Rectangular Pits Created on KBr (001) Surface by Electron Stimulated Desorption and Imaged by Au Decoration and C Replication*

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The surface morphology of KBr (001) irradiated by electrons is observed by first decorating the surface with Au particles and then replicating it with C foils. For the electron irradiation and the subsequent decoration, we integrated an electron-beam gun and a vacuum evaporator. The sample surface was irradiated by a 1.5 keV electron beam; small Au particles were then evaporated onto the surface. Although the decorated sample was prepared in an ultra-high vacuum condition, the C foil was evaporated in a separate high vacuum evaporator. To avoid deliquescence of the sample surface, contact between the sample and the ambient air was minimized by transporting the sample between the two vacuum chambers in a N2-gas-filled enclosure. Imaging the surface with a transmission electron microscope revealed many rectangular monolayer pits. The mean area of the pits and the associated standard deviation are presented versus temperature; the mean pit area increases with temperature.

1. Introduction

Over the last decade, we have studied electron-stimulated desorption (ESD) from surfaces of alkali-halide crystals, and now in particular, temperature dependence of their morphology. Because these crystal surfaces are easy to damage by electron irradiation, secondary-electron microscopes (SEMs) cannot be used to image them. Thus, to image such surfaces, we inspect scattered ions at glancing angles from the surface with the aid of a computer simulation or imaged the surfaces in air by atomic force microscopy (AFM). The ion-scattering experiments with computer simulation provided evidence of layer-by-layer ESD from the KBr surface. However, the method is not optimum for analyzing surface morphology because the surface morphology must be assumed in the simulation. In addition, AFM imaging in air does not produce an accurate image of the surface because some alkali-halide-crystal surface morphologies are easily modified by contact with air molecules. At present, SEMs or surface-probe microscopes (SPMs) are being developed to image surfaces. As a substitute for SPM imaging in ultra-high vacuum (UHV) for studying the morphological evolution of surfaces during irradiation by electrons, we propose herein a replica method whereby the sample surface is decorated with small Au particles in UHV and then replicated by a C foil.

The replica method is a simple technique developed for imaging surfaces of organic or inorganic solids with a transmission electron microscope (TEM). The surface is replicated by imprinting it onto a film (e.g., a carbon foil), which is then imaged with a TEM. The replica method has also been widely used to image surfaces and is a simple technique for surface imaging when SEM or SPM in UHV is not possible.

The first use of this method dates back to the 1940s, and it has since evolved significantly because of the use of the pre-shadowed C replica method that uses metal atoms such as Au, Pt or Pd. In the early days, the resolution ranged from 2.5 to 10 nm in the surface plane. To observe step structures on cleaved surfaces of alkali-halide crystals, the C replica method was introduced around 1960. The resolution in the surface plane was 3 nm and 0.3-nm-high monolayer steps were discerned. In these pioneering works, the term “preshadow process” was not used; instead, the procedure was called “decoration” of the alkali-halide surfaces because the metal atoms diffuse over the surface and create nanoparticles along the lines of the surface steps. After these works, in the 1990s, Höche et al. used decoration in addition to the replica method to show that rectangular pits grow on NaCl (001) surfaces when these surfaces are irradiated by photons; these experiments provided evidence of layer-by-layer desorption using helium-atom-scattering study. After this study, such pits were also observed by AFM measurements in UHV, which revealed one or several kinks in their arrangements.

Recently, we studied Au nanoparticles grown on the surface of alkali-halide crystals previously irradiated by electrons. Based on the measured size distribution of the Au particles, we concluded that the experimental conditions could be tuned to preferentially grow particles with diameters less than a few nanometers. Thus, we expect rectangular monolayer pits larger than several nanometers grown on the surface by ESD to be decorated by Au nanoparticles, thereby allowing them to be imaged by the replica method. In this paper, we present recent results from KBr (001) surfaces irradiated by 1.5 keV electrons in UHV and then imaged by Au decoration and C-foil replication.

