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IONIC CRYSTAL DECOMPOSITION WITH LIGHT* **

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We report on RbI crystal decomposition due to electronic excitations in a vicinity of the top of the crystal band gap by UV photon irradiation. Dynamic force microscopy (DFM) studies reveal that randomly spread rectangular pits of monolayer depth in the topmost layer of the crystal are formed during irradiation. Growth and coalescence of the pits lead to almost 'layer-by-layer' desorption mode. Similarly to electron stimulated desorption, periodic changes of surface topography were found to have a profound effect on the desorption process. Since excited F-centre recombination with alkali atom emission was possible exclusively at low-coordinated sites the desorption yields were found to go hand in hand with the number of low-coordinated sites on the surface. Furthermore, simultaneous irradiation of the crystal by UV photons and visible light within the F-centre absorption band increases average F-centre mobility which has a profound effect on process efficiency. Such processes could be applied in controlled surface nanostructuring.

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1. Introduction

The phenomenon of desorption induced by electronic transitions (DIET) of ionic insulators due to interaction with ionising radiation has been investigated for a long time [1]. Most of the work, however, was focused on details of what is emitted (desorbed) from the surface rather than on the surface modification. It is well established that projectiles (electrons, photons) of energy exceeding the bandgap hitting the ionic crystal create the cascade of excitations, mainly in the form of pairs of conduction band electrons and valence band holes as well as phonons. The excitations undergo the process of trapping, which ultimately leads to creation of Frenkel defects (F- and H-centres) in the bulk [2, 3]. An H-centre is formed by a halogen atom in a interstitial position, whereas an F-centre is formed by a halogen vacancy with an electron bound in. Subsequent evolution of the defects (diffusion and recombination with the surface) leads to surface erosion.

Recent work concerning electron stimulated desorption (ESD) of alkali halides has shown that due to a complicated way of interaction between F-centres and the surface, its topography has a profound effect on the process of desorption [4]. The efficiency of the desorption was found to be dependent on the density of low-coordinated sites (edge and kink atoms) on the surface. Since the surface was eroded in 'layer-by-layer' scheme the number of low-coordinated sites was changing periodically. As the result, desorption yields of both crystal components (alkali and halogen atoms) were found to vary according to changes in the surface topography.

Similar experiments were previously performed for photon induced desorption (PSD) of alkali halides [5]. However, despite the fact that the authors also found 'layer-by-layer' erosion of the crystal surface, they concluded that the topography change did no affect the efficiency of the desorption process, whatsoever.

The experiments described in this paper were aimed at clarifying the discrepancy between the results for ESD and PSD and at explaining the role of F-centres in the process of alkali halide desorption.

2. Experimental

The experiment was carried out in a UHV chamber with a base pressure of the order of 10^{-10} Torr. RbI crystals were cleaved in air and subsequently mounted on a sample holder in the chamber which temperature could be changed between room temperature and 700 K as measured by a thermocouple. Desorption and surface modification was stimulated by UV-light (200–250 nm) generated by a deuterium lamp. The yields of emitted atoms were measured by a quadrupole mass spectrometer for both crystal components, or alternatively, a surface ionisation detector for alkali atom detection. The white light for F-centre band excitation was provided by a 150 W halogen bulb. Dynamic force microscopy (DFM) was used to image irradiated surfaces. In DFM a sharp tip is mounted on a cantilever which is driven in its resonant frequency just over the sample. The surface topography is measured by analysing the change in cantilever frequency due to tip interaction with the surface. PSI VP2 microscope with Nanosurf easyPLL demodulator was used in the experiment. The cantilever resonant frequency was 173 kHz and applied detunings were not larger than 100 Hz.

Rapid annealing of the crystals to 600 K for a period shorter than a minute was found to be an efficient way of removing surface modification introduced by UV-light. That procedure was applied routinely before every irradiation in order to assure the same starting experimental conditions.

