トピックス

I. X-Ray Structural Study of Ge(001):Te 1×1 Performed at the Advanced Photon Source. II. Current Status of the Surface-Interface Structure Beamline at SPring-8

Osami SAKATA

*Japan Synchrotron Radiation Research Institute**

Abstract

This article is composed of two parts. In the first half, we describe a study that we performed at 5ID–C of the Dupont-Northwestern University-Dow (DND) CAT in the Advanced Photon Source, the Argonne National Laboratory for 1998 to 2000. A surface structure of Ge(001): Te 1×1 was determined by least-squares fits of x-ray scattered intensities with calculations based on some surface atomic structural models. The fitted structural model has a characteristic that a direction of a Ge–Ge dimer bond on the first Ge atomic layer is perpendicular to a Te missing row. It was distinct from those based on first-principles total energy calculations. In the second half, we introduce up-to-the-minute status of BL13XU for surface-interface structural studies at SPring-8. Scientific research goals we desire are mentioned as well.

1. A structure of a Ge(100):Te 1×1 surface

Heteroepitaxial crystal growth is classified into three growth modes: Frank-Van der Merwe (FM; 2D) growth[1], Volmer-Weber (VW; 3D) growth[2], and Stranski-Krastanov (SK; 2D followed by 3D) growth[3]. Whether a film undergoes FM, VW, or SK growth depends on the balance between surface, interface, and film free energies. Copel *et al.*[4] proposed an elegant method to amend the kinetics at a growth surface by using surface-active species (surfactants). They demonstrated that island formation and interdiffusion were avoided with a surfactant. Such surface mediated epitaxy can specifically control the kinetics at the growth surface.

Te has proven to be an effective surfactant in forming a sharp interface in Ge/Si heteroepitaxial structures grown by molecular beam epitaxy.[5] To understand this growth mechanism on an atomic scale, we aimed at determining structural parameters, such as adsorption sites and bondlengths for a Ge(100): Te 1×1 surface.

There were two research articles related to the surface structures as far as we knew. One was an experimental study using low energy electron diffraction (LEED) and x-ray standing waves.[6] The researchers' finding was that Te atoms are located at a well defined position in the [004] direction but has a spread in its surface plane. From these results, the researchers expected Te lateral displacements from the bridge-sites in the 5×1 Te missing row model and dimerized Ge surface atoms (**Fig. 1**). The other article was about a study on the surface structure based on first-principles total energy calculations.[7] Two structural models were therein proposed which are the 2×1 Te zigzag model (**Fig. 2**) and the 5×2 missing row model. The energy difference between the two models was not shown due to difficulties in comparing the energies for the two models which used different size clusters. It was noted that the orientation of Ge dimers in the 5×2 model differed by angle 90 degrees from those in the 5×1 model.

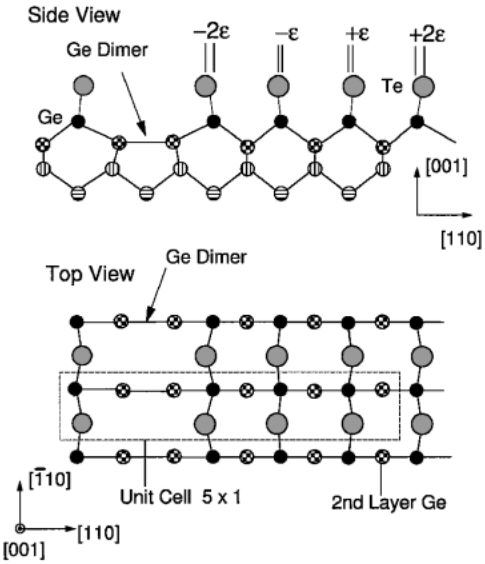

Figure 1. 5×1 Te missing-row model for the Ge(001): Te 1×1 surface.

