Identification of the Structure Model of the Si(111)-(5 × 2)-Au Surface

Tetsuroh Shirasawa,[1,2,*] Wolfgang Voegeli,[3] Takehiro Nojima,[1] Yusaku Iwasawa,[1] Yudai Yamaguchi,[1] and Toshio Takahashi[1]

[1]*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

[2]*JST, PRESTO, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan*

[3]*Department of Physics, Tokyo Gakugei University, 4-1-1 Nukuikitamachi, Koganei, Tokyo 184-0015, Japan*

(Received 13 June 2014; revised manuscript received 4 September 2014; published 15 October 2014)

The atomic structure of the Si(111)-(5 × 2)-Au surface, a periodic gold chain on the silicon surface, has been a long-debated issue in surface science. The recent three candidates, the so-called Erwin-Barke-Himpsel (EBH) model [S. C. Erwin, I. Barke, and F. J. Himpsel, Phys. Rev. B 80, 155409 (2009)], the Abukawa-Nishigaya (AN) model [T. Abukawa and Y. Nishigaya, Phys. Rev. Lett. 110, 036102 (2013)], and the Kwon-Kang (KK) model [S. G. Kwon and M. H. Kang, Phys. Rev. Lett. 113, 086101 (2014)] that has one additional Au atom than the EBH model are tested by surface x-ray diffraction data. A two-dimensional Patterson map constructed from the in-plane diffraction intensities rejects the AN model and prefers the KK model over the EBH model. On the basis of the arrangement of Au obtained from the Patterson map, all the reconstructed Si atoms, such as the so-called honeycomb chain structure, are directly imaged out by utilizing a holographic method. The KK model reproduces out-of-plane diffraction data as well.

DOI: 10.1103/PhysRevLett.113.165501 PACS numbers: 61.05.cp, 68.35.Ct

Self-assembled metal atomic chains on silicon surfaces have been a subject of intensive study as prototypes of one-dimensional (1D) metallic chains [1–5]. Among them, the Si(111)-(5 × 2)-Au surface is the oldest structure, discovered about a half century ago [6]. The surface and its relatives, gold atomic chains on Si(111) vicinal surfaces [7,8], have been widely studied for finding and understanding the physics peculiar to quasi-one-dimensional metals [8–11]. Structure determination is a necessary step for understanding the nature of a system, but in the case of these quasi-1D structures the structure analysis is not straightforward due to a large unit cell with a low symmetry and the incoherence in the chain-chain ordering. For the Si(111) vicinal surfaces, successful structure models were proposed by surface x-ray diffraction (SXRD) experiments [12,13]. However, the Si(111)-(5 × 2)-Au structure still remains controversial, although more than a dozen structure models were proposed along with the development of surface science techniques [14–26].

Until recently, the Au coverage was considered to be 0.4 ML. In 2009, however, Barke *et al.* recalibrated the Au coverage by detailed STM and photoemission spectroscopy experiments and revised the Au coverage to be 0.6 ML [27], which triggered remodeling of the surface structure. Erwin, Barke, and Himpsel proposed a new structure model (hereafter, EBH model) that contains three Au rows (with six Au atoms) per unit cell as shown in Fig. 1(a) [28]. Meanwhile, Abukawa and Nishigaya proposed a different model (hereafter, AN model) that can account for the so-called *Y*-shaped units observed by STM [19,24], on the basis of the three-dimensional Patterson map constructed from reflection high-energy electron diffraction (RHEED) data [29]. While the AN model does not contain the Si honeycomb chain of the EBH model [see Fig. 1(a)], a recent optical reflection anisotropy spectroscopy measurements suggest its existence [30]. Their first-principles calculations show that the AN model has a higher formation energy than the EBH model [30].

Furthermore, very recently, Kwon and Kang have proposed a new model (hereafter, KK model), a modified version of the EBH model, using first-principles calculations [31]. They added one more Au atom to the EBH model [Fig. 1(b)] to show that it is energetically favored over the EBH model. The KK model reproduces the characteristic features of STM images and well explains electronic structures and their modification driven the by Si adatom. The Au coverage of the KK model is 0.7 ML that is consistent with the latest experimental value of 0.65–0.67 ML [32]. The KK model contains Au-Au dimer as indicated in Fig. 1(b). Its existence is strongly suggested by the RHEED Patterson map [29].

Both the EBH and KK models successfully explain the major experimental observations, but the similar structure models have not been examined by diffraction experiment. In this Letter, we study the 5 × 2 structure using SXRD. Direct structure analysis of in-plane SXRD data justifies the KK model. The KK model satisfactorily reproduces out-of-plane SXRD data as well.

