Phys. Status Solidi C **10**, No. 4, 611–613 (2013) / **DOI** 10.1002/pssc.201200797

physica status solidi pss c
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current topics in solid state physics

Surface tracks on ultra-thin polymer films

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Received 5 October 2012, revised 19 November 2012, accepted 19 November 2012
Published online 13 March 2013

Keywords MeV ions, nanostructure, surface track

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In this work, crater formation by single 20 MeV Au ions on ultra-thin poly(methyl methacrylate) (PMMA) films was systematically investigated as a function of the thickness *t* of the layers (2 nm<*t*<100 nm). The samples were bombarded at grazing angles of incidence (79°and 84° to the surface normal) and morphological changes analyzed employing scanning force microscopy in the tapping mode. For thicknesses from 100 nm down to approximately 20 nm no major changes were observed in the size and morphology of the impact features. For t<20 nm rims (hillocks) start to diminish, but crater hole size showed very little changes even for very thin samples of ~ 8 nm. Similar results were observed for both impact angles. The results indicate a different depth of origin for crater and ridge formation due to a fast ion impact.

1 Introduction It has been known since many years that the interaction of an energetic ion with insulators causes the ejection of material and plastic deformation at the surface, resulting in permanent hillocks and craters [1-4]. These effects are due to energy transfer from electronic excitations along the trajectory of the projectile. The energy transferred can be quickly converted into atomic motion, creating defects in the bulk and sputtering and mass transport at the surfaces. Fast transient thermal processes (the so called thermal spikes) [5] and pressure pulses emanating from the core of the impact [6] are considered to be the major sources of mass transport and ejection at the surface for polymers, although alternative mechanisms (such as the ion hammering [7] or coulomb explosions [8]) may play an important role in certain types of materials.

Recent studies on the interaction of individual ions in polymeric thin films indicated that the surface effects are altered as the thickness of the material is reduced [9]. The effects of fast ions on confined structures is not completely understood [10,11] and may vary from those observed for bulk matter, having a major influence from interface interactions. In this contribution, we report on the impact features produced by 20 MeV Au ions on quase-monodisperse poly-(methyl methacrylate) (PMMA) films as a function of the thickness *t* of the layer (2<t<100 nm) at grazing angles of incidence. The results observed indicated a clear thickness-dependent effect on the cratering process for very thin layers.

2 Experimental Thin films of PMMA (Polymer Laboratories, M_w=132,000 u, polidispersity 1,03) were spin-coated from anisol solutions onto Si substrates. The thicknesses *t* ranged from 2 to 100 nm and the root mean square roughness around 0.25 nm. The films were bombarded by 20 MeV $^{197}Au^{7+}$ ions at low fluences (~10^9 cm^{-2}). The electronic stopping power, $(dE/dx)_{el}$, estimated by the TRIM code, was around 235 eV/Å. The irradiations were performed in vacuum (2x10^{-6} Torr) at the Porto Alegre 3MV Tandetron ion implanter. Two distinct angles of incidence (79° and 84° to the surface normal) were employed. The size and the shape of the impact features were characterized offline on a Nanoscope IIIa (Digital Instruments) scanning force microscope in the Tapping Mode™ (TM-SFM), with standard Si tips (with nominal radius of curvature 10 nm) and a 1–2 Hz scanning frequency. Typical drive amplitudes were set to give a detector signal around of 2.8 V. Only images collected with high quality tips were stored and used for quantitative analysis. The dimensions of the impact features were extracted from cross-sectional profiles and mean values were calculated from data taken in more than 20 impact features.

3 Results and discussion Figure 1 show a series of SMF images of PMMA films bombarded by 20 MeV Au ions. For the thick films, two different structures at the impact site are observed, an elliptical crater hole and an elongated hillock or tail extending along the direction of ion penetration, as usually seen for polymers [4]. For thicknesses around and below 16 nm, changes in the size of the impact features, particularly in the hillock volume and the crater depth, start to occur. For sufficiently thin layers, the hillocks are completely suppressed, but the crater holes, although shallower, are still present.

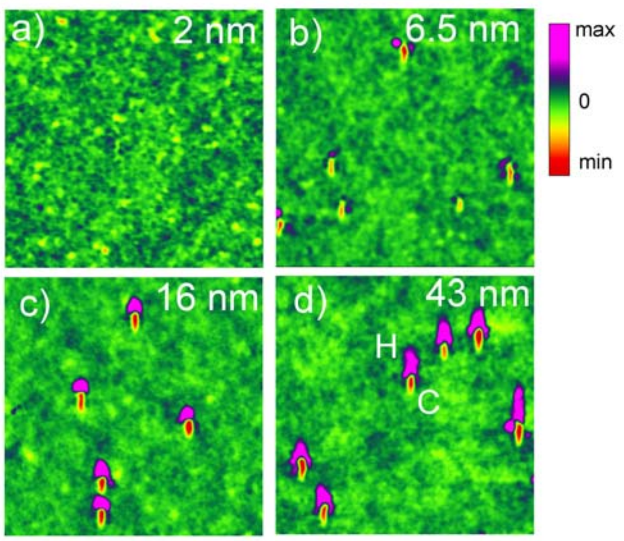

Figure 1 SFM images of PMMA thin films of distinct thicknesses, bombarded at 79° to the surface normal by 20 MeV Au ions: (a) 2 nm; (b) 6.5 nm; (c) 16 nm; (d) 43 nm. The min in the height scale is -2.5 (2.5 nm below the surface level in a) and -4 nm in b)-d). And max is 2.5 nm in a) and 4 nm in b)-d). The image size is 500X500 nm^2. In the frame d) the crater and the hillock are identified by letters C and H, respectively.

