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Surface Modifications of BaF₂ and CaF₂ Single Crystals by Slow Highly Charged Ions

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Abstract

Ion-irradiation of solid surfaces is considered as one of the promising and powerful techniques for material nanostructuring. Recently, slow highly charged ions (HCI) have shown their potential in creating surface nanostructures in various solids. Here, we focus on the surface modifications of BaF₂ and CaF₂ single crystals by HCI. Despite the fact that both materials belong to alkaline-earth fluorides with the same crystalline structure, they exhibit different sensitivity for HCI-induced nanostructure. We discuss similarities and differences for the creation of HCI-induced nanohillocks and etch pits in both materials and their dependence on potential and kinetic energy deposition. Furthermore, we compare the results with modifications induced by swift heavy ions (SHI), in order to reach a better understanding of the mechanisms responsible for the creation of nanostructures in ionic fluoride single crystals.

Keywords: highly charged ions; nanostructures; ion-surface interaction; BaF₂; CaF₂

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1. INTRODUCTION

It is widely accepted that the interaction of ions with surfaces plays an important role not only in understanding the associated basic interesting phenomena but also in a wide range of up-to-date surface science technological applications [1, 2]. Swift heavy ions, SHI, were used efficiently for a long time to fabricate surface nanostructures in different materials [3-5]. Due to their high kinetic energy in the range of MeV - GeV, and consequently large ion penetration depth, modification by SHIs occurs not only in the surface but also in the bulk [6,7], which should be avoided in special applications (e.g. thin films nanoelectronics). This drawback was overcome recently by using slow highly charged ions (HCIs) with kinetic energies in the range of eV - keV, which modify only the surface and near-surface regions, leading to the creation of nanostructures of different shapes (hillocks [8-12], pits [13], craters [14,15], caldera-like [16], and nanopores [17]) and sizes in various materials. The formation of these structures is mainly attributed to the deposition of a large amount of potential energy (sum of binding energies of the removed electrons), carried by HCI, in a nanometric volume at the ion impact position. The enhancement in the sensitivity of surface analysis has been successfully used in Time-of-Flight Secondary Ion Mass Spectroscopy (TOF – SIMS) using HCI [18].

In comparison to conducting and semiconducting materials, insulators are more sensitive to structural modifications induced by electronic excitation [19]. Among insulators ionic halide crystals are the most investigated category of materials regarding defects creation by both classical radiation (electrons, x-rays, gamma rays) and ion beams [20]. Motivated by the already existing knowledge, regarding ion-induced defects, as well as the fact that comparison between targets with common and different properties is needed for reaching a better understanding of the mechanisms responsible for the HCI-induced nanostructures, we selected two different alkaline-earth fluorides, namely calcium fluoride (CaF_2) and barium fluoride (BaF_2). Both materials exhibit the same fluorite crystalline structure and are used in advanced

electronic and optoelectronic device applications [21]. The key issue is the lattice match to Si and wide range of III-V semiconductors. Here, we mainly focus on a direct comparison for HCI impact on CaF_2 and BaF_2 by presenting the new results as well as including the outcomes from recent published results trying to explain the rather surprising differences but also the similarities.

2. EXPERIMENTAL

BaF_2 and CaF_2 thin platelets were cleaved along the (111) planes from high-purity single crystal blocks (Korth Kristalle GmbH Kiel, Germany) grown from melt in an inert atmosphere. The samples were irradiated in a UHV chamber (pressure $\sim 1 \times 10^{-8}$ mbar) with $^{129}\text{Xe}^{q+}$ ($q=10-37$) ions extracted from the Dresden-EBIT (electron beam ion trap) at the Ion Beam Center at Helmholtz-Zentrum Dresden-Rossendorf [9]. The irradiation was performed at room temperature and under normal incidence. The kinetic energies of the used ions are determined by the extraction potential, which is typically 4.5 kV. In addition, a two stage-decelerated system was used resulting in a wide range of kinetic energies (45 - 165 keV) for the extracted ions, in particular obtaining ions of the same charge state and different kinetic energies. The beam flux varied between 10^4 - 10^6 ions/s. In addition, an Electron Beam Ion Source (EBIS) was also used for Au^{55+} ions extracted at 2.0 kV. The gold ions were injected into the EBIS from an external liquid metal ion source [22, 23]. The chemical etching of the ion-irradiated BaF_2 samples was done using HNO_3 (1% vol.) solution at room temperature. In the case of CaF_2 HNO_3 (10 % vol.) was used. The irradiated samples were immersed in the etchant for constant etching time and subsequently washed in ethyl alcohol. The drying was performed by using a stream of dry nitrogen and by the insertion in the slots of our home made spin-dryer. A rectangular copper grid was inserted above the sample during irradiation to differentiate between the features created by ion impact and other etch features from natural occurring dislocations.

