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Nanometer-scale surface modification of KBr (001) single crystal by Ar ion bombardment

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ABSTRACT

Morphological development on alkali halide crystal surfaces, under ion irradiation, has been investigated by means of Atomic Force Microscopy in UHV conditions. The KBr (001) surface has been exposed to Ar^+ beam with varying incident angles (from 5° to 75° off-normal) and energies (from 1.0 to 5.0 keV). Different kinds of nanostructures, depending on ion incident angle, have been observed on the irradiated surfaces such as nanocavities, or nanorings and nanodots, preferentially for close to normal incidence, and ripples for the oblique incidence. The formation of ripple structures on KBr surfaces as a function of the incidence angle and energy has also been observed. The orientation of the ripples has been found to be incident angle dependent and it is perpendicular, or parallel to the ion beam projection on the irradiated surface for angles of 30° and 75°, respectively. Moreover, it has been observed that the wavelength of the ripples also depends on energy of the projectile ions. The AFM images acquired with atomic resolution reveal well ordered, crystalline structure of the ripples even after bombardment with high fluence. The results have been discussed in terms of electronic and ballistic processes of sputtering and existing theories for surface modifications.

1. Introduction

The fabrication of nanoscale surface structures such as ripples, nanorods, quantum dots and wires have attracted considerable attention due to their technological applications in optical and electronic devices [1]. Yet, the nanostructures obtained in various-assembled ways have a size distribution wider than required by applications, and display random alignment. Lithographic methods are often considered as prime candidates to overcome these shortcomings, but due to their limited resolution they are open for further challenges. Consequently, there is continued high demand for alternative methods that would allow low cost and efficient mass fabrication of nanoscale surface structures. In the light of these technological and scientific driving forces, the recent demonstration of nanostructure development by energetic ion beam has captured the interest of the scientific community as alternative and promising tool for the cost-efficient fabrication of large-area nanostructured surfaces via self-organization rather than lithography techniques [2,3]. Various morphological evolutions of surfaces created by ion bombardment are of both fundamental and technological interest, ranging from metals to insulators [4–9]. One such appealing morphology is the ripple structure formation. The underlying mechanism for this evolution of regular nanometer structure is a self-organization process caused by the interplay and competition between surface roughening by curvature dependent sputtering and smoothening due to surface diffusion process commonly attributed to the Bradley–Harper (B–H) theory [10]. Several researchers extended B–H theory by the inclusion of viscous flow relaxation [6,11,12], ion enhanced or inhibited diffusion [13], preferential sputtering without actual mass transport [14], interlayer diffusion (Ehrlich–Schwoebel barrier influence), crystallographic dependence of the surface and bulk diffusion [15,16], the random or noisy arrival of ions and the statistical variation of the sputtering rate [17], and the effect of recoiling-adatom diffusion induced by ion irradiation [18]. As a result, the exact mechanism for ripple formation remains controversial even after two decades from its first observation. Recently, Makeev, Cuerno and Barabasi (MCB theory) [19] derived a stochastic nonlinear continuum equation to describe the morphological evolution of amorphous surface eroded by ion irradiation, adding nonlinear and fourth-order terms in surface relaxation to address the inadequacies of the B–H theory. The MCB theory introduced an ion-induced smoothing mechanism via preferential sputtering without mass movement on the surface. Being ion induced, the smoothing remains effective when the thermal diffusion is negligible, and therefore makes the wavelength temperature independent at low temperatures. In addition, this theory has many compelling trends including a linear increase of the ripple wavelength with ion energy, and saturation of the ripple amplitude at a longer

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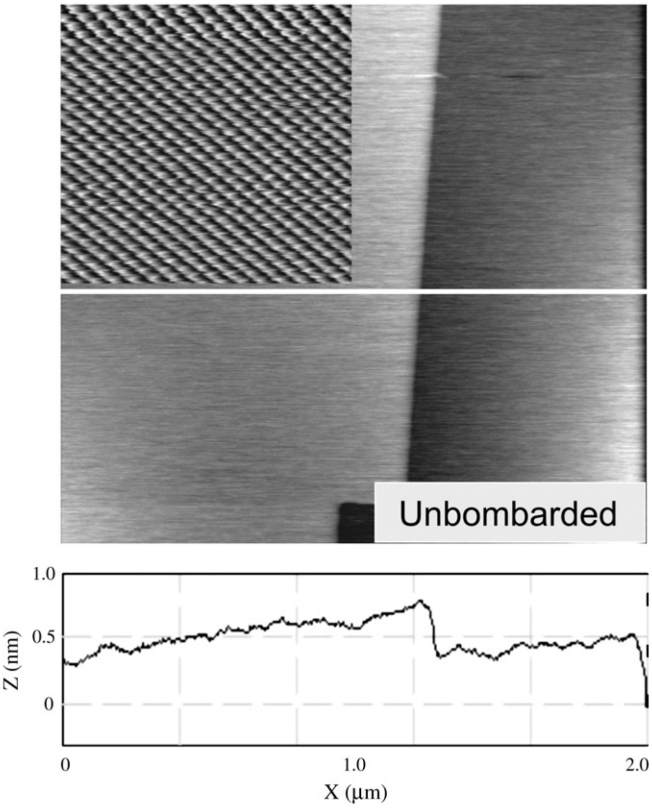

Fig. 1. 2 μm×2 μm AFM image of typical KBr (001) substrate after cleavage in air followed by annealing in UHV at 425 K for 90 min.

time scale of irradiation. The well defined self-organized ripple structures appeared on CaF_2 [8]. It is suggested that the developed nanostructures arise from self-organization of the surface into periodic stress domains after fluorine preferential erosion. Also, the nanometric ripples were created on irradiated LiF surface by 800 eV Ar ion bombardment at an angle 35° and temperature about 80 °C [9].

