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Atomic force microscope study of crater formation in ion bombarded polymer

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Polyimide Kapton films with a thickness of 62 μm were bombarded by Ar^+, N^+, He^+ and D^+ ions at energies from 10–50 keV. After bombardment at room temperature, the surface topographic changes of the polymer were investigated using an atomic force microscope (AFM). The most common feature of the ion-bombarded Kapton surface is the formation of craters which often have circular shape and rims. The crater sizes suggest they are unlikely to have been caused by a single ion but by the collective effects including diffusion and trapping of gas atoms and gas molecules in ion-bombarded polymer. A model for the formation of these craters is proposed.

1. Introduction

Crater formation in ion bombardment of polymer surfaces is a very interesting phenomenon. Many different models have been proposed to explain the mechanism of crater formation. Among them, the pressure-pulse model, the thermal-spike model and the shock-wave model, are widely cited. The pressure-pulse model is a hydrodynamic type model. In the pressure-pulse model, the angular distributions of target molecules are asymmetrical and the energy density resulting from the ion–solid interaction propagates in the solid by diffusion. The thermal-spike model assumes that the energy deposited by the incident ion creates a thermal spike characterized by a temperature, and the energy is transported in the solid due to heat conduction. The third model, namely the shock-wave model, suggests that the target molecule redistribution is due to a propagating shock wave which is caused by the sudden pressure change in the ion-bombarded region. All three models consider energy transfer in the solid but only the first model treats the energy transfer as a result of mass transport in the solid. However, mass transport is very important in understanding the crater-formation mechanism.

Because of the complex structure and composition of polymeric materials, the mechanisms of forming craters are still unclear. Unlike ion damage in metals, radiation causes scission and cross-linking of polymer chains which usually alter the molecular weight, structure and composition of the polymer [1, 2]. One of the most important chemical changes related to chain scission on a polymer is the release of free radicals and gases after ion radiation. For polyimide, the released gases are usually H_2, CH_4, CO, CO_2 and CN [3]. Along with chain scission, the incident ions create great amounts of defects when they collide with the target atoms or molecules. These ions may also capture electrons to form gas atoms and gas molecules. The present study suggests that diffusion and trapping of gas molecules and gas atoms in an ion-bombarded polymer may be the fundamental cause of observed crater formation on Kapton polymer surface.

2. Experimental procedure

Polyimide Kapton films with thickness of 62 μm were bombarded by Ar^+, N^+, He^+ and D^+ ions at room temperature. The energy of incident ions varied from 10–50 keV for different Kapton samples. The fluence was 10^{13} ions cm^{-2} for all experiments. During ion bombardment, the vacuum of the target chamber was kept at 10^{-6} torr (1 torr = 133.322 Pa). After ion bombardment, the Kapton samples were stored in a sealed container for 4 wk or more before being analysed under an atomic force microscope (AFM). Before being analysed, the Kapton samples were treated with a mild solution of NaOH for less than 30 s. A SFM-BD2 atomic force microscope (AFM), designed and built by Park Scientific Instruments, was used to analyse both the pristine (non-irradiated) and ion-bombarded Kapton surfaces at ambient conditions. The AFM works in contact mode with a standard silicon nitride tip. The size of the Kapton samples was 2×2 cm^2 and the maximum scanning size was 11 μm × 11 μm for this atomic force microscope.

3. Results and discussion

First, a pristine Kapton film was analysed by AFM. Lines of different orientations were observed on an

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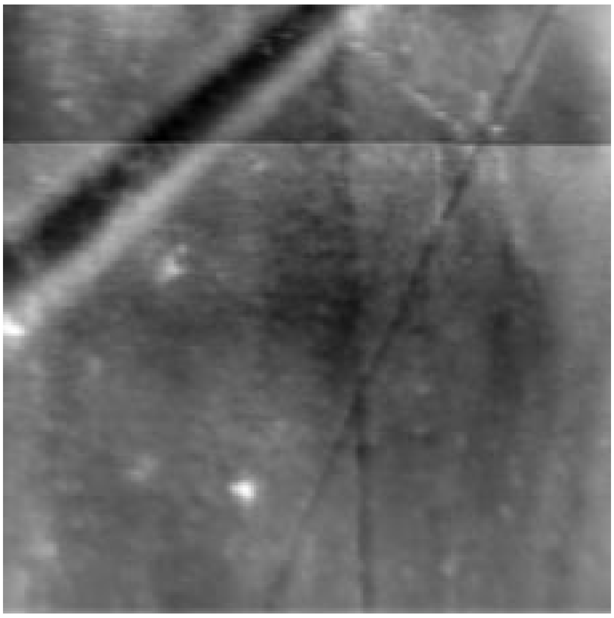