2. Experimental procedure

Previous imaging of NaCl surfaces by other groups
used C replication of Au–particle-decorated samples and showed that the resolution was sufficient to detect monolayer steps\textsuperscript{6,7,9}. Our previous imaging of spiral monolayer steps grown on thermally desorbed KBr surfaces shows that nearly identical resolution is obtained with the method we used\textsuperscript{10}. Although we found evidence of layer-by-layer ESD\textsuperscript{11}, we have not yet obtained clear images of rectangular monolayer pits created on the surface after treatment by ESD\textsuperscript{12}. These monolayer pits are believed to be unstable compared with spiral steps\textsuperscript{13}. In this experiment, the pits were created and preserved on the surface throughout the procedure prior to depositing the carbon foil onto the surface in a high-vacuum (HV) evaporator.

KBr crystals cleaved in air along the (100) face were mounted on a heater and placed into a UHV chamber with a base pressure of $1 \times 10^{-7}$ Pa. Although the pressure could be measured by using an ionization gauge (IG), it was switched off to avoid irradiating the sample by photons from the IG filament. Instead, the pressure was regularly monitored based on the ion-pump current. To clean the surface, the sample was heated to 425 K and maintained at this temperature for 24 h (simultaneously baking the UHV chamber), following which it was heated to 525 K and maintained at this temperature for 1 h. Two $4 \times 5 \times 5$ mm$^3$ samples were fixed in two holes in a Cu block on a sample heater that heated five faces of the block, except the single face on which the sample was held. This arrangement ensured a uniform sample temperature. The surface temperature of the sample was monitored by using a thermocouple thermally connected to the Cu block.

After cleaning the sample surface and adjusting the sample temperature, the sample surface was irradiated by 1.5 keV electrons from an electron gun while evaporating a small quantity of Au (producing a mean deposition thickness on the sample surface of $\leq 1$ nm). A scheme of the setup is shown in Fig. 1(a). The sample holder in the UHV chamber held two samples, as shown in Fig. 1(a), and the chamber itself was connected with another device. A shutter consisting of a Faraday cup (FC) was positioned in front of the sample to control exposure to the electron irradiation and Au evaporation. Figure 1(b) shows details of the evaporator, electron gun, and beam-scan mechanism. The electron gun had a V-shaped W filament packed in a Wehnelt cathode supported by electrodes on an insulator that served as electrostatic lenses. At the entrance of the UHV chamber, the electron beam was collimated by a $2 \times 10$ mm$^2$ slit and horizontally scanned (line scan) by a 20 Hz magnetic field to produce uniform irradiation. The electron-beam current density impinging on the sample surface was 1.3 nA/mm$^2$. The electron-beam current was monitored by using the FC with an electron suppressor ($-50$ V), as
shown in Fig. 1(a). The FC was inserted in front of the sample into the path of the electron beam by a 130° rotation and the electron suppressor fixed in front of the FC consisted of a fluorescent screen that allowed us to verify the position of the scanning electron beam.

Figure 1(b) shows the W spiral basket containing the Au for evaporation. The basket was moved out of the path of the electron beam during sample irradiation and was moved by bellows into the path of the electron beam for evaporation of the Au atoms. To prevent Au from depositing onto the electron gun, it was shielded by a stainless-steel plate during Au evaporation. With respect to the KBr–surface, the angles of incidence of the electron beam and the evaporated Au particles were 50°, as shown in Fig. 1(a).

After Au evaporation, the sample was cooled in UHV for 12 h to room temperature, with the IG maintained off. After cooling, pure N₂ gas was introduced into the UHV chamber. Simultaneously, the enclosure shown in Fig. 1(c) was filled with N₂ gas. The sample holder and the sample were removed from the chamber and immediately inserted into the N₂-filled enclosure, following which the ensemble was transferred to a HV evaporator (JEE-5B; JEOL) in an adjoining room. Figure 1(c) shows the sample holder with the fluorescent screen in front of the FC. The sample was removed from the sample holder by opening a 70×120 mm² window in the enclosure and set on a glass in the HV evaporator, where a C foil was evaporated onto it at room temperature. The pressure of the evaporator was 3×10⁻⁴ Pa, as measured by a Penning gauge instead of the IG. A C foil several tens of nanometers thick was evaporated onto the sample by electrically heating C rods.

