Fabrication of Mesoscopic Structure on PMMA Surface by Atomic Hydrogen and Evaluation of the Surface Functionality

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Surface properties of polymers such as wettability and adhesiveness play an important role in industrial applications. The properties can be enhanced by fabricating a mesoscopic structure to the surface. In this study, we examined a chemical etching which is a simple and direct technique for the surface profile control, using atomic hydrogen generated by hot-wire catalytic method. Several tens of nanoscale structures were fabricated on poly(methyl methacrylate) (PMMA) surface by atomic hydrogen irradiation, and the size and pitch of the structure could be controlled by reaction temperature and time. The wettability of PMMA film surface changed from hydrophilicity to hydrophobicity by formation of mesoscopic structures.

Keywords: Atomic hydrogen, Hot-wire catalyst, Poly(methyl methacrylate), Mesoscopic structure

1. Introduction

Surface structure in polymer material greatly influences its surface physical properties such as wettability and adhesiveness [1,2]. In particular, mesoscopic structure having a size of several tens nanometer to several hundred nanometer can impart optical characteristics such as antireflection in addition to the above characteristics. Yabu et al. have reported that when a honeycomb structure is formed on the surface of fluorinated polymer, the maximum contact angle becomes 170°, resulting in a superhydrophobic surface [3]. Superhydrophobic surfaces have been used as transparent coatings with anti-fogging properties and self cleaning properties. Photolithography and self-organization technique are used as a precise manufacturing method of the mesoscopic structure [4,5]. In recent years, direct microstructure formation using plasma has also been studied as a different method [6-8]. Surface modification of polymers by plasma treatment is due to functionalization of polymer side chains and formation of surface roughness [9].

The hot-wire CVD (chemical vapor deposition) is a method of forming a thin film using radicals generated on the surface of a heated catalyst. Hydrogen radicals are produced by decomposing molecular hydrogen on a metal hot-wire catalyst. The atomic hydrogen possesses high reactivity, and is possible to decompose some polymers by reduction reaction. We have previously reported that the photoresist polymers could be removed from Si wafer using atomic hydrogen generated by hot-wire catalytic method [10]. In the hot-wire method, it is easy to control the reaction conditions depending on the catalyst temperature and typical hydrogen pressure. The tungsten hot-wire catalytic process produces atomic hydrogen only and is not composed of some charged particles, e.g. ions and electrons, as compared to typical plasma methods. Therefore, polymer is perhaps chemically etched by only atomic hydrogen. For the reasons mentioned above, atomic hydrogen produced by the tungsten hot-wire catalyst must be effective in the fabrication and control of the microstructure on the polymer.
We have attempted to the fabrication of fine structure on the surface of PMMA based polymer by atomic hydrogen generated by hot-wire method as a simple and direct technique [11]. A few tens of nanometer size fine structure was fabricated on the PMMA surface, but the control of the size and pitch has not been investigated to enough. In this study, for the purpose of controlling the mesoscopic surface structure, the correlation between the PMMA surface structure and the processing conditions with atomic hydrogen was investigated in detail. Additionally, the surface characteristics of PMMA film with mesoscopic structure were evaluated.

2. Experimental procedure

PMMA (Sigma-Aldrich Co. LLC., $M_w$ 120,000) were used. Ethyl lactate was utilized as solvent. The PMMA solutions were spin-coated onto silicon wafer by using spin coater, and then the wafers were baked for 1 minute on a hot plate at 100 °C.

Figure 1 shows a schematic illustration of the generation and irradiation of atomic hydrogen by hot-wire catalytic method. Hydrogen-nitrogen mixed gases (H$_2$/N$_2$=10/90 vol%) flowed from the upper nozzle. The gas flow rate was fixed at 300 sccm using a mass-flow controller. The total gas pressure was 32 Pa. The current applied to the tungsten catalyst was 20 A. The temperature of tungsten catalyst was measured by two wavelength radiation thermometer (ISR12-L0 from Impac Electronic Corp.), and was 1800 °C. The distance between the catalyst and the sample substrate was 100 mm. The substrate temperature was controlled by heater and monitored with a thermocouple. Initial substrate temperature was changed so that an arbitrary temperature would be obtained with irradiation time of 9 minutes. Irradiation was carried out continuously up to an arbitrary time. The surface morphology was evaluated by AFM (Digital Instrumental Nanoscope IIIa in tapping mode.) The average roughness ($R_a$) and maximum roughness ($R_{\text{max}}$) were calculated from AFM images. The aspect rate was calculated from the ratio of interval of the microstructure and $R_{\text{max}}$. The water contact angle was measured using a contact angle meter (FT 1000 Drop Shape Instrument B Frame System, manufactured by First Ten Angstroms). Distilled water was used as droplets and the contact angle was measured 3 seconds after the dropwise addition.

3. Results and discussion

Surface profiles of PMMA after irradiating atomic hydrogen at each substrate temperature and irradiation time were shown in Table 1. The AFM images were shown in Fig. 2. The etching rate of PMMA was calculated from the PMMA film thickness before and after irradiating atomic hydrogen when the irradiation time was the longest.