3. Results and discussion

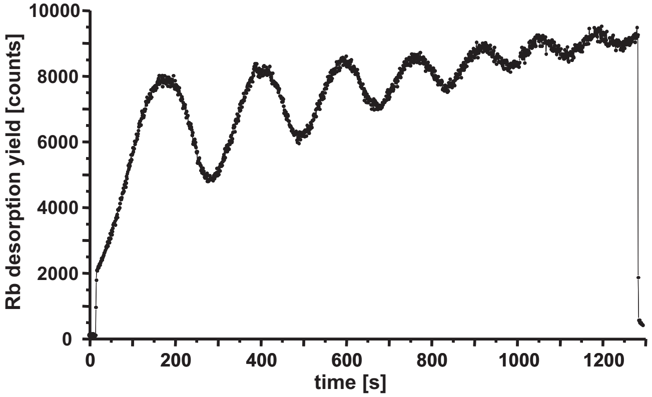

Fig. 1. Rb desorption yield from the RbI crystal due to UV irradiation.

In Fig. 1 the oscillatory dependence of Rb desorption yield emitted from a RbI crystal on the time of UV irradiation is presented. Similarly to ESD experiments reported earlier, the oscillatory dependence is dumped and disappears after a certain number of cycles. Every cycle of efficiency of the process corresponds to removal of a single monolayer and the 'layer-by-layer' erosion process is observed as checked by DFM. However, there is some damage in the deeper layer created before the upper one is completely removed. Therefore, after several cycles the well defined periodicity in the surface topography is lost and as the result, the changes in desorption efficiency are no longer observed [6].

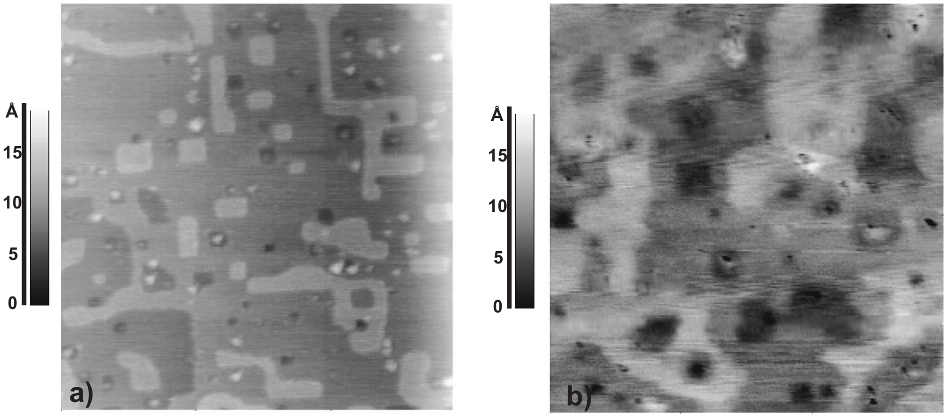

Fig. 2. 300×300 nm^2 DFM images of RbI crystal irradiated with UV-light; (a) irradiation was stopped at the maximum of the first cycle; (b) irradiation was stopped at the minimum of the first cycle.

The surface topography altered by UV-light is presented in Fig. 2. Freshly cleaved crystals have large (up to 1×1 μm^2) terraces. Under irradiation rectangular pits of monolayer depth with edges oriented along the main crystallographic directions are created on the surface. During surface erosion they grow and coalesce leading to 'layer-by-layer' desorption. In Fig. 2(a) the topography of the crystal which irradiation was stopped in the first maximum of the desorption efficiency is presented. The islands remained from the topmost layer can be observed. In contrast, the surface of the crystal irradiated by the dose required to remove a single monolayer is presented in Fig. 2(b). The main features observed are pits created in the second layer, whereas no islands can be seen. The most important difference between the topographies in these two stages of desorption is a much higher density of steps present on the surface when the desorption efficiency is maximal in comparison to the surface exhibiting low efficiency.

