

Creation of surface nanostructures by irradiation with slow, highly charged ions

A. S. EL-SAID^{†§}, W. MEISSL[†], M. C. SIMON[†], J. R. CRESPO LÓPEZ-URRUTIA[‡],
I. C. GEBESHUBER[†], J. LAIMER[†], H. P. WINTER[†], J. ULLRICH[‡]
and F. AUMAYR^{*†}

[†]Institut für Allgemeine Physik, Technische Universität Wien, Wiedner Hauptstr.
8/E134, A-1040 Wien, Austria

[‡]Max-Planck Institut für Kernphysik, D-69029 Heidelberg, Germany

(Received 4 December 2006; revised 2 January 2007; in final form 3 January 2007)

It has recently been demonstrated that slow ($v \ll 1$ a.u.) highly charged ions (HCIs) are able to generate nano-sized hillocks on cleaved $\text{CaF}_2(111)$ surfaces. The aim of the present study was to explore whether surface nanostructures can also be formed on other target materials by the impact of slow HCIs. To this purpose, we have irradiated $\text{LiF}(001)$, diamond-like carbon (DLC) and $\text{Au}(111)$ with slow Xe HCIs (up to charge state $44+$) from the Heidelberg electron beam ion trap. After irradiation, the crystals were investigated by scanning force microscopy. Nanometric hillocks protruding from the surface were found in the topographic images for the case of Xe^{q+} on $\text{LiF}(001)$ for charge states $q \geq 28$, but not for DLC and $\text{Au}(111)$.

Keywords: Highly charged ions; Surface nanostructures; LiF; Ion-surface interaction; Inelastic thermal spike model; Diamond like carbon; HCIs

PACS: 79.20Rf; 68.37Ps; 68.35Dv

1. Introduction

It has long been known that irradiation of crystalline solid targets with swift, heavy ions can lead to severe structural modifications at the surface and in the bulk (see, *e.g.* refs. [1–4] and references therein). Examples are the formation of latent tracks in the solid, the creation of (mostly hillock type) nanostructures on the surface and the occurrence of phase transitions, *e.g.* from crystalline to amorphous or from superconducting to insulating. Usually, track formation is linked to a critical energy loss (dE/dx) of the projectiles and occurs particularly in insulators (*e.g.* polymers, oxides, ionic crystals).

Although there is no question that the intense electronic excitation of a confined volume around the ion trajectory because of the electronic stopping of the swift ions is the major

*Corresponding author. Tel.: +43 1 58801 13430; Fax: +43 1 58801 13499; Email: aumayr@iap.tuwien.ac.at
[§]On leave from Physics Department, Faculty of Science, Mansour University, 35516, Mansour, Egypt

cause for this modification [5], the exact mechanism of how this energy is transferred to the lattice is still under discussion and probably strongly depends on the type of material. Several simple mechanisms have been proposed. In the Coulomb explosion model [6], the positively charged lattice atoms created by the slowing projectile via ionization processes repel each other, thus leading to a shock wave. In the thermal spike model [7], the kinetic energy of the electrons is transferred to the lattice atoms efficiently enough to increase the lattice temperature locally above the melting temperature, followed by a rapid quenching. For ionic crystals such as alkali halides (LiF) or fluorides (CaF₂), sublattice effects exist, in which the electronic excitation is mainly deposited in the anion sublattice, leading to specific point defects or even defect clusters (resulting from self-trapped excitons, V_k centers etc.) that are connected to track formation, surface hillock production and increased sputtering yields [8–12].

Highly charged ions (HCIs) carry a large amount of potential energy [13]. This internal energy is equal to the total ionization energy, which has to be spent for producing the high charge state from its neutral ground state (*e.g.* 51 keV in the case of Xe⁴⁴⁺). Upon interaction with solid surfaces, the HCIs deposit their potential energy within a very short time (a few femtoseconds) within a nanometer-size volume close to the surface [13–16]. Recently it has been demonstrated that hillock-like surface nanostructures on CaF₂ single crystals can not only be produced by swift, heavy ions but also by slow (*i.e.* in a velocity regime well below the kinetic electronic stopping power threshold) HCIs as long as these ions are sufficiently highly charged [17, 18]. Surprisingly, instead of a critical energy loss, hillock formation by HCIs exhibits a sharp potential energy threshold around 14 keV [18]. With increasing potential energy, both the basal diameter and the height of the hillocks became larger. No effect of the kinetic energy on the size of the observed hillocks was observed in the range $2 \text{ keV/amu} \leq E_{\text{kin}}/m \leq 4 \text{ keV/amu}$. Estimations of the energy density deposited on the atoms indicated that the threshold might be linked to a solid–liquid-phase transition [18]. The calculations took into account the excitation of the electronic subsystem and included the energy spread via the electron–phonon mean free path as developed within the inelastic thermal spike model for swift, heavy ions [19, 20].