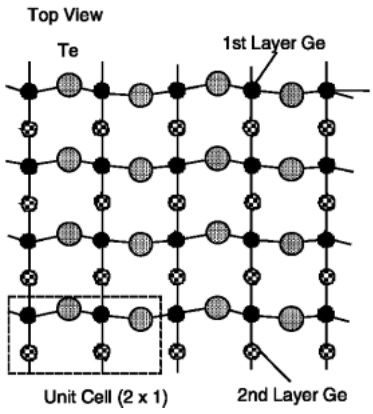

Figure 2. 2×1 Te zigzag model for the Ge(001): Te 1×1 surface.

* Kouto 1-1-1, Mikazuki, Sayo, Hyogo 679-5198
Tel: 0791-58-2750 Fax: 0791-58-0830 E-mail: o-sakata@spring8.or.jp

Our question was which structural model between the 5×1, the 5×2, and the zigzag one was most favorable from an x-ray scattering point of view. To answer the question, we measured x-ray scattered intensities of crystal truncation rods (CTR's) and compared the intensities with those calculated from the above-mentioned structural models (, which could be a sort of modified bridge-site ones).

The experiments were carried out in an ultrahigh vacuum (UHV) surface chamber at the 5ID–C station on the DND undulator beamline. Te was deposited at a substrate temperature of 540 K on a clean Ge(001) surface followed by annealing to 690 K. After Te deposition we observed a 1×1 LEED pattern with streaks between the 00 and 01 spots **(Fig. 3)**. This indicates that the surface had 1×1 long-range order but was locally disordered.

We measured x-ray scattered intensities along the 1 0 L, 1 1 L, and 3 0 L CTR's. (The reflection indices are here expressed using a tetragonal unit cell with a base defined by the 1×1 surface unit cell of Ge(001).) The results of analyses of the data were compared to simulations corresponding to the bridge, top, anti-bridge, and hollow site models. Te at the bridge site was in best agreement. More complex surface structural models based on modifications of Te at the bridge site were then compared to the data with the missing-row model being in better agreement than the zigzag model **(Fig. 4)**. The missing-row model could result from an in-plane strain relief mechanism. Finally, the CTR data were used to refine the structural parameters of the 5×1 missing row model for determining surface relaxation. In this structural model, the displacement of the Te atomic layer along the Z direction from the bulk Ge position is +0.01(nm), where + sign stands for atoms shifted outwards. The first through fourth Ge atomic layers are shifted vertically by 0.002, −0.003, −0.004 and −0.001(nm), respectively, from the bulk Ge positions. For further information, you could refer to our original article[8].

2. The latest information on BL13XU

The design of BL13XU was written by Goto *et al.*[9]; a previous status of BL13XU was described a year ago.[10] Stages for the beamline monochromator have been upgraded since then for making a direct beam intensity more stable. In addition, preliminarily experimental results with a UHV system have been obtained. Let me first refresh your memory as to the outline of BL13XU and second introduce up-to-the-minute information. We are hoping that the description below would be helpful like a guided-tour brochure when you plan to utilize the beamline facilities.

The light source is the standard SPring-8 in-vacuum undulator (ID)[11] with a 32 mm period and its number of 140. The gap of the ID is opened up to 50 mm and closed down to 9.6 mm. The fundamental energy range available is correspondingly from 18.9 to 5.5 keV. **Figure 5** depicts the beamline lay-

