Direct observation of X-ray induced atomic motion using SR-based STM

The interaction of X-ray photons with materials plays an essential role in various fields such as imaging, diffraction and spectroscopy. As a higher throughput of measurements requires a higher photon density of synchrotron radiation (SR), the strong irradiation effects become an important issue either for applications to the fabrication process [1] or for radiation damage that limits the structural studies [2]. Although the X-ray induced reaction or damage on materials by SR has long been observed under various conditions, the direct observation of the atomic motion induced by hard X-rays in ultrahigh vacuum (UHV) has not yet been reported at an atomic scale, about which we report here the results obtained by scanning tunneling microscopy (STM). Also, we visualized successfully the tracks of the atomic motion [3].

To observe precisely the X-ray induced atomic motion, it is essential to compare the atomic structure on the same surface area before and after X-ray irradiation. The *in situ* SR-based STM (SR-STM) system has already been installed for our past research studies dedicated to a chemical analysis with nanometer resolution assisted by element-selective core-hole excitation using SR (Fig. 1) [4]. To overcome the small efficiency of core excitation by hard X-rays, we installed the STM system at **BL19LXU** having a 27 m long undulator and focused the beam two-dimensionally to increase the photon density. To avoid an excessive heat load by X-rays, small incident beams (ϕ10 μm) were used and controlled with an accuracy of ~1 μm under the total reflection condition that can effectively reduce the X-ray penetration depth.

The Ge(111)c-(2×8) surface is a standard well-defined stable clean surface and BL19LXU can effectively excite the Ge atoms. During X-ray irradiation, the STM tip was under the tunnel-off condition and the sample bias (Vs) was kept at 0 V. Also, the STM observations were performed only under the beam-off condition. Thus, the atomic motion was not produced by the electric field around the STM tip under X-ray irradiation, but solely by X-ray irradiation.

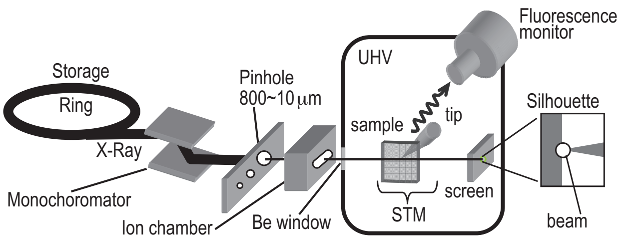

Fig. 1. Schematic view of the SR-STM system.

Figure 2 shows the STM images in the same area on a Ge(111) clean surface before (upper) and after (lower) X-ray irradiation for 3 min (11.119 KeV > Ge *K*-absorption edge, photon density = 2×10^{15} photons/s/mm^2). The low-magnification images (left) show that the X-ray induced atomic motion rate is so low that structural changes are hardly detectable, even by other surface analysis techniques, such as diffraction analysis giving average information. However, the magnified images (right) revealed a clear change in the atomic structures, as indicated by the open circles. The atomic motions are found to occur mainly around defects on the surface, differently from a close-packed 2×8 structure. The origin of the atomic motion is then suggested to be an effect of surface diffusion (the number of atoms does not change after X-ray irradiation), which is different from desorption caused by core excitation [1].

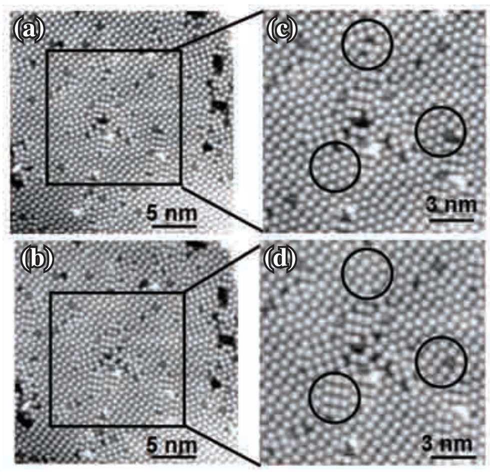

Fig. 2. STM images with different scales within the same area on a Ge(111) clean surface obtained before (**a**, **c**) and after (**b**, **d**) X-ray irradiation (3 min). Open circles indicate the area in which the Ge atomic shift is observed. Vs= 2.0 V and tunneling current It= 0.3 nA.