Scanning force microscopy (SFM) (Nanoscope III, Digital Instruments) was used for topographic investigations of the irradiated BaF₂ and CaF₂ surfaces. The SFM was operated in contact mode using Bruker cantilevers with a force constant of $k = 0.1$ N/m. Nanotec Electronica SL WSxM software (version 4.0 Develop 9.3) was used for image processing of the obtained micrographs [24].

3. RESULTS

Barium fluoride (BaF₂)

After irradiation of freshly cleaved BaF₂(111) surfaces with 4.5 keV* q Xe ^{q^{+}} ($q=11-37$) ions, the measured SFM micrographs did not show any surface topographic changes (even for the highest ion charge states $q = 37$ used). In order to make any ion-induced surface modifications visible, we used the technique of selective chemical etching for the irradiated samples. Figure 1 shows a typical SFM topographic image of BaF₂ irradiated with 85 keV Xe¹⁹⁺ and subsequently etched with HNO₃. The image shows a pattern of irradiated and virgin areas resembling the geometry of the used mask. As observed in Ref. [11], the irradiated areas contain triangular etch pits. By comparing the applied fluence and the etch pit areal density we conclude that each pit is created by a single ion impact. This particular geometrical shape originates from the (111) crystal lattice symmetry of the BaF₂ single crystal. The size of the measured etch pits, obtained at constant etching conditions, increases as a function of potential energy [11]. The fact that we were not able to observe hillocks for impact of 4.5 keV HCl up to $q=38$ comes as a surprise, since in a previous investigation we have observed that the deceleration of Xe³³⁺ to final impact energy of only 0.12 keV/amu can lead to the creation of nanohillocks on the surface of BaF₂ [25]. Using EBIS capable of producing Au⁵⁵⁺ ions with a potential energy of 74 keV at a kinetic energy of 110 keV, we were finally able to create hillock-type nanostructures on the BaF₂ surface, as shown in Fig. 2. The number of observed hillocks corresponds with the applied ion fluence.

Calcium fluoride (CaF₂)

Utilizing the technique of chemical etching for a CaF₂ surface irradiated with HCl of potential energy below and above the threshold needed for nanohillocks formation, as described in [26], reveals the appearance of etch pits of regularly structured 3-faced symmetric triangular depressions, which are similar to those observed for BaF₂. Figure 3 shows a typical example of etch pits created after irradiation with 123 keV Xe²⁸⁺ and chemically etched with HNO₃. Keeping the etching conditions (etching time and etchant concentration) and the ions' kinetic energy ($E_{kin}=40$ keV) constant allows us to study the effect of potential energy on the creation of etch pits. Figure 5 shows that the mean width of the etch pits increases with increasing potential energy. This is taking into consideration that we estimated lateral etching speed of ~ 20 nm/s. Etch pits are, however, not observed below a certain minimum potential energy (threshold around $E_{pot} \sim 4$ keV). As reported in [26] the exact value of this threshold varies with kinetic energy, i.e. HCl of lower kinetic energy requires more potential energy to create etchable damage and vice versa. For example, etch pits were observed after irradiation with 112.5 and 40 keV Xe²⁵⁺ ions, whereas they were absent in case of irradiation with 20 and 11 keV Xe²⁵⁺ ions.

4. DISCUSSIONS

In order to understand the results presented above, in particular the differences for BaF₂ and CaF₂, we first discuss damage production by impact of swift heavy ions (SHIs). The energy deposition into a near surface region during single ion impact is considered as the most important factor for the creation of surface modifications [4]. In the case of SHI, the electronic energy loss $(dE/dx)_e$ is dominating the interaction for SHIs and enables the creation of surface nanostructures (hillocks) and of damage in the bulk (e.g. color centers, defects clusters, aggregates and colloids) in various ionic-fluoride single crystals (LiF [27], CaF₂ [28,29], BaF₂ [30], CaF₂ [28], MgF₂ [31], and LaF₃ [32]). For HCl interaction with solid surfaces the potential energy deposition is the key parameter responsible for the created