The presence of visible light within the spectral range corresponding to F-centre band absorption was found to have a very strong effect on the desorption process. In Fig. 3 the yield of Rb atoms emitted from the RbI surface due to UV-photon irradiation is presented. After removal of 1.5 monolayer (*i.e.* in the maximum of the second cycle of oscillations of the yield) the F-band light was turned on. As the result, an instant desorption signal increase is recorded, as well as decrease of the period of oscillatory dependence. Both those effects occur as a result of considerable increase of the desorption yield.

Our previous work on ESD of ionic surfaces demonstrated that such processes are controlled by dynamics of Frenkel defects [7]. Surface modification

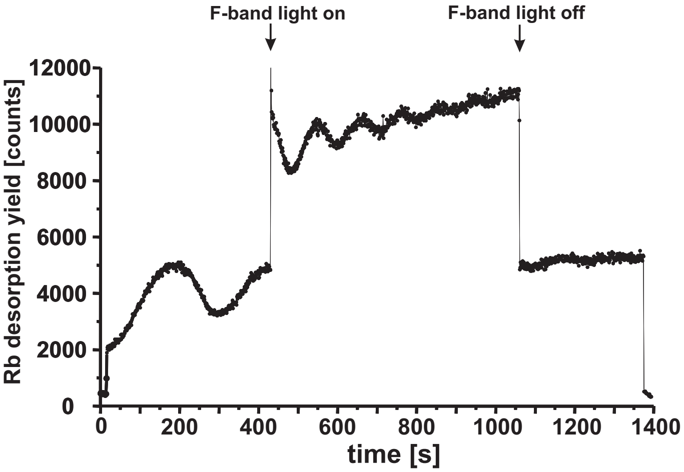

Fig. 3. Dependence of Rb desorption signal on time of UV-photon irradiation for RbI (001) surface and simultaneous co-excitation by F-band light. The moments of turning on and off F-band light are shown by arrows.

is exclusively due to surface recombination of F-centres since H-centres are essentially interstitials and their recombination leaves the surface structure intact. Moreover, ground state F-centres are not only immobile in the crystal but also have insufficient energy to induce emission of alkali atoms [8]. It is only $2p$ excited state F-centre which can diffuse efficiently [9] and if it makes for a low-coordinated site (a kink, an edge) it can induce emission of an alkali atom. Emission from the perfect surface, however, is virtually impossible due to deficiency of energy, therefore an excited F-centre, unless it gets to a low-coordinated site, is reflected back to the bulk and it deexcites there to its ground-state, immobile form. F- and H-centres can recombine in mutual recombinations. Therefore, the population of accumulated ground-state F-centres form traps for H-centres and alternate the desorption yield of halogen atoms. Since the density of low-coordinated sites is changing periodically during irradiation (reaching its maximum if approximately a half of the layer is still present on the surface and its minimum if approximately a complete layer is removed) so does the probability of F-centre recombination on a low-coordinated site and subsequent alkali atom desorption.

The profound effect of co-excitation by F-band, visible light strongly supports described mechanism in case of PSD, as well. The light converts a certain part of stored F-centres into excited form enhancing their effective diffusion rate. Therefore, created defect can faster reach the sites from where they can induce dosorption and as the result, an instant increase of desorption yield is observed.

4. Conclusions

UV-photon irradiation of the ionic surfaces leads to their erosion in 'layer-by-layer' mode by creation, growth and coalescence of rectangular pits in the topmost layer of the crystal. In contrast to previous reports, however, we found that the periodically varying surface topography had a profound effect on the desorption process itself. The desorption yields of atoms emitted from the surface were found to exhibit oscillatory dependence on the dose with a period corresponding to removal of a single monolayer. Furthermore, the desorption was strongly enhanced by co-excitation by visible light of wavelength within the F-centre absorption band.

All these phenomena can be understood in terms of the model proposed recently for electron stimulated desorption. Kinetics of F-centres and periodically varying density of low-coordinated sites on the surface are the key factors in understanding the process.

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