Next, we developed a technique to recognize atomic motions directly to comprehend their behavior. By merging the STM images obtained before and after X-ray irradiation, the atomic motion track could be newly presented as several continuous lines (Fig. 3), whereas other stable atoms are shown as spheres. The appeared atomic track is the direct evidence and visualized information of the atomic diffusion at an atomic scale.

Using the visualized atomic track, we compared quantitatively dependences of the atomic motion on some parameters to consider the origin of the atomic motion that can be attributed to quantum effect (core-hole excitation) or the thermal effect [1]. For core excitation, in Fig. 3 showing the number of atoms (~1000), the total number of core-hole events is estimated to be ~40 for 3 min of irradiation in one STM image. The observed atomic motion rate (~100 atoms in total track length), for which one core-hole event corresponds to a 2.5 atomic motion, appears very high. The next possibility is then the atomic motion induced by electronic transitions stimulated by impacts of photo-, Auger and secondary electrons generated multiply by one core-excitation event.

For the thermal effect, in which the core excitation is included as the average absorption effect for mass volume, the local increase in temperature (ΔT) on the surface was calculated from the incident heat flux, the specific heat of the sample, and the thermal diffusion rate. The photon density dependence (from 1.2×10^{15} to 4.8×10^{15} photons/s/mm^2 for 11.119 KeV) of the atomic motion rate was found as the moving atomic number increased from 30 to 70 per STM image, where ΔT was estimated to be 23 and 92 K, respectively. (The incident energy dependence of the atomic motion rate was not apparently found owing to a relatively low photon density.) It is worth comparing our results with previous conventional thermal STM observations on the same surface [5], where the atomic motion was found to occur in the form of domain (Fig. 4) and begin at ~220°C. However, our results show the atomic track having a local chain distribution. This locality in diffusion may be attributed to the anisotropy of the surface structure, and probably the origin of atomic motion, to core excitation. In fact, considering ΔT (92 K from RT), our atomic motion rate appears very high in comparison with the past report. Many aspects on the atomic motion still require to be discussed in detail.

The radiation damage by Coulomb explosion has long been an important issue in XFEL. In our experiments, even at a much lower photon density

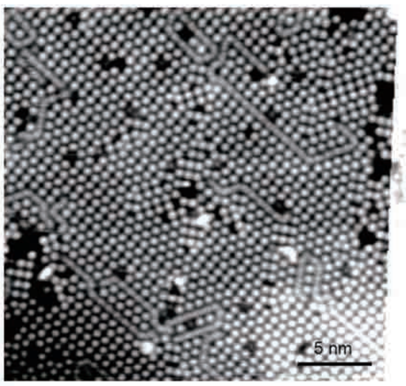

Fig. 3. Merging the STM images before (Fig. 2(**a**)) and after (Fig. 2(**b**)) X-ray irradiation. The atomic motion tracks can be newly presented.

(12~48 photons/s/Å^2 at 11.119 keV) than the conventional barrier derived from the dynamics of damage analyses [2], the surface structure was found to start to break, which has never been observed directly for hard X-rays in UHV at RT. The new feature is probably marginal for the brilliance from the long undulator with focusing. Actually, the photon density lower than 1×10^{14} photons/s/mm^2 scarcely induced the atomic motion. Our observation of the damage barrier has potential importance as an indicator for a damage threshold in the near future for analyzing low-dimensional materials. On the other hand, the dense X-rays are also suggested to have new applications, such as direct X-ray lithography. Also, our results show a new application of the *in situ* SR-STM system. Our method for observing the atomic track will serve to provide new information not only for the effects of the radiation process on various optical devices in new X-ray generators, such as XFEL, but also for basic science by observing photon-matter interactions.

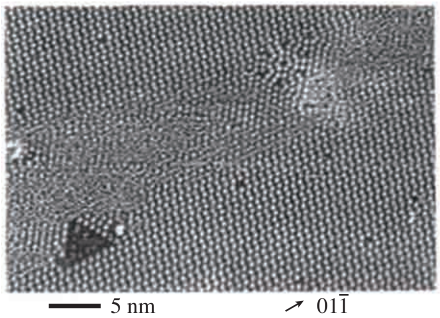

Fig. 4. STM image of the Ge(111) clean surface obtained at 235°C. A band of disordered surface area, located at a domain boundary, extends through the center of the image [5].

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