Encouraged by these promising results, we have started to explore possibilities to produce similar nanostructures on other target materials by irradiation with slow HCIs. One important aim of these studies is to find materials of practical relevance in which slow HCIs could be used as a nanostructuring tool [21]. On the other hand, we aim for a basic understanding of the mechanisms that lead to damage creation by slow HCIs in different materials with different electronic and crystalline structures.

2. Experiments

In the present investigations, we have used LiF(001) and Au(111) single crystals as well as thin films of diamond-like carbon (DLC) as target materials on Si substrates. The samples were cleaved or cleaned, mounted on a target holder and transferred into the irradiation chamber, which was then evacuated to a finite pressure in the 10^{-10} mbar range. Irradiation took place at normal incidence with slow, highly charged ¹²⁹Xe^{*q*+} (*q* = 26, 28, 44) ions from the Heidelberg electron beam ion trap (EBIT) [22] using an ion impact energy of $10q$ keV (10 kV extraction voltage times projectile charge state *q*). The ion flux from the EBIT varied between 10^3 and several 10^4 ions/s, as monitored via electron emission detection with close to 100% detection efficiency [23]. An irradiation time between 2 and 10 h resulted in typical total ion fluences between 0.5 and 2×10^9 ions/cm². After irradiation, the samples were investigated by an MFP-3D scanning force microscope (SFM) (Asylum Research, Santa

Barbara, USA) under ambient conditions. This system allows for simultaneous SFM and optical measurements of transparent and opaque samples owing to top-view optics and an inverted optical microscope base. The measurements have been performed in contact mode at a constant loading force of <10 nN, using non-conductive Si_3N_4 sensors (Veeco Instruments, France) with cantilevers with force constants of about 0.1 N/m (cantilever tip radius typically $4\text{--}5$ nm).

3. Results and discussion

3.1 $\text{LiF}(001)$

Lithium fluoride single-crystal samples, freshly cleaved along one of the (100) planes (thickness ≤ 1 mm), were irradiated with Xe^{26+} , Xe^{28+} and Xe^{44+} ions. The irradiation parameters are listed in table 1. The TRIM code in its present form (SRIM 2006 [24, 25]) was used to estimate the ion range as well as values for electronic and nuclear energy losses.

SFM topographic investigations of the samples reveal nano-sized hillocks protruding from the surface after irradiation with 2.2 keV/amu Xe^{28+} (figure 1) and 3.4 keV/amu Xe^{44+} ions (figure 2). The measured mean diameter and height of the hillocks are listed in table 1.

However, for the case of 2.0 keV/amu Xe^{26+} projectiles, no hillocks or any other surface modifications were observed (table 1). This points to a similar but slightly lower potential energy threshold ($10\text{--}11$ keV) in the case of $\text{LiF}(001)$ compared with $\text{CaF}_2(111)$ [18].

Table 1. Ion-beam parameters and measured hillock sizes for irradiation of a $\text{LiF}(001)$ single crystal by slow Xe HCIs of different charge states.

