Formation of Ordered Nanometer-sized Polymer Dots on Silicon by Friction Rubbing Method

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Regular arrays of poly(ethylene) deposits, about 10 nm high and 160 nm in diameter, separated by 340 nm, were formed by simply rubbing the polymer plate against the surface of silicon just below the melting point of the polymer.

Ordering of polymers on solid surfaces in nanometer scales is of great importance not only for understanding properties of polymers near surfaces but also for creating functional surfaces on highly versatile materials, such as silicon. Langmuir-Blodgett method,[1] epitaxial growth during polymerization,[2] and adsorption of block copolymers[3] are some of the methods commonly applied to place structural regularities in the polymers near solid surfaces.

Recently, new techniques that involve technically simple, yet highly complex processes have been reported to produce ordered patterns on surface. For instance, Wittmann and Smith have shown that a thin, highly crystalline continuous film of poly(tetrafluoroethylene) is formed by moving a bar of the polymer against a glass surface near the glass transition temperature of the polymer.[4] This so-called friction transferred film is shown to be an excellent substrate for oriented growth of other materials. We think that the extremely high melt viscosity of the polymer plays an important role in this method. Karthaus, Ijiro and Shimomura have found that ordered patterns of poly(styrene) aggregates are formed on a mica surface by rinsing the mica with a dilute benzene solution of the polymer and allowing the benzene to evaporate.[5] They speculated that the driving force for pattern formation is dewetting of the mica surface by the increasingly viscous polymer solution.

In this letter, we report on a simple method of producing regular arrays of polymer deposits on the surface of a silicon wafer. The nanometer sized dots are produced by simply rubbing a thin polymer plate on the silicon surface at temperatures below but close to the bulk melting point of the polymer.

High density poly(ethylene) (PE(HD)) was shaped into a thin plate having a narrower width of about 0.5 mm. The wider length was about 10 mm, although it was not relevant for the present experiment as long as the pressure remained constant. Low density (LD) and linear (LN) (molecular weight 30000, M_w/M_n = 1.14) poly(ethylene) were similarly shaped. The 21 x 11 x 0.4 mm Si(111) substrate had natural oxide on its surface and the mean roughness was less than 1 nm over several μm.[6] Mica was cut into a similar shape and freshly cleaved in air. The polymer was moved on the substrate surface so that the wider face pointed in the direction of rubbing. The average pressure on the polymer plate was kept at approximately 0.03 kg/mm^2. Atomic force microscopy (AFM) was used to observe surface features of the samples made at controlled substrate temperatures and rubbing rates. Since the substrate surface was open to air, the surface temperature was lower than the bulk temperature. This small difference was not so critical in the present experiment as a non-uniformity of contact areas (and thus heat produced by friction) limited accuracy in the temperature of the contacting region to a few degrees. The melting point of the polymer was determined by an endothermic peak in differential scanning calorimetry.

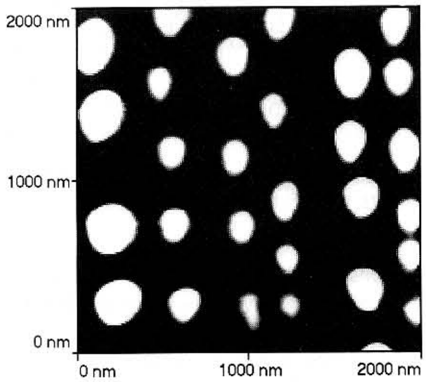

Figure 1. AFM image of poly(ethylene) dots on silicon. The dots have an average height of 11 nm.

Figure 1 displays an AFM image of the silicon surface after rubbing PE(HD). The transferred polymer exists as a nanometer scale dot. These dots form straight lines in the direction of rubbing. On the average, the dots made at 120 °C with a rubbing rate of 20 mm/s have a height of 11 nm, a diameter of 162 nm, and are separated by 341 nm along the line. These are the absolute values directly measured from the images without considering the fact that the dots within a single line are more similarly sized than those from other lines. Also, the dots with larger diameters tend to be more separated from each other.

Ordering of dots can be seen more easily by examining a distribution of the spacing along the rubbing direction. Since an ordering pattern depends on a line, we can normalize each spacing along a line by the average spacing of that line. A narrow distribution of the normalized spacing as shown in Figure 2 demonstrates a regular positioning of the dots along the rubbing direction.

In some regions, a regular alignment of the dots from neighboring lines can be also seen. In this case, the average spacing between the dots from adjacent lines is 530 nm. We think that ordering on the dots from different lines depends on the uniformity of the contact area between the polymer plate and the silicon surface. With the present geometry of a thin plate moved against the flat substrate, it was difficult to achieve uniform contact for a large area. As long as the contact length remains short in the direction perpendicular to rubbing (so as to keep the transferred materials in small quantities), other configurations like a polymer rod rolled against the substrate surface may improve ordering in two dimensions.