Figure 1 Scratch lines observed on a pristine Kapton surface specimen by an atomic force microscope. The size of the image area is 4 × 4 μm^2.

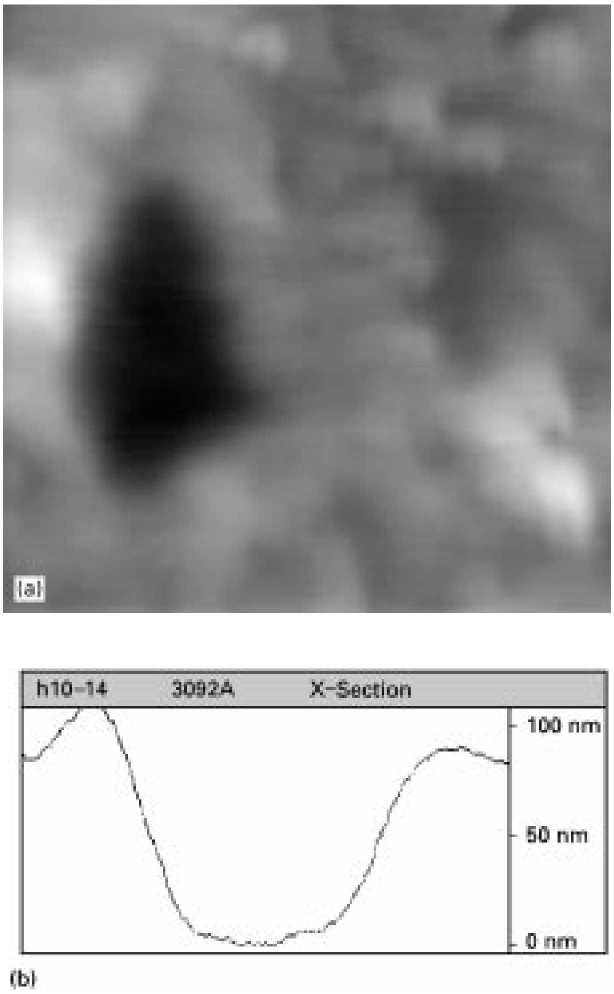

Figure 2 (a, b) Crater formed on 20 keV He$^+$ ion-bombarded Kapton surface. The size of the image area is 280 × 280 nm^2.

otherwise smooth surface as shown in Fig. 1. No other type of feature was found on the surface of pristine Kapton films. These lines can be simply interpreted as scratch lines. It was noticed that the optical reflection of the film was slightly different from one side to the other. After both sides had been examined by AFM, more lines were observed on the rough side. This also indicates that the observed lines were scratch lines.

While craters have been reported from ion-bombarded polymers in previous studies [4, 5], the mechanism of crater formation is still not clear. In the current investigation, craters of various sizes and depths were found on the surface of ion-bombarded Kapton. Most of these craters were circular in shape and had rims as shown in Figs 2 and 3. As discussed in the previous section, the crater depth changes with incident ion energy but is always shallower than that calculated by transport ion in matters (TRIM). On considering gas release and diffusion effects in the ion-bombarded polymer, it appears that diffusing ions and released gases play an important role in crater formation. It also noted in these figures that the cross-sections of these craters have a characteristic profile. Such features provide an understanding of the formation of craters.