	Xe^{26+}	Xe^{28+}	Xe^{44+}
Kinetic energy (keV/amu)	2.01	2.17	3.41
Ion range (nm)	83	89	130
Electronic energy loss (keV/nm)	0.99	1.03	1.28
Nuclear energy loss (keV/nm)	2.59	2.57	2.39
Potential energy (keV)	8.9	12.0	51.1
Mean hillock diameter (nm)	–	24.0 ± 4.2	33.3 ± 4.8
Mean hillock height (nm)	–	0.6 ± 0.2	0.9 ± 0.2

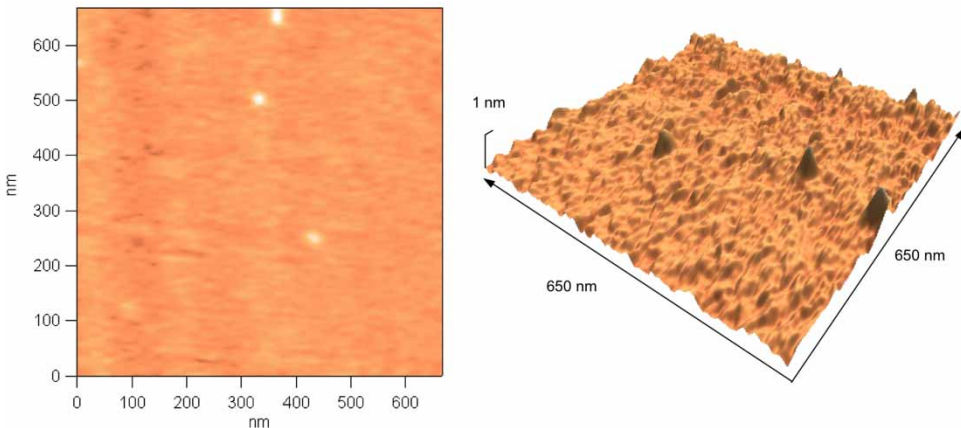


Figure 1. Topographic contact mode SFM image of a $\text{LiF}(001)$ surface irradiated by 2.2 keV/amu Xe^{28+} ions showing hillock-like nanostructures protruding from the surface.

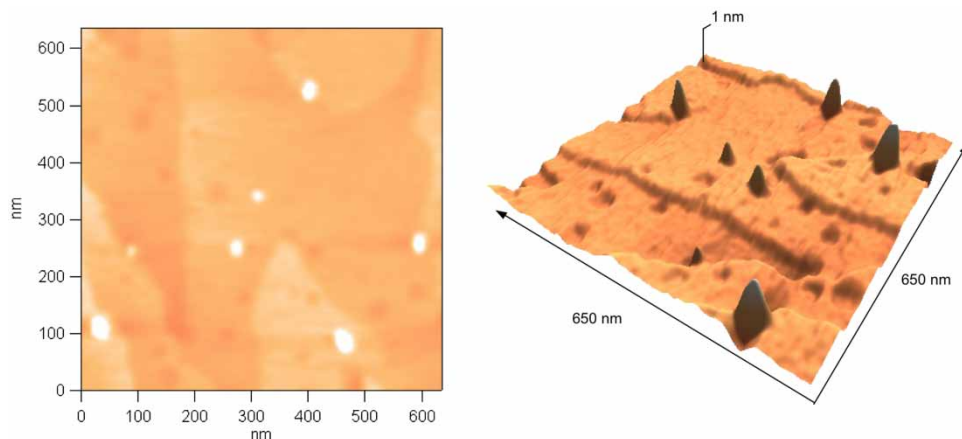


Figure 2. Topographic contact mode SFM image of a LiF(001) surface irradiated by 3.4 keV/amu Xe⁴⁴⁺ ions.

The number of hillocks per unit area was found to be in good agreement with the applied ion fluence, *i.e.* above the threshold; the majority of projectiles produce an individual hillock. Similar to the case of CaF₂(111), the size (*i.e.* height and diameter) of the hillocks increases considerably with increasing charge state. Because of the finite curvature radius of the SFM tip (nominally 4–5 nm), the diameter (but not the height) of the hillocks is subject to a systematic error.

We again note a remarkable similarity with the case of swift, heavy ions, which are known to induce similar hillocks on cleaved LiF surfaces, if the corresponding electronic energy loss $(dE/dx)_e$ exceeds a threshold of about 4–5 keV/nm [9]. Above this threshold, the size of these hillocks also increases as a function of $(dE/dx)_e$. Although, for swift, heavy ions electronic energy loss processes initiate the nano-sized hillock (and track) formation, slow HCIs deposit their potential energy to the electronic system of the target material in a small region close to the surface, thus causing the formation of the observed nanostructures.