Although the sample transport process took 20 min, the sample was in contact with the ambient air outside the enclosure for at most 3 min. Based on the work by Bassett⁷), we expected that two evaporations done without opening the vacuum system was the most suitable procedure. However, C foils may be evaporated in vacuum systems by using other sample-treatment procedures. For example, sample transport between vacuum systems via remote-controlled manipulators is well developed and may be used. However, because a rigid sample holder was used in this work to control the temperature of the sample surface, we concluded that the present transport process was the best approach to maximally suppress deliquescence in the surface layer. The procedure was simple but effective, considering the fact that the monolayer steps (e.g., the spiral steps on the surface of alkali halides) can survive much longer than a few minutes in dry air²,¹²,¹⁴).

The C foil was removed from the substrate by immersing it in distilled water and the floating foil was scooped up by an observation mesh for imaging by TEM (JEM-2100; JEOL).

3. Results and discussion

Figure 2 shows typical TEM images of the C replicas of irradiated and subsequently decorated KBr surfaces. The temperature and electron-irradiation fluence are the relevant parameters. Figure 2(a) shows the rectangular pits and the kinks³), which explains the lack of perfect rectangles. The pit shown in Fig. 2(b) shows a clipped rectangle. Note that some samples exhibit no rectangles; for example, images such as the circle shown in Fig. 2(c) or irregular shapes having only two sides [see Fig. 2(d)] may result from poor C–foil replication, wherein the entire pit area is not replicated. Overlapping rectangular

![Fig. 2 Typical TEM images of C replicas. (a) Pits obtained at 473 K and with a total electron-beam irradiation of 0.20×10¹⁴ cm⁻². (b) Expanded view of rectangular pits from panel (a). (c) Expanded view of circular pits from panel (a). (d) Irregular shapes (missing two sides) obtained at 431 K, 0.80×10¹⁴ cm⁻² (1.5 ML desorption). (e) Overlapping pits obtained at 523 K, 0.17×10¹⁴ cm⁻². The thin straight lines in panels (d) and (e) are to guide the eyes.](image-url)
pits also appear, as shown in Fig. 2(e). Although we have observed yet many irregular pits shown by the examples, this experiment has also provided many images of rectangular monolayer pits for various surface temperatures (see Fig. 3).

The imaging of the rectangular pits is probably because of the care taken to create and preserve the pits before C evaporation. In other words, in addition to suitably tuning the electron-irradiation fluence and the amount of Au for decoration, the introduction of N₂ into the UHV chamber and the transport of the sample to the HV chamber in a N₂-filled enclosure may be important. Although we are not sure what mechanism is at the origin of the circular pits seen in Fig. 2(c), it may result from the effect of deliquescence on originally rectangular pits. Considering that no rectangular pits are detected before the decoration procedure, the Au nanoparticles that fix at the surface steps are expected to move with the surface atoms upon deliquescence. Other irregular pits (e.g., pits missing two sides; see Fig. 2(d)) might be related to overlapping pits, as implied in Fig. 2(e). Although overlapping portions of pits do not produce straight lines, other straight lines produced by non-overlapping portions still remain.

Since it would be recognized that the temperature dependence of the morphology is an important information for understanding ESD of alkali-halide crystals, it must be confirmed that the size of the detected rectangles represents the actual area of the rectangular pits formed at fixed temperature in UHV. The area of the rectangles was measured and is plotted as a function of temperature in Fig. 4(a). The points represent the mean area of the 20–50 nearly rectangular shapes and the vertical bars give the standard deviation in the area. Figure 4(a) shows the results for two different irradiation fluences. The open symbols correspond to desorption of about 0.5 monolayer (ML) of the surface atoms while the closed symbols correspond to desorption of about 1.5 ML of the surface atoms. In both cases, the mean area increases rapidly with temperature above ~350 K. Although the temperature range is small, these results are fairly consistent with those obtained from irradiating a NaCl (001) surface by photons¹⁰. These data were measured at an irradiation corresponding to a desorption from the sample surface inferior to 0.5 ML. The mean area and standard deviation from these results are also shown in Fig. 4(b).