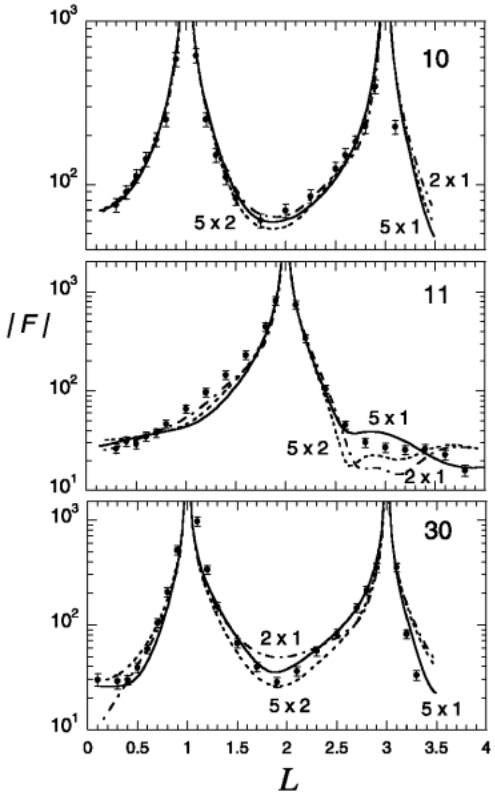

Figure 4. Crystal structure factors measured along the 1 0 L, 1 1 L, and 3 0 L for the Ge(001): Te 1×1 surface. 5×1 (——) and 5×2 (------) stand for the 5×1 and 5×2 Te missing-row model, respectively. 2×1 (−·−·) means the 2×1 zigzag model.

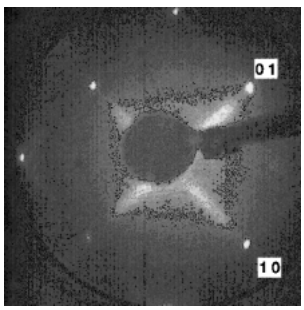

Figure 3. LEED pattern with streaks for the Ge(001): Te 1×1 surface. E=35 eV.

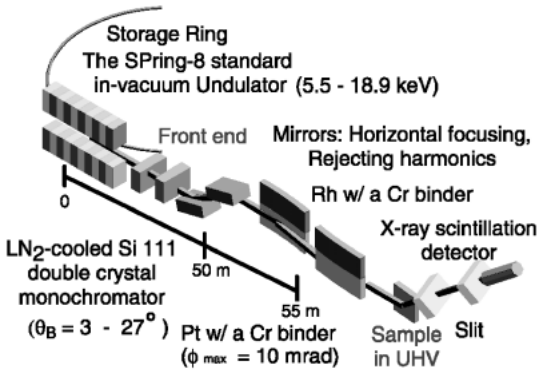

Figure 5. Layout of BL13XU. The inside of EH 3 is additionally illustrated. ϕ stands for an incidence angle.

out. The beamline double crystal monochromator with an Si 111 reflection is cooled down with a liquid nitrogen chiller[12]. The two mirrors have two stripes of a rhodium (Rh) and a platinum (Pt) film with a Cr binder. They are for rejecting higher harmonics of incident photons and for focusing an x-ray beam in a horizontal scattering geometry in an optics hutch. The beamline has three experimental hutches (EH's). You can utilize three UHV chambers that can be independently mounted on an S2+D2 (2 degrees of freedom (DOF) on a sample and 2 fully independent DOF on an x-ray detector) diffractometer (3.2×3.2×2.3 m in dimension) in EH3. EH1 is furnished with a multi-axis diffractometer and precision-rotary tables.

It was observed that an intensity of x-rays diffracted from the BL13XU monochromator quickly faded away.[10] This mainly arose from temperature variation of the stage for the second crystal. The stage was radiatively heated by Compton x-rays scattered from the first crystal surface.[13] We had adopted a constant temperature unit by water flow and sandwiched it in. The unit was designed for BL29XUL by Tamasaku *et al.*[14]. (It is called a chiller but a de factro heater against the second crystal, which is funny.) The x-ray intensity from the monochromator has been more stable than it was before. **Fig. 6** shows a stability test at an ID gap of 10 mm. It is noted that the intensity was considerably stable although the ID almost gave the maximum heat load to the monochromator. The temperature of the second stage was successfully controlled within fluctuations of 0.1 K (**Fig. 7**). It has been found that variations in the intensity were ascribed to the temperature fluctuations of the first crystal stage (compare **Fig. 6** with **Fig. 7**).