More systematic studies are presently under way to determine precisely the position of the potential energy threshold as well as the dependence of the hillock size on potential energy and other ion irradiation parameters.

3.2 DLC and Au(111)

DLC films of about 40 nm thickness were deposited via plasma-assisted chemical vapor deposition on an Si substrate. DLC is usually an insulating material. However, after irradiation with swift, heavy ions, it becomes conductive along the ion track owing to a nano-scale conversion of material along the track from DLC (sp³) to graphite-like (sp²) carbon [26]. Simultaneous topography and conductivity recording showed that nano-sized hillocks are emerging from the surface with a clear increase of conductivity at every hillock position [27]. Following this interesting work, we tried to use slow HCIs to induce similar effects and thus irradiated DLC films with 3.4 keV/amu Xe⁴⁴⁺ ions. In our SFM images, however, no ion-irradiation effects could be observed (figure 3), despite the fact that our DLC films are rather flat, which would allow small surface modifications to be observed. So either the created dots are too small to be observed within our SFM resolution (1 nm spatial, 0.1 nm vertical) or the potential energy of our Xe⁴⁴⁺ projectiles lies below a threshold for such a material modification. We plan to irradiate DLC samples further with HCIs in still higher charge states.

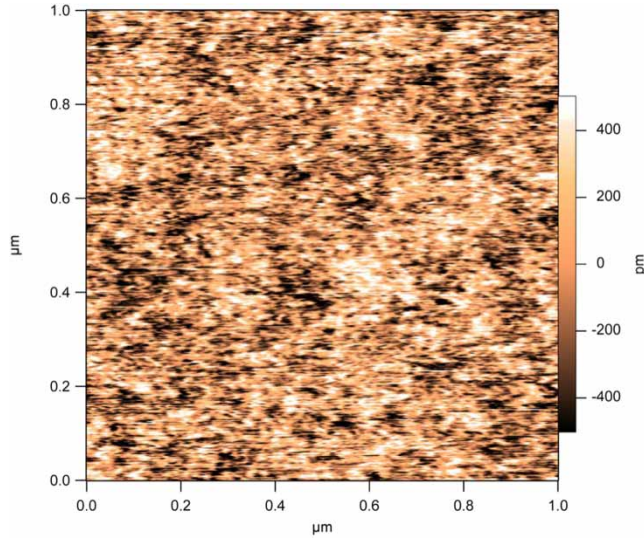


Figure 3. Topographic contact mode SFM image of a DLC film on an Si substrate irradiated by 3.4 keV/amu Xe^{44+} ions.

In contrast to insulators, the interaction between slow HCIs and metal surfaces is relatively well understood [14]. Because of the large mobility of electrons in conductors, HCIs are less likely to create a local charge depletion region in metals, thus decreasing the probability to create permanent defects. We nevertheless have irradiated an Au(1 1 1) single-crystal target with 3.4 keV/amu Xe^{44+} ions because interesting surface modifications have recently been reported for Au(1 1 1) as a result of slow Xe^{44+} impact [28]. Although irradiation of Au(1 1 1) by Xe^{44+} ions resulted in an electron yield of almost 150 electrons per ion [23, 29], we so far have not been able to detect any permanent surface modifications as a result of HCI irradiation during SFM inspection. One explanation could be that the roughness of our Au(1 1 1) surface is still too high. Although, meanwhile, another group [30] also failed to reproduce the findings of Pomeroy *et al.* [28], it is planned to continue these investigations with HCIs in higher charge states and better prepared Au(1 1 1) surfaces.

4. Conclusions

We have started to explore possibilities to produce nanostructures on various target materials by irradiation with slow HCIs. So far we have not been able to find any surface modifications on HCI-irradiated DLC and Au(1 1 1). On the other hand, for LiF(0 0 1) and $\text{CaF}_2(1 1 1)$, nano-sized hillocks are produced as a result of the deposition of potential energy by the HCIs. Here the formation of these protrusions seems to require a minimum potential energy that is slightly lower in the case of LiF(0 0 1) than $\text{CaF}_2(1 1 1)$. Analogies to hillock formation by swift, heavy ions are striking and are due to the fact that both swift heavy ions as well as slow HCIs deposit their energy primarily into the electronic subsystem of the target material.