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Table 1. PMMA surface profile after irradiating atomic hydrogen at various conditions in stainless chamber.

| Temp. (°C) | Time (min) | Rate (µm/min) | $R_a$ (nm) | $R_{\text{max}}$ (nm) | Aspect rate |
|------------|------------|---------------|-----------|---------------------|-------------|
| Not irradiation | 0 | 0 | 0.2 | 2 | n.d.$^a$ |
| 80 | 15 | 0.2 | 2 | n.d.$^a$ |
| | 30 | 0.4 | 4 | n.d.$^a$ |
| | 45 | 0.2 | 2 | n.d.$^a$ |
| | 60 | 0.2 | 2 | n.d.$^a$ |
| 100 | 15 | 0.9 | 8 | n.d.$^a$ |
| | 30 | 1.3 | 14 | n.d.$^a$ |
| | 45 | 5.9 | 42 | 0.13 |
| | 60 | 4.8 | 35 | 0.11 |
| 120 | 15 | 2.3 | 19 | n.d.$^a$ |
| | 20 | 13.1 | 120 | 0.24 |
| | 25 | 12.1 | 114 | 0.19 |
| | 30 | 13.2 | 118 | 0.20 |
| 140 | 10 | 9.1 | 73 | 0.18 |
| | 15 | 54.0 | 342 | 0.33 |
| | 20 | 81.0 | 486 | 0.28 |
| 160$^b$ | 9 | 0.43 | 17.3 | 100 | 0.08 |
| 170$^b$ | 9 | 0.54 | 2.0 | 16 | 0.02 |

$^a$Not determined. $^b$ In glass chamber.
at each substrate temperature. The film thickness of PMMA was not changed with atomic hydrogen irradiation at the substrate temperature of 80 °C, and the surface morphology was almost the same as the untreated PMMA at all irradiation times. At substrate temperatures of 100, 120 and 140 °C, the film thickness was decreased and the etching rates at 100, 120 and 140 °C were 0.02, 0.06, and 0.09 μm/min, respectively. At a substrate temperature of 100 °C, when the irradiation time of atomic hydrogen was less than 30 minutes, the surface roughness of PMMA was almost the same as that of the untreated PMMA. When the irradiation time was extended to 60 minutes, the surface became rough and the values of \( R_a \) and \( R_{\max} \) were approximately 4.8, and 35 nm, respectively. Mesoscopic structure was formed on PMMA surface by irradiation of atomic hydrogen. At the substrate temperature of 120 and 140 °C, the microstructure was formed. The values of \( R_a \) and \( R_{\max} \) were increased with increasing substrate temperature. The aspect ratio of microstructure was also the same manner. At comparison of the irradiation time at the same temperature, the values of \( R_a \) and \( R_{\max} \) were increased with increasing the irradiation time but the aspect ratio was constant. On the other hand, the values of \( R_a \) and \( R_{\max} \) and aspect ratio were extremely lower above 160 °C of substrate temperature and the surface morphology after irradiation of atomic hydrogen at 170 °C became smooth. It is thought that plasticity of PMMA was caused by heating at the temperature exceeding the \( T_g \) of PMMA at approximately 110 °C. These results showed a fine structure is formed by decomposition of PMMA with atomic hydrogen at the substrate temperature in the vicinity of \( T_g \).

Figure 3 shows the water contact angle of PMMA before and after irradiation of atomic hydrogen. The wettability of the liquid is correlated with the roughness of the solid surface, and Wenzel equation and Cassie-Baxter equation were known as models of the relationship between the surface wettability and the roughness. The Wenzel equation is shown in equation 1 [12,13].

\[
\cos \theta_y = \gamma \cos \theta \quad (1)
\]

Where \( \theta_y \) is the contact angle on the rough surface, \( \theta \) is the contact angle on a smooth surface, and \( \gamma \) is the area ratio of the rough surface to the smooth surface. From equation 1, hydrophilicity and hydrophobicity of rough surface were enhanced by increasing the specific surface area. When the aspect ratio of the fine structure is large, air enters between the solid surface and the droplet. In this case, the contact angle is expressed by the Cassie-Baxter model in equation 2 [14].

\[
\cos \theta_R = A_1 \cos \theta_1 + A_2 \cos \theta_2 \quad (2)
\]

Where \( A_1 \) and \( A_2 \) are the proportion of substances 1 and 2 on the surface, and \( \theta_1 \) and \( \theta_2 \) are the contact angles of substances 1 and 2. In the case of one substance is air, the contact area with the air is increased by forming a fine structure, i.e. hydrophobic surface is formed. Figure 3 showed that the water contact angle of untreated PMMA was 73°. The water contact angle of PMMA after irradiation of atomic hydrogen at 120 °C was 110° when the irradiation time was 20 min, although its
The angle was 85° when the time was 15 min. The water contact angle at 120 °C increased with increase in the irradiation time. The wettability of PMMA surface was changed from hydrophilicity to hydrophobicity by forming a fine structure on the surface. The change of wettability may be ascribed to the formation of an air layer between the PMMA surface and the droplets, i.e. Cassie-Baxter state. At the substrate temperature of 140 °C, the contact angle is 90° and higher than untreated PMMA. The value became lower than it was at 120 °C. The pitch between structures at 140°C may be too large to form the air layer between the sample and the droplet.

4. Conclusion

The mesoscopic structure on the PMMA surface was formed by using atomic hydrogen generated by hot-wire method. We clarified that decomposition of polymer by atomic hydrogen is necessary at substrate temperature near $T_g$ in order to form microstructure. In addition, the size and the aspect ratio of fine structure were controllable to the substrate temperature and processing time. Furthermore, wettability of PMMA surface was changed depending on the formation of microstructure.

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