We revised measured photon flux densities as a function of an incident photon energy with a silicon pin photo diode (**Fig. 8**). The data were followed by correction of absorption of a 150 μm-thick Be window of the photo diode and taking into consideration of detection efficiency of the diode in 300 μm thickness of Si. The x-ray beam came in through a 0.3 mm graphite filter(, which was 0.1 mm in the previous article[10]) and three Be windows in total thickness of 0.75 mm. In this revision, we removed harmonics contribution carefully; the flux densities for an energy range less than 9 keV look much weaker than those shown in the previous article[10].

A UHV vacuum system includes three UHV chambers and the S2+D2 diffractometer. The chambers are equipped with standard surface-structure-analysis apparatus and sample-growth tools. Chamber 1 (**Fig. 9**) is suitable for a structural

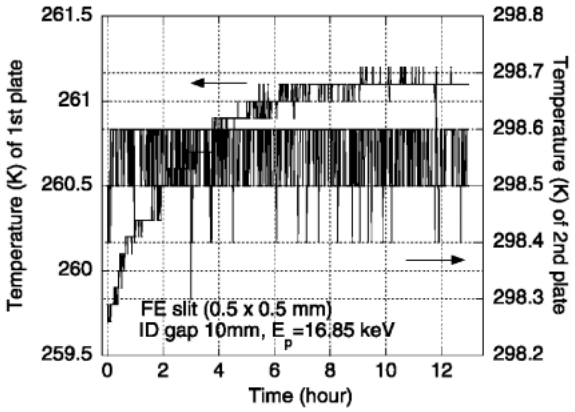

Figure 7. Temperature of monochromator stages versus time.

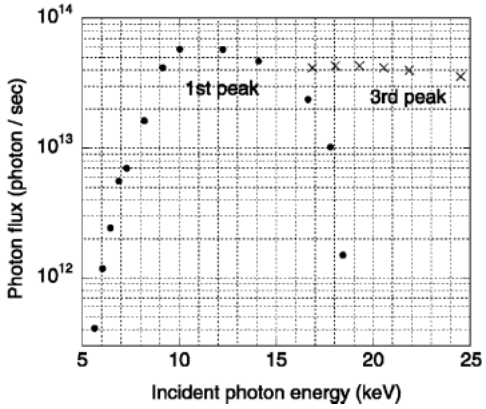

Figure 8. An absolute x-ray photon flux measured. An FE slit opening used was 1×0.8 mm^2. The data were taken without the mirrors. '1st' and '3rd' mean the fundamental light and third harmonics generated from the undulator, respectively.

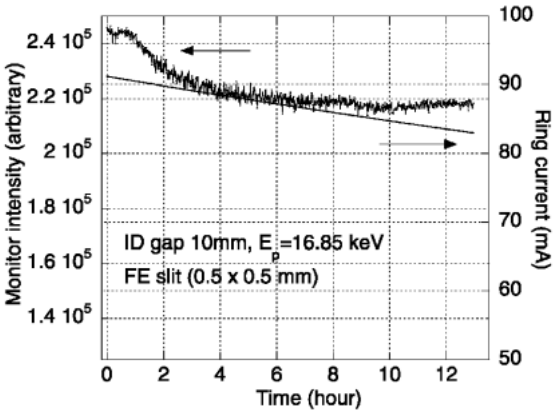

Figure 6. X-ray beam intensities and ring currents versus time. After we opened the MBS, time was measured.