Upon changing the rubbing conditions, we have noticed four

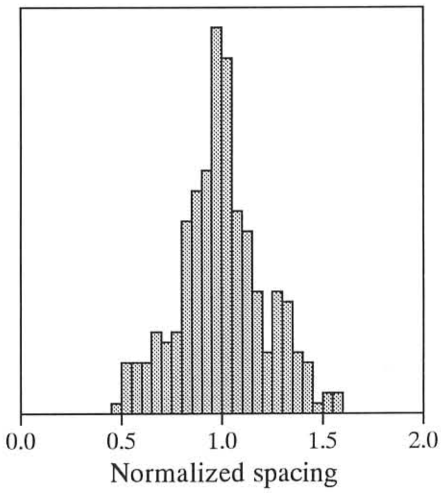

Figure 2. Distribution of spacing in the rubbing direction normalized with respect to the average spacing on a line.

different situations resulted on the silicon surface. As an extreme case, no polymer may be transferred. If the polymer is successfully transferred to produce nanometer sized objects, it may form either ordered dots as shown above or aggregates without any ordering. Finally, the polymer may be deposited in macroscopic scales with thickness of more than a few hundreds nanometers. Figure 3 summarizes the effects of changing the substrate temperature or the rubbing rate. For PE(HD) (mp: 131 °C) on silicon rubbing at 20 mm/s, there was no transfer at low temperatures (Figure 3(b)). At 15 °C below mp, the polymer was transferred without ordering. From 120 to 130 °C, ordered dots were formed. Above mp, macroscopic deposition took pace. At the temperature of 120 °C, the rubbing rate must be within the range from 15 to 25 mm/s to produce ordered dots. Rates either slower or faster than this resulted in no transfer. We did not see significant differences in the dot sizes for these ranges.

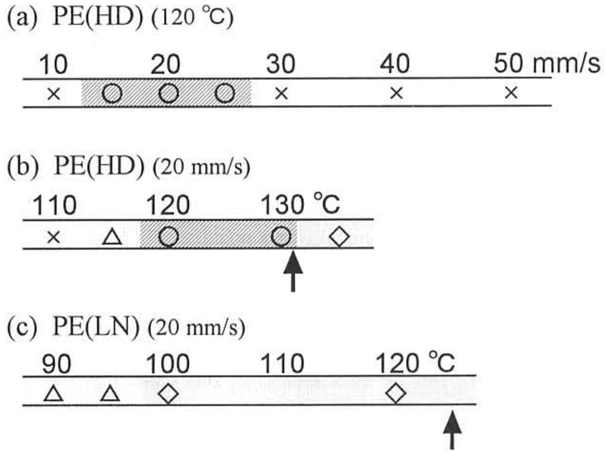

Figure 3. Effects of (a) rubbing rate and (b) temperature with PE(HD), and (c) temperature with PE(LN) on polymer transfer to the silicon surface. The marked points represent where the experiment has been conducted. ×: no transfer, ○: transfer with ordering, △: transfer without ordering, ◇: macroscopic deposition. The arrows denote the melting points.

PE(HD) was also rubbed against mica under similar conditions. In all cases, no polymer was transferred onto the mica surface. We have noted that macroscopically sized poly(ethylene) in melt does not wet mica.

For PE(LD) (mp: 107 °C) on silicon at 105 °C, rubbing at 20 mm/s produced ordered dots, but 30 mm/s resulted in transfer without ordering. PE(LN) (mp: 125 °C) rubbed on silicon at 20 mm/s gave transfer without ordering below 95 °C and macroscopic depositions above that temperature (Figure 3(c)). Thus, PE(LD) possesses the similar dots formation condition as PE(HD), while PE(LN) only transfers without ordering under the conditions investigated.

These results indicate that the ordering of polymer dots and transfer of nanometer-sized polymers must be considered separately. In order for polymer to be transferred, the polymer in contact with the surface must melt by friction. This explains the absence of transfer at low temperatures or slow rubbing rates. Transfer occurred on a pair of polymer and substrate that shows good wetting. Even in this wetting condition, no transfer occurred at high rates. This suggests that sticking is a necessary process for transfer of nanometer-sized polymers. Too strong sticking efficiency, however, leads to macroscopic depositions, as demonstrated by the higher temperature experiments. These characteristics represent the fundamental differences between our method and the rinsing method of Karthaus et al.[5]

When the substrate temperature is just below mp, only small quantities of polymer could be melted by friction. While this condition and suitable sticking seem to be sufficient for transfer, it does not guarantee ordered dots formation. We have noticed that the ordered dots are circularly shaped, while the polymer without ordering has no regular shape. Thus, the transferred portion must rupture to be separated, and at the same time, it must flow to be circularly shaped. Since the polymer wets the surface, either interfacial energies of the system or elastic contributions from shearing are responsible for shaping. However, the surface tensions of these polymers are nearly equal.[7] This leaves the flow and mechanical properties of polymers as the relevant factors for the ordered dots formation. Since the transferred polymer is cooled to the substrate temperature during shaping, the present ordering phenomenon may be classified as a far-from-equilibrium process.

References and Notes

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