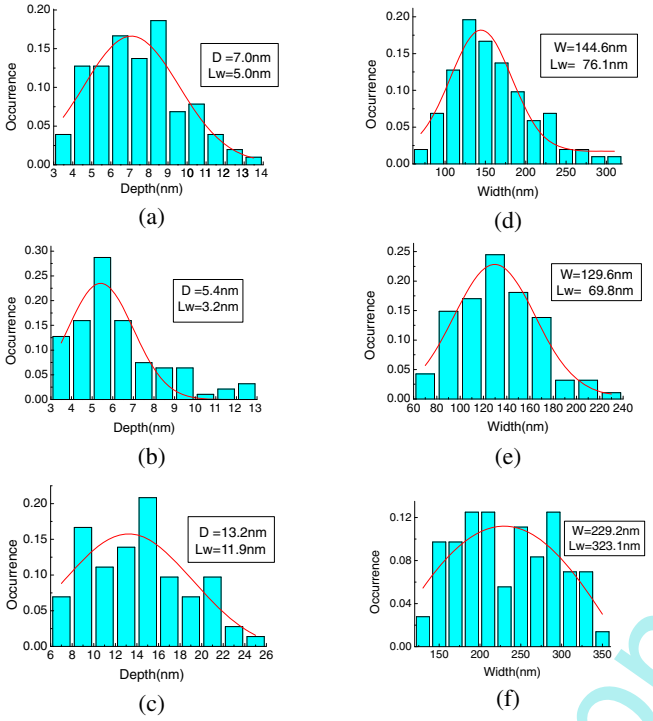

Fig. 2. (Color online) Distributions of (a–c) depth and (d–f) width of nanosized pits on PMMA films prepared using 2.26% solution and annealed at ambient temperature, 75 °C, and 120 °C, respectively. Data in the inset show the most probable value of depth (D) or width (W) and the linewidth (Lw) of their Gaussian fitting shown as red lines.

distributions of the depth and width of each pit, as shown in Fig. 2, where the PMMA films were prepared using 2.26% solution. Figures 2(a)–2(c) show the distributions of the depth of nanosized pits on PMMA films annealed at ambient temperature, 75 °C, and 120 °C, respectively. The data were Gaussian-fitted as the red lines in the figure. The most probable values of depth and linewidth were achieved, as shown in the inset. It is found that the most probable depth of nanosized pits on the sample annealed at 75 °C is smaller than that of naosized pits on the sample annealed at ambient temperature, which indicates that the pits become shallower. At the same time, the linewidth of the depth distribution of nanosized pits is smaller at 75 °C than at ambient temperature. However, the situation seems to be obviously different when the sample is annealed at 120 °C, which exceeds the glass transition temperature (T_g)[13–15] of PMMA. The pits on this sample are deeper than those on the samples annealed at the other two temperatures. Accordingly, the linewidth of the depth distribution is larger as well. Similarly to the results in Figs. 2(a)–2(c), the distributions of the width of nanosized pits on the films annealed at different temperatures are

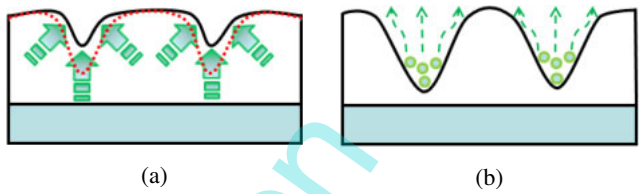

Fig. 3. (Color online) Evolution model for the pits on PMMA films annealed at (a) ambient temperature (dot line), 75 °C (solid line), and (b) 120 °C. In (a), green arrows indicate the thermal expansion of the polymer film resulting in a shallower and narrower pit. The green circles in (b) show the evaporation of the inner residual toluene solvent forming a deeper and wider pit.

demonstrated in Figs. 2(d)–2(f). The narrowest pits are formed on the film annealed at 75 °C, while the widest pits are formed on the film annealed at 120 °C.

In Table I, we summarize the most probable values and distributions of the depth and width of nanosized pits on PMMA films, which were prepared with three different solution concentrations and annealed at three different temperatures.

When the PMMA solution is 0.41%, the most probable values of pit depth are 9.9, 6.6, and 12.4 nm on PMMA films annealed at 25, 75, and 120 °C, respectively. It is found that the shallowest pits are formed on the PMMA film annealed at 75 °C and the deepest pits are formed on the PMMA film annealed at 120 °C. The linewidths of the pit depth distribution are 3.2, 3.6, and 9.6 nm on PMMA films annealed at 25, 75, and 120 °C, respectively, which indicates that the linewidth is larger at 120 °C than at the other two temperatures. Moreover, the distributions of the width of nanosized pits on the films annealed at ambient temperature, 75 °C, and 120 °C are also analyzed. It is shown that the narrowest pits and the smallest linewidth of the pit width distribution are observed on the film annealed at 75 °C, whereas the widest pits and largest linewidth are observed on the film annealed at 120 °C.

The formation of the pitted structures is suspected to be due to the evaporation of toluene exposed to air during the spin-coating process at room temperature.[10–12] When the PMMA film is annealed at a temperature lower than T_g, the film would be in the glassy state in which the molecules vibrate rather gently and independently.[13–16] The thermal energy induced by the annealing process would turn into the vibration energy of the PMMA molecules, increasing the average distance between them.[17] As illustrated in Fig. 3(a), the thermal expansion of the polymer film results in a shallower and narrower pit at an annealing temperature of 75 °C than at ambient temperature. However, when the annealing temperature is 120 °C, which is higher than T_g, the PMMA film becomes a super cooling liquid[16,18–20] in which

the molecule becomes more flexible and mobile. As shown in Fig. 3(b), the inner residual toluene solvent in the PMMA film exposes to the surface and it evaporates, and then a deeper and wider pit is formed accordingly.

4. Conclusions

We have proposed a robust method to manipulate the pit size by controlling the annealing temperature in this paper. Nanosized pits are formed when the toluene solvent evaporates rapidly. Compared with the pits on the film annealed at ambient temperature, the nanosized pits on the film annealed at 75 °C are shallower and narrower, because PMMA molecular vibration expands the film. However, the nanosized pits become deeper and wider at 120 °C, resulting from the inner residual toluene solvent evaporating in the PMMA film. The controllable nanosized pits on porous polymer films could be coupled to single quantum systems such as single atoms,[21] single molecules,[22] and single quantum dots[23] to enhance the interaction between photons and a quantum system.

Acknowledgements

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