Acknowledgements

This work has been supported by the Austrian Science Foundation FWF (project nos M894-N02 and P17449). The experiments were performed at the distributed

LEIF-Infrastructure at MPI Heidelberg, Germany, supported by Transnational Access granted by the European Project RII3#026015.

References

- [1] L.T. Chadderton, *Radiat. Meas.* **36** 13 (2003).
- [2] R.L. Fleischer, P.B. Price and R.M. Walker, *J. Appl. Phys.* **36** 3645 (1965).
- [3] H. Dammak, A. Dunlop, D. Lesueur *et al.*, *Phys. Rev. Lett.* **74** 1135 (1995).
- [4] G. Schiewietz, E. Luderer, G. Xiao *et al.*, *Nucl. Instrum. Meth. Phys. Res. B* **175** 1 (2001).
- [5] H. Gnaser, *Low-Energy Ion Irradiation of Solid Surfaces*, volume 146 (Springer, Berlin, 1999).
- [6] D. Lesueur and A. Dunlop, *Rad. Eff. Def. Sol.* **126** 163 (1993).
- [7] M. Toulemonde, C. Dufour and E. Paumier, *Phys. Rev. B* **46** 14362 (1992).
- [8] C. Müller, A. Benyagoub, M. Lang *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **209** 175 (2003).
- [9] C. Müller, M. Cranney, A.S. El-Said *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **191** 246 (2002).
- [10] N. Khalfaoui, C.C. Rotaru, S. Bouffard *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **240** 819 (2005).
- [11] A.S. El-Said, M. Cranney, N. Ishikawa *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **218** 492 (2004).
- [12] A.S. El-Said, R. Neumann, K. Schwartz *et al.*, *Rad. Eff. Def. Sol.* **157** 649 (2002).
- [13] F. Aumayr and H.P. Winter, *Phil. Trans. R. Soc. (London)* **362** 77 (2004).
- [14] A. Arnau, F. Aumayr, P.M. Echenique *et al.*, *Surf. Sci. Rep.* **27** 113 (1997).
- [15] H.P. Winter and F. Aumayr, *J. Phys. B: At. Mol. Opt. Phys.* **32** R39 (1999).
- [16] H.P. Winter and F. Aumayr, *Euro. Phys. News* **33** 215 (2002).
- [17] A.S. El-Said, W. Meissl, M.C. Simon *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **256** 346 (2007).
- [18] A.S. El-Said, W. Meissl, M.C. Simon *et al.*, [arXiv.org cond-mat/0609246](http://arXiv.org/cond-mat/0609246) (2006).
- [19] M. Toulemonde, C. Dufour, A. Meftah *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **166/167** 903 (1992).
- [20] A. Meftah, J.M. Constantini, N. Khalfaoui *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **237** 563 (2005).
- [21] F. Aumayr and H.P. Winter, *e-J. Surf. Sci. Nanotech.* **1** 171 (2003).
- [22] J.R. Crespo López-Urrutia, B. Bapat, B. Feuerstein *et al.*, *Hyperfine Interact.* **146/147** 109 (2003).
- [23] W. Meissl, M.C. Simon, J.R. Crespo Lopez-Urrutia *Rev. Sci. Instr.* **77** 093303 (2006).
- [24] J.F. Ziegler, J.P. Biersack and U. Littmark, *The Stopping and Range of Ions in Matter*, volume 1 (Pergamon, New York, 1985).
- [25] J.F. Ziegler, <http://www.srim.org> (2006).
- [26] J.-H. Zollond and A. Weidinger, *Nucl. Instr. Meth. Phys. Res. B* **225** 178 (2004).
- [27] M. Waiblinger, M.C. Sommerhalter, B. Pietak *et al.*, *Appl. Phys. A* **69** 239 (1999).
- [28] J.M. Pomeroy, H. Grube, A.C. Perrella *et al.*, *Nucl. Instr. Meth. Phys. Res. B* **258** 189 (2007).
- [29] H. Kurz, F. Aumayr, D. Schneider *et al.*, *Phys. Rev. A* **49** 4693 (1994).
- [30] M. Tona, private communication (2006).