Like craters, hillocks were frequently observed in previous studies [6]. In this research, areas with hillocks were usually avoided in order to obtain a better look at the craters. However, hillocks of different sizes were largely present on the surface. Barlo Daya *et al.* reported that conical-shaped hillocks having nearly circular shaped bases were observed on a

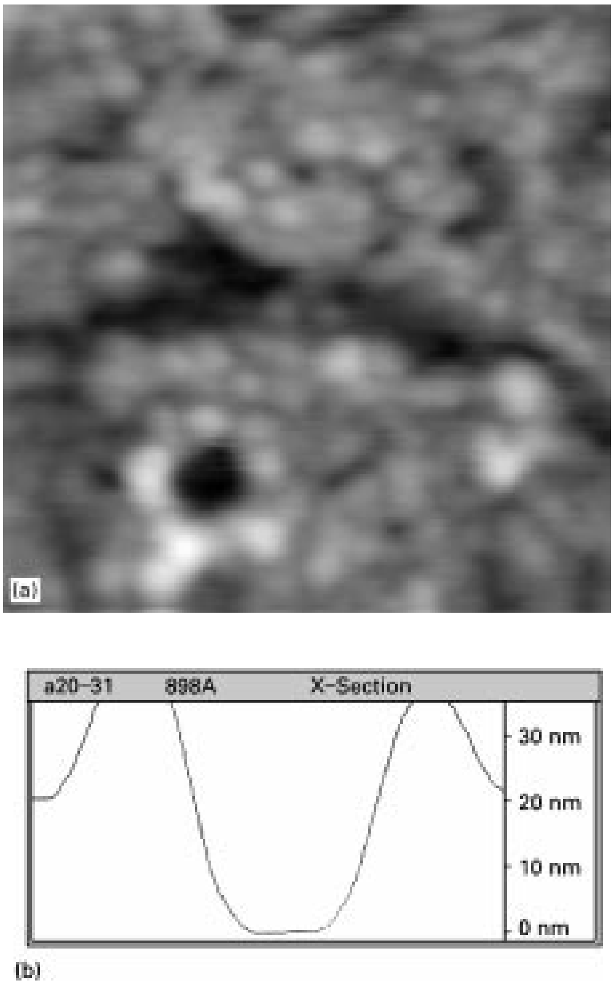

Figure 3 (a, b) Crater formed on 20 keV Ar$^+$ ion-bombarded Kapton surface. The size of the image area is 280 × 280 nm^2.