The SXRD experiments were done at beam line 15B2 of the Photon Factory at KEK by using a surface diffractometer equipped with an ultrahigh vacuum chamber. The chamber pressure was 1×10^{-8} Pa during the measurements. The x-ray wavelength was 0.86 Å. The Si(111)-(5 × 2)-Au structure was prepared by depositing Au on the Si(111)-(7 × 7) clean surface at 730 °C and postannealing at the same temperature for 10 min. The Au

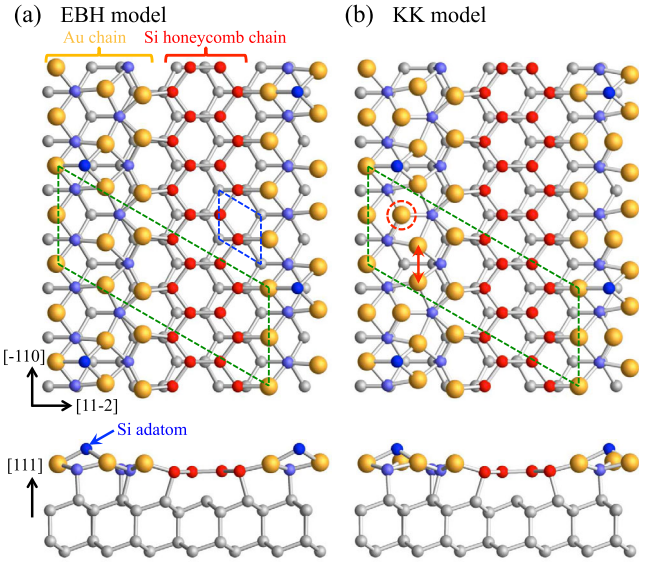

FIG. 1 (color online). Structure models for the Si(111)-(5 × 2)-Au surface. (a) EBH model [28] and (b) KK model [31]. The 5 × 2 and 1 × 1 unit cells are outlined by parallelograms. The larger circles are Au atoms, and the reconstructed Si atoms are highlighted. In (a), the EBH model is characterized by three Au rows and the Si honeycomb chain. In (b), the additional one Au atom is indicated by a dashed circle, and the Au-Au dimer is indicated by a double-sided arrow. In the top view (upper part), the bottom Si bilayer of the side view is omitted for clarity. Note that the 5 × 2 structures are decorated by the Si adatoms with the 5 × 4 periodicity.

coverage was calibrated by *ex situ* x-ray fluorescence spectroscopy to be ~0.6 ML [13], which falls within the range of others reported as 0.56–0.67 ML [32,33]. All the measurements were done at room temperature.

In the in-plane SXRD experiment, the reflections of 1/5-order rods at $l = 0.5$ were measured with an incident angle of 0.5°, where the reciprocal space indices of (hk) rod and l are based on the Si(111)-(1 × 1) unit cell and $c = 9.407$ Å. On a flat Si(111) surface, due to its threefold symmetry, there are three equivalent chain growth directions. In averaging of the equivalent reflections over the three domains, the intensity data of 37 symmetry-inequivalent reflections were obtained within $1 \le |h| \le 14$ and $0 \le |k| \le 4$. For the out-of-plane measurement, a single-domain 5 × 2 structure was prepared on a vicinal Si(111) surface (1.8° miscut along the $[\bar{1}\bar{1}2]$ direction), in order to avoid the overlap of the reflections from the three rotational domains on integral-order rods (crystal truncation rods, CTRs). Two 1/5-order rods and four CTRs were measured within $0.4 \le l \le 4.3$.

It is known that the Si(111)-(5 × 2)-Au surface does not show half-order rods. Instead, half-order streaks appear in reciprocal space because the phase of the ×2 periodicity along the chain direction is incoherent between the chains. For this reason, we could not include the half-order reflections in the following structure analysis.

A promising way to solve such a complex structure without ambiguity is to derive structural information directly from measured diffraction data. We calculated the two-dimensional (2D) Patterson map of the 5 × 2 surface by Fourier transforming the in-plane reflection intensities of the 1/5-order rods. We note that since the half-order reflections are not included, the essential unit cell of the Patterson map is 5 × 1 and the ×2-modulated atomic positions are folded into the 5 × 1 unit cell. In Fig. 2, the experimental Patterson map [Fig. 2(a)] is compared with the simulated ones for [Fig. 2(b)] the EBH model, [Fig. 2(c)] the AN model, and [Fig. 2(d)] the KK model. For the EBH and KK models, the simulation was carried out for the surface atoms illustrated in the right part of the figures, and for the AN model Au, reconstructed