The area as a function of irradiation fluence shows a large mean area at 1.5 ML desorption and 473 K compared with that obtained at 0.5 ML desorption. However, because there are rectangular pits difficult to be identified and the standard deviations are rather large, we cannot determine the physics behind this result. One possible mechanism is that the pits may be influenced by the removal of a second atomic layer because the surface flatness is not completely recovered after removal of the first layer.

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**Fig. 3**  Effect of temperature on TEM images of C replicas. (a) Pits obtained at 493 K and with a total electron-beam irradiation of $0.18 \times 10^{14}$ cm$^{-2}$. (b) Pits obtained at 503 K, $0.18 \times 10^{14}$ cm$^{-2}$. (c) Pits obtained at 523 K, $0.17 \times 10^{14}$ cm$^{-2}$. The thin straight lines are to guide the eyes.

**Fig. 4**  Mean area of rectangular pits as a function of temperature. Bars give the association standard deviation. (a) Present results for ESD of KBr (001). The open symbols correspond to the mean pit area for a fluence giving about 0.5 ML desorption of surface atoms and the closed symbols correspond to the mean pit area for a fluence giving about 1.5 ML desorption of surface atoms. (b) Photon-surface-desorption from NaCl (001) surface; summary of data from Höche et al¹⁰.
4. Conclusion

We imaged surfaces of KBr (001) irradiated by 1.5 keV electrons by decorating the surface with Au particles and then using the C replica method. For this experiment, an electron gun and vacuum evaporator were introduced into the UHV sample chamber. The C replication foil was evaporated onto the sample surface in a HV evaporator. The sample was transported from the UHV chamber to the HV evaporator in a N$_2$-gas-filled enclosure. By minimizing the time during which the sample was in contact with ambient air, we obtained TEM images of many rectangular pits on the sample surface. The mean area of the pits increases to large values upon increasing the sample surface temperature in the UHV chamber, which is consistent with the results of photon stimulated desorption from NaCl.

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References

1) Y. Fukazawa, K. Kihara, K. Iwamoto and Y. Susuki: J. Vac. Soc. Jpn., 56 (2013) 428.
2) Y. Matsumoto, Y. Fukazawa and Y. Susuki: J. Vac. Soc. Jpn., 52 (2009) 411 [in Japanese].
3) M. Szymonski, J. Koledziej, B. Such, P. Piatkowski, P. Struski, P. Czuba and F. Krok: Progress in Surf. Sci., 67 (2001) 123.
4) H. Mahl: Z. tech. Physik., 21 (1940) 17 [in Germany].
5) R. C. Williams and R. W. G. Wyckoff: J. Appl. Phys., 15 (1944) 712.
6) A. Fukami: J. Electron Microscopy, 6 (1958) 18.
7) G. A. Basset: Phil. Mag., 3 (1958) 1042.
8) H. Bethge: Phys. Stat. Sol., 2 (1962) 3 and 775 [in Germany].
9) H. Bethge: Surf. Sci., 3 (1964) 33.
10) H. Höche, J. P. Toennies and R. Vollmer: Phys. Rev. B, 50 (1994) 679.
11) Y. Fukazawa, S. Shibata, M. Ikemoto, H. Kawatoko and Y. Susuki: J. Vac. Soc. Jpn., 57 (2014) 147.
12) R. M. Wilson and R. T. Williams: Nucl. Instrum. Meth. B, 101 (1995) 122.
13) R. M. Wilson, W. E. Pendleton and R. T. Williams: Rad. Eff. Def. In solids, 128 (1994) 79.
14) K. Miura and Y. Shukuya: Jpn. J. Appl. Phys., 32 (1993) 4752.