surface features. In all crystals, including BaF_2 and CaF_2 , nanohillocks were observed after surpassing a $(dE/dx)_e$ threshold of ~ 5 keV/nm [28,30]. Both SHIs and HCI produce strong electronic excitations in the impact region followed by effective lattice heating via electron-phonon coupling. Within the inelastic thermal spike model the hillock creation is explained by rapid quenching of the molten volume created by localized ion energy deposition [26, 33]. Due to this similarity between SHI and HCI in the observed structure and the creation mechanism, we did not expect to observe large differences in the potential energy threshold for hillock creation in BaF_2 and CaF_2 , especially since we also estimated a similar critical distance for the electron transfer from both surfaces to the HCI (≈ 1.0 nm in case of $q = 33$) [34]. Despite this difference in sensitivity of hillocks creation by HCI in BaF_2 and CaF_2 also a common behaviour was observed, where the potential energy threshold for hillocks creation is shifted down at smaller ion velocities. As an example, for CaF_2 , it is shifted from ~ 14 keV to ~ 11 keV by reducing the extraction voltage from 10 kV to 150 V. In case of BaF_2 the same effect was observed by the formation of hillocks only after the reduction of the extracted voltage from 4.5 kV to 1.5 kV for Xe^{33+} ions. In fact this is similar to the so called velocity effect in the case of SHIs, where at smaller ion velocity the energy density will be higher leading to larger damage cross-section [35].

The importance of the potential energy has also appeared in controlling the size of the created hillocks on CaF_2 surface [26]. Similarly, by taking into consideration that both the nuclear energy loss, $(dE/dx)_n = 3.3$ keV/nm, and electronic energy loss, $(dE/dx)_e = 0.5$ keV/nm, calculated by SRIM 2010 [36], of the 110 keV Au^{55+} are well below the threshold for creating hillocks in BaF_2 , the increase of hillocks size in case of Au^{55+} with respect to 15 keV Xe^{33+} ions can be ascribed to the increase of the potential energy from 21.2 to 73.8 keV. However more systematic experiments are needed for studying the size evolution of hillocks in BaF_2 as a function of potential energy. This observation is similar to the case of SHI, where the hillocks size increases as a function of $(dE/dx)_e$ [28-32].

In case of CaF_2 , simulations for HCI energy transport to the lattice were performed by calculating the average energy density deposited in the target along the ion trajectory as a function of the distance [26, 37]. The results showed that a minimum volume should be heated above the threshold energy density needed for melting, and consequently the formation of a hillock. This volume was not reached in the case of high kinetic energy where the deposited energy is dissipated in a very short time, and the melting process is suppressed. The inability of hillocks formation in BaF_2 , using the same irradiation conditions used for the observed hillocks in CaF_2 , can in principle be interpreted by assuming that the minimum required heated volume and/or threshold energy density needed for melting is larger for BaF_2 than CaF_2 . One reason for this is the larger thermal conductivity of BaF_2 in comparison to CaF_2 , which leads to a significant reduction of the heat localization. In addition, a major difference between the two targets regarding the sensitivity to radiation damage can be ascribed to the large number of electrons for Ba (57) in comparison to Ca (20). This leads to a less “*ionicity*” [38] for BaF_2 and consequently a higher resistivity for HCI-induced damage (hillocks) in comparison to CaF_2 , where the resistance to radiation damage in insulators is governed by the competition between the short-range covalent and long-range ionic forces [39]. Due to the strong ionic binding character, amorphization is not possible in ionic fluorides. This is different from other materials e.g. lanthanide oxides, where the hillocks are produced by ion-induced amorphization [40].

The damage produced in BaF_2 and CaF_2 surfaces by HCI, below the threshold for hillocks formation, could be revealed only after using the technique of selective chemical etching. The potential energy delivered to the surface is enough to create large clusters and/or defects aggregates, which are required for the formation of the observed pyramidal etch pits. Despite the facts that we found a clear potential energy threshold (e.g. $E_p \sim 3$ keV for 40 keV Xe^{q+} ions, $q=10-33$) of etch pits creation in CaF_2 , no threshold was found for BaF_2 down to 49.5 keV Xe^{11+} . The requirement of defects aggregation exist also in case of SHI, where the

etching of ion tracks is only possible after exceeding a minimum $(dE/dx)_c$ needed to create large defects aggregates rather than point defects (e.g. F- and H- centers) [41]. The SHI-induced defects aggregates were observed in BaF_2 and CaF_2 by performing UV-Vis spectroscopy for the irradiated crystals, where the spectra are dominated by broad band attributed to defect aggregation, which is confirmed by bleaching experiments [30, 42]. In addition, it was demonstrated for CaF_2 that F-centers are stable only by irradiation at temperature below 150K, whereas at higher temperatures various aggregate centers are produced [43]. Furthermore, J. Jensen et.al observed nano-clusters along ion tracks by means of transmission electron microscopy (TEM) [44].