In this context, alkali halides definitely appear as promising materials as they are transparent in nature acquiring a distinctive color after an appropriate chemical or physical treatment. Although different kind of radiation can be exploited to induce the electronic defects, the use of low energy ions is particularly appealing because it allows getting thin layers with high concentration of active centers at the surface of the crystalline materials. Among the alkali halides, potassium bromide (KBr) is of special interest due to its numerous applications in research and technology.

In this paper, we report on the nanostructure formation on KBr (001) surface by Ar^+ beam irradiation as a function of varying incident angle and energy. It is observed that the orientation of the developed anisotropic nanostructures is incident angle dependent while the wavelength and RMS surface roughness depend on the projectile energy.

2. Experimental

KBr crystals purchased from Kelpin Crystal (Neuhausen, Germany) has been cleaved in air parallel to the (001) cleavage plane. The samples of the dimensions of 5×5 mm^2 were mounted on a molybdenum plate with the help of titanium clamps and fixed on the sample holder which can be resistively heated up to 1000 K. The experiments have been performed in an ultrahigh vacuum system, with the base pressure in the range of low 10^{-10} mbar. The system consists of three main chambers for sample introduction (load-lock), sample preparation, and SPM imaging. The chambers are interconnected with the redistribution chamber allowing for transferring of the samples between the chambers in UHV conditions. The SPM chamber is equipped with Omicron VT-AFM microscope. In the preparation chamber the sample is mounted on the sample manipulator, characterized by linear and rotated motion for experimental parameter adjustments. Prior to ion irradiation the sample is heated for 1 h at 425 K to remove the surface water overlayers. The temperature is measured with the thermocouple fixed to the sample holder. The nanostructuring of the sample surface is performed with rastered Ar^+ focused beam (with the spot diameter about 1 mm). The scanning area of ion beam irradiation exceeds the sample surface area in order to prevent the charging of the KBr surface during ion beam bombardment. The Ar^+ beam current density measured on a molybdenum plate is in the range of 1.0 μA/cm^2 to 5.0 μA/cm^2, depending on the ion energy. The secondary electron emission of the Mo was suppressed by applying the positive bias to the plate. The experiments are performed with different parameters such as the incidence angle of the ion beam chosen in the range of 5°–75° with respect to the surface normal, and beam energy in the range of 1.0–5.0 keV with the fixed ion fluence of about 5×10^{17} ions/cm^2 at room temperature (RT). After the ion irradiation the sample is transferred to the microscope chambers for imaging with UHV contact mode atomic force microscope (C-AFM). The average pattern wavelengths are deduced from AFM images, as well as from their two dimensional (2D) Fourier transformations (FFTs). The imaging is carried at different places on the sample surfaces in order to get better statistics. The RMS surface roughness is measured directly from AFM topography images.

3. Results and discussion

A typical image of KBr(001) surface after cleavage in air followed by annealing in UHV at 425 K for 1 h is shown in Fig. 1. In this figure, there is a clear observation of extended atomic terraces with typical sizes exceeding 1.0 μm separated by monoatomic step. The modification of KBr(001) surfaces by 4 keV Ar ions for a fluence of 5×10^{17} ions/cm^2 as a function of incident angle of 5°, 15°, 20°, 45°, 60° and 75°, respectively is presented in a sequence of images presented in Fig. 2 (a–f). The formation, shape and ordering of patterns depend on process parameters like the ion beam incidence angle. By varying the ion incidence angle, a change in the evolution of patterns on the irradiated surfaces has been observed. Nanocavities and nanodots (marked with circle) are the prominent features for 5° and 15° of incident angle irradiation. Moreover, it is interesting to see that the nanodots are accumulated to get the shape of initial nanorods for 15°of the irradiation. Also, these nanorods seem to be connected to each other. The developed nanostructures have dimension of 50–90 nm in width and 3–8 nm in height.

For the angle of incidence of the impinging ions increased to 30°, there is clear observation of ripple structures which are perpendicular to the projection of the ion beam on irradiated surface. The ripple wavelength is about 100 nm and the ripple height in the range of 10 nm. Further increase in the angle of incident ions leads to disappearance of the surface structures anisotropy (see Fig. 2d with the $\theta=45°$). For the ion incidence angle approaching 75° off-normal, the clear anisotropy pattern (ripple pattern) appears, which is parallel to ion beam projection on the surface. The observed change of ripple orientation is consistent with the B–H theory.

Fig. 3 shows the (RMS) surface roughness (calculated from AFM images) versus the incidence angle. It is clear from the graph that initially for incident angles up to 45°, the RMS surface roughness hardly depends on the angle, whereas for higher incidence angles it increases gradually by a factor of ~2.

In Fig. (4a–e) images of the KBr surface modified by Ar^+ beam for varying energy of 1 keV, 2 keV, 3 keV, 4 keV and 5 keV, respectively are shown. The angle of incidence is kept at 75°off-normal and the fluence