Figures 2 and 3 display the results of quantitative data analysis of the hillock and crater dimensions as a function of t, for the case of 79° incidence. The crater width showed only slight changes even for very thin samples, reducing from ~20 nm for the thicker layers down to ~15 nm for the thinnest films. The small variation in the hole diameter indicates the melted and vaporized radius around the point of impact does not shrink very much as the thickness is decreased. The crater depth, obviously diminish as the thickness goes down, but it never reaches the level of the Si substrate. For shallow craters (<1 nm) the uncertainty in the crater radius is larger, because the natural roughness of the surface may not be clearly separated from the crater topography.

The crater length diminished more markedly (by ~30%) between the thickest and thinnest films. But still these changes are moderate. The evolution of the hillock size as a function of thickness is clearly different. For films with t<16 nm, there is a strong decrease of the hillock length and height (Fig. 3). The protrusions disappear completely at t~4 nm and lower, being barely distinguishable from the pristine surface roughness.

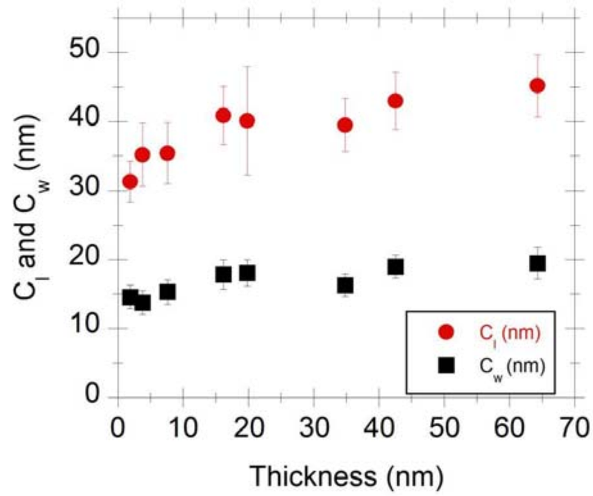

Figure 2 Average width (C_w) and length (C_l) of craters produced by 20 MeV Au ions on PMMA films of different thickness.

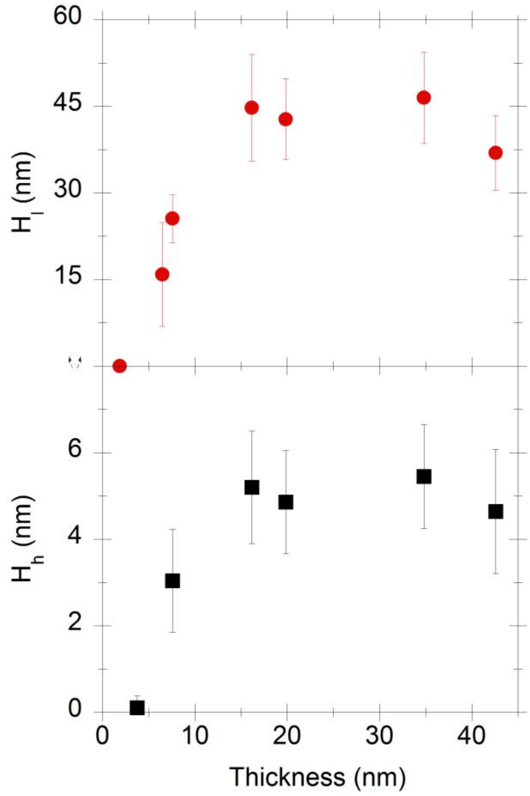

Figure 3 Average length (H_l) and height (H_h) of the hillocks as a function of thickness.

The absence of a thickness effect in thinner layers for the crater sizes (C_l and C_w) shows that the main contributions to craters formation occur by near-surface events, at distances smaller than ~8 nm below the surface. It indicates that the depth of the excited region contributing to the hillock formation is deeper than the depth of origin of the hole. The effect of the thickness reduction on the surface track dimensions was similar to both angles of incidence.

Thus, below a critical thickness (~15 nm for our films) the ion track effects start to weaken. As the generation of the raised regions demands contributions from excited regions deeper into the film, they quickly decrease in size. Craters on the other hand, are less sensible to the spatial constrain: the weaker thickness effect suggests their formation is very much dependent on the near surface excitation events, as was indicated recently by charge-state dependent impact craters due to 600 MeV Au ions [9]. Further mechanistic considerations, including cooperative effects and transport and dissipation of the deposited energy will be discussed in a separate paper.

4 Conclusions

We have studied surface tracks produced by single 20 MeV Au ions on thin films of PMMA as a function of the layer thickness. It was found a dependence of the surface track sizes on the thickness. The crater hole and hillocks start to present a decrease in their size for films below ~ 16 nm. The hillock volume showed a sharp decrease below this critical thickness The weak dependence of the crater size on the thickness indicates that the hole formation is dominated by near-surface, short-range effects, while the strong changes of the hillock dimension indicates a deeper depth of origin for protrusion formation, related to long-range cooperative interactions.

Acknowledgements The Brazilian agency CAPES and CNPq is acknowledged for financial support.

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