It is worthwhile mentioning here that, in addition to thermal spike model, a possible mechanism of defect formation in insulating materials is the change of the atom interaction potential under high density excitation (non-thermal melting) [45,46].

While increasing the kinetic energy of HCl reduces the efficiency for hillocks creation in BaF_2 and CaF_2 , it improves the sensitivity of etch pits creation. This is confirmed by the finding that faster ions needs less potential energy to form etchable damage. This synergistic or at least additive effect between the potential energy and kinetic energy is so far confirmed only for CaF_2 [47]. However this effect was already demonstrated for one of the alkali halides, namely KBr, for the HCl-induced defect stimulated desorption, leading to the creation of surface pits without chemical etching [48]. The damage creation efficiency in the simple cubic lattice of alkali halides, e.g. LiF and KBr, is higher than in BaF_2 and CaF_2 crystals [49], where the separation of electron and hole centers is hindered geometrically (the cube of F^- ions is surrounded by the cube of Ba^{2+} and Ca^{2+} ions, respectively), and consequently the stimulated desorption is weakened.

5. SUMMARY

We were able to create hillocks on the surface of BaF_2 using HCl of much higher potential energy ($E_p=73.2$ keV) than the ones used in previous experiments. These structures are

similar to those observed in CaF_2 . Furthermore, additional pyramidal etch pits were observed in BaF_2 and CaF_2 after irradiation with HCI of potential energies below the threshold for hillocks creation. Unlike hillocks, the kinetic energy of HCI enhances the lattice damage and consequently its etchability. At a constant kinetic energy, the pit size increases as a function of potential energy. While quenching of the nanometric melted volume is responsible the hillocks formation, the creation of defects aggregates is required for the etchability, and thereby the observed triangular etch pits. The similarity between HCI and SHI in producing strong electronic excitations in the impact region was confirmed by observing the same structures. However, despite the fact that for both materials similar $(dE/dx)_e$ threshold for hillocks creation by SHI was observed, CaF_2 showed more sensitivity (lower potential energy threshold) for HCI in comparison to BaF_2 .

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FIGURE CAPTIONS

Fig. 1 SFM image of etch pits on BaF₂ surface irradiated with 85 keV Xe¹⁹⁺ ions. The surface was irradiated through a structured mask and chemically etched using HNO₃.

Fig. 2 SFM image of nanohillocks on BaF₂ surface irradiated with 110 keV Au⁵⁵⁺ ions. line profile along one hillock is shown.

Fig. 3 SFM image of a CaF₂ surface showing etch pits after irradiation with 128 keV Xe²⁸⁺ ions. The sample was irradiated through a mask and subsequently chemically etched using HNO₃. The inset in the lower right corner shows a magnification of the etch pits. Line profile along one of the created etch pits is shown.

Fig. 4 SFM image of CaF₂ surface irradiated with 40 keV Xe^{q+} (q=15, 25 and 33) ions and chemically etched using HNO₃.

Fig. 5 Mean width of etch pits as a function of potential energy for CaF₂ surface irradiated with 40 keV Xe^{Q+} (Q=10- 33) ions.

Fig. 1

Fig. 2

Xe^{+28} (123 keV)

Fig. 3

Fig. 4

Fig. 5

Highlights

The 1st observation of surface nanostructures induced by irradiation of BaF₂ surface with highly charged ions (HCI) at higher potential energy is shown.

Evidence for the significance of the deposited potential energy in the creation of surface hillocks in BaF₂ is confirmed.

The existence of potential energy threshold for the creation of surface etch pits in CaF₂ is shown.

Similarities and differences for the creation of HCI-induced nanohillocks and etch pits in CaF₂ and BaF₂ of the same crystalline structure are discussed.

We compare the results with modifications induced by swift heavy ions.