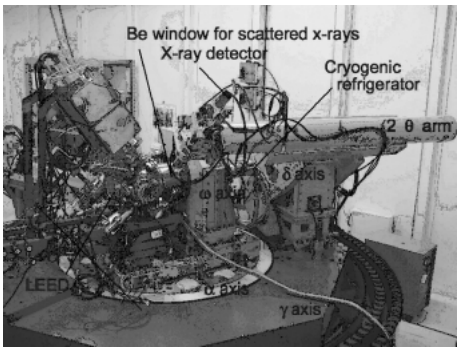

Figure 9. A UHV chamber for studying a metal surface mounted on the S2+D2 diffractometer in EH 3.

study of a metal surface.[15] Chamber 2 and 3 target determination of a semiconductor surface structure using x-ray scattering/diffraction and x-ray standing waves, respectively. The optimal chamber between the three ones for a user's experiment can be mounted on the diffractometer at will. We performed preliminary experiments for commissioning purposes. One of the experiments was a structural study on an O/Pt(111) surface that Prof. M. Ito proposed. (The other UHV chambers have been being prepared.)

A main idea for cleaning a metal surface like Pt is as follows. In combination with sputtering and annealing, surface segregation occurs; accordingly the concentration of impurities (such as Si, Ca, Al, S, C, and P) is enhanced. Oxygen exposure then produces a volatile compound of such an element and oxygen. Oxides like these will readily remove the surface. A sample-surface cleaning series including sputtering, oxygen exposure, and annealing was typically repeated three times. The surface was cleaned by Ar^+ (1.5×10^{-3} Pa) sputtering at room temperature and followed by oxygen exposure at a temperature of 770 K with an O_2 pressure of 2×10^{-5} Pa for 10 min to remove the volatile oxides. The successive flash at 1270 K for 2 min made the flat and clean surface, which was ensured by a sharp LEED pattern (like a hexagon) taken at room temperature. (Electron bombardment heating was used.) 2-Langmuir O_2 was deposited at a substrate temperature of 100 K. The sample was annealed at 250 K for 2 min to dissociate to atomic oxygen; its surface structure became ordered. After this process, LEED patterns showed 2×2 spots at 25 K. Closed-cycle cryogenic refrigerator was utilized for the cooling. The high temperatures were monitored using an alumel-chromel thermocouple and the low temperatures were done using an Au+0.07% Fe-chromel one. The base vacuum pressure was 5×10^{-8} Pa. We recorded scattered intensities along an integer rod (**Fig. 10**) and a fractional rod (**Fig. 11**) from the surface at 25 K in chamber 1. The both plots would have ample L ranges for atomic-scale structure analysis of a crystal surface.

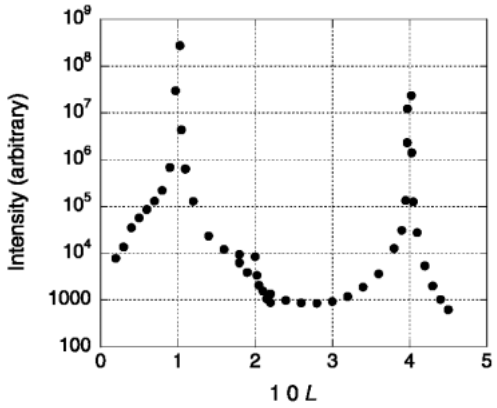

Figure 10. Scattered x-ray intensity along an integer (1 0 L) rod at 25 K.

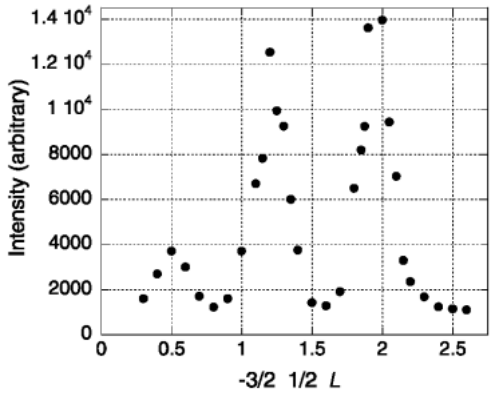

Figure 11. Scattered x-ray intensity along a fractional ($-\frac{3}{2}\frac{1}{2}L$) rod at 25 K.