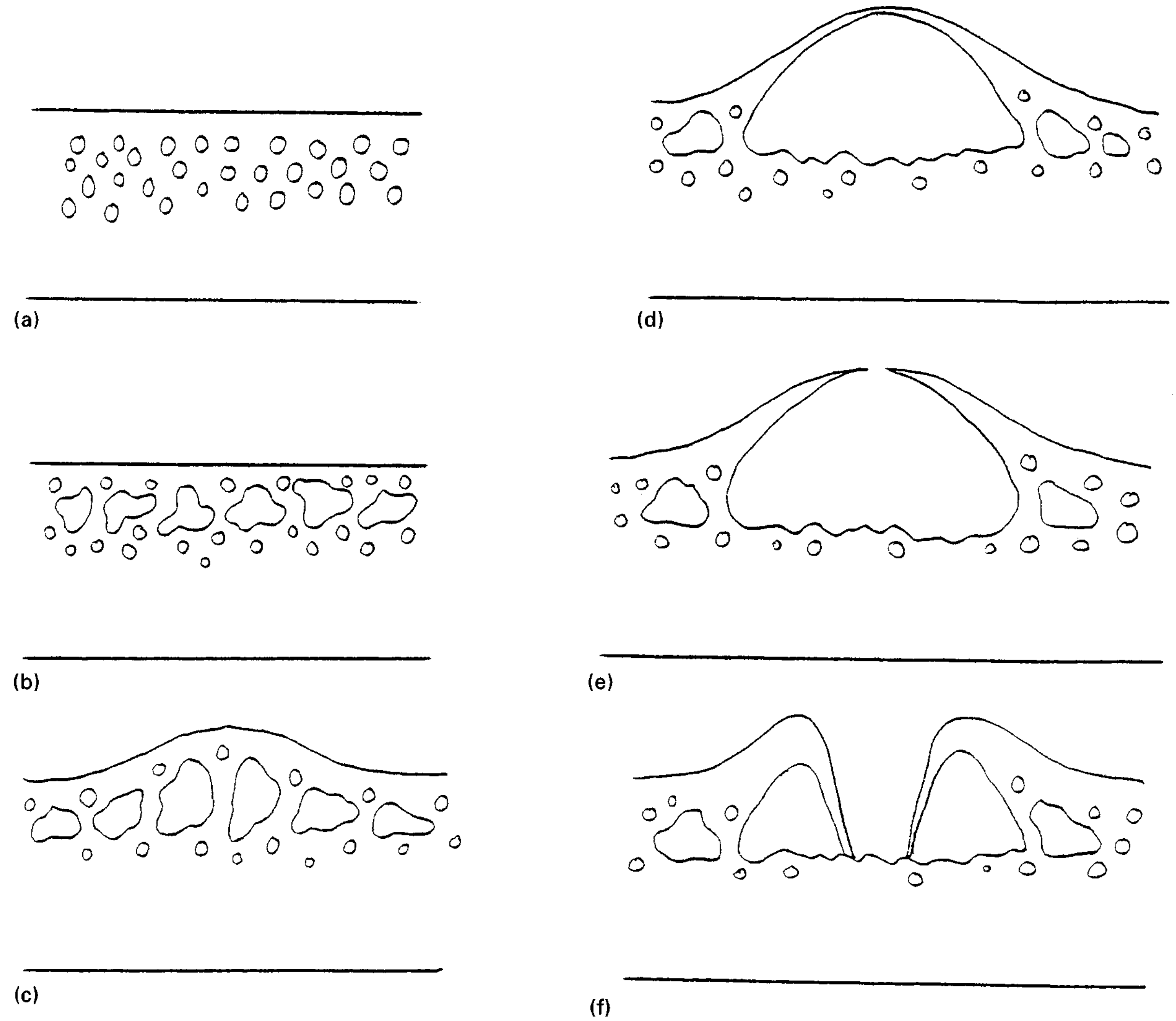

Figure 4 Schematic drawing of crater formation on an ion-bombarded polymer: (a) defects created by ions; (b) gas trapped by defects to form bubbles; (c) surface deformation caused by bubbles; (d) blister formed by the coalescence of bubbles; (e) rupture of blisters and release of gas; (f) surface collapses to form crater.

78.2 MeV ^{127}I bombarded mica surface [7]. Because those hillocks could be erased by the probe tip to reveal craters, they suggested that the hillocks could be thick blisters created by hydrodynamic pressure. This is substantiated by other studies which also suggest a similar process.

Previous research on ion-bombarded polymer shows that there are released gases (H_2, CH_4, CO, CO_2) in the target as the result of chain scission when polyimide is bombarded with ions [8, 9]. The incident ions also create a large amount of defects [10]. For instance, one 30 keV N^+ ion can create 197 defects in a Kapton target according to TRIM calculation. These gases are moving inside the target through diffusion and can be trapped by defects to create cavities [11]. This diffusion–trapping process may be the foundation of crater formation [12, 13]. Thus, based on these observations, a model is proposed as shown in Fig. 4.

The basic process in the proposed model involves the diffusion and trapping of gases, forming bubbles on the surface, breaking of blisters with gas release, and eventual formation of craters on the surface. Initially, incident ions create great amounts of defects and cause chain scission, which releases free radical gases (Fig. 4a). The incident ions may also capture electrons to become gas atoms or gas molecules. These gases diffuse in the polymer and are trapped by defects to form bubbles (Fig. 4b and 4c). While the concentration of the gas builds up, the coalescence of bubbles forms blisters (Fig. 4d). The internal pressure on the surface causes surface deformation and eventually breaks the blister (Fig. 4e). Therefore, a crater with depth close to the projected range of incident ions is formed and gas is released. After gas release, the ruptured surface collapses, resulting in a cross-section as shown in Fig. 4f.

This described cross-section can be found in the cross-sections measured by AFM, as shown in Figs 2 and 3 and leads to the conclusion that this model is able to explain the various observations, including shallower depth and damage profile which are observed on ion-bombarded Kapton surfaces.

4. Conclusion

In this study, the ion-bombarded polyimide Kapton surface was analysed by an atomic force microscope

(AFM). Circular-shaped craters, often with rims, were observed and their depth profiles were measured. To explain the mechanism of crater formation, a model based on diffusion and trapping of ion bombardment-induced gases is proposed. With this model, many observations found in crater formation can be explained.

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