Capabilities of the instruments include x-ray scattering studies in grazing incidence, studies of CTR's, reflectivity measurements, x-ray standing waves, and many others in UHV and in air. While surface x-ray measurements would take so long time, they have not reached an accurate structure analysis so far. We have two long-term goals of science that look opposite. The keywords are high throughput (convenience or to very efficiently get research outputs) and accurate measurements. The latter goal is to determine an electron-charge density map of a crystal surface. (We hope we have an opportunity to write the details after achieving the goals.) Determining a structure of a locally disordered surface is, moreover, tempting as shown in the first part.

3. Acknowledgments

The scientific research written in the first half of this article was carried out by Prof. M. J. Bedzyk's Group at Northwestern University. We are grateful to friendly researchers for working together, who were Drs. P. F. Lyman, B. P. Tinkham, D. A. Walko, D. L. Marasco, T.-L. Lee, W. P. Rodrigues, and Prof. M. J. Bedzyk. The commissioning job related to the beamline in the second half was performed with Drs. S. Goto, Y. Furukawa, T. Mochizuki, T. Uruga, K. Takeshita, T. Ohata, T. Matsushita, S. Takahashi, T. Ishikawa, and H. Tajiri. The author discussed alteration of the stages for the beamline monochromator with Drs. K. Tamasaku, M. Yabashi, and S. Goto. The UHV chamber for studying the Pt surface was mainly prepared by Prof. M. Ito's Group at Keio University and Prof. T. Takahashi's Group at the University of Tokyo. In particular, young gentlemen, Dr. M. Nakamura and Mr. K. Sumitani, performed excellent work for sample-surface preparation and x-ray measurements. **Fig. 5** is modified marginally—like a mirror image—from a drawing (for the 5ID–C experimental setup) being originally prepared by Dr. T.-L. Lee. The x-ray measurements were carried out under proposal numbers of 2001B0504–ND–np, 2002A0128–ND1–np, and 2002A0201–ND1–np. Encouragement, suggestions, and supports have been provided by Drs. T. Ishikawa, T. Ueki, and H. Suematsu.

References

1) F. C. Frank and J. H. Van der Merwe: Proc. Roy. Soc. Lon-

don **A 198**, 205 (1949).
2) M. Volmer and A. Weber: Z. Phys. Chem. **119**, 277 (1926).
3) I. N. Stranski and Von L. Krastanow: Akad. Wiss. Wien. **146**, 797 (1938).
4) M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp: Phys. Rev. Lett. **63**, 632 (1989).
5) S. Higuchi and Y. Nakanishi: Surf. Sci. **254**, L465 (1991).
6) P. F. Lyman, D. L. Marasco, D. A. Walko, and M. J. Bedzyk: Phys. Rev. **60**, 8704 (1999).
7) N. Takeuchi: Surf. Sci. **426**, L433 (1999).
8) O. Sakata, P. F. Lyman, B. P. Tinkham, D. A. Walko, D. L. Marasco, T.-L. Lee, and M. J. Bedzyk: Phys. Rev. **61**, 16692 (2000).
9) S. Goto, K. Takeshita, and T. Ishikawa: SPring-8 Information **5**, 100 (2000).
10) O. Sakata, Y. Furukawa, S. Goto, T. Mochizuki, T. Uruga, Y. Shimada, K. Takeshita, H. Ohashi, T. Ohata, T. Matsushita, S. Takahashi, and T. Ishikawa: SPring-8 Information **6**, 450 (2001).
11) H. Kitamura: J. Synchrotron Rad. **7**, 121 (2000).
12) The following article does not describe the chiller for BL13XU but for a similar one. T. Mochizuki *et al*., Nucl. Inst. and Meth. **A 467–468**, 647 (2001).
13) K. Tamasaku, M. Yabashi, T. Mochizuki, and T. Ishikawa: SPring-8 Information **5**, 390 (2001).
14) K. Tamasaku, M. Yabashi, D. Miwa, T. Mochizuki, and T. Ishikawa: Proc. SPIE **4782**, to be published.
15) The chamber numbers here are different from those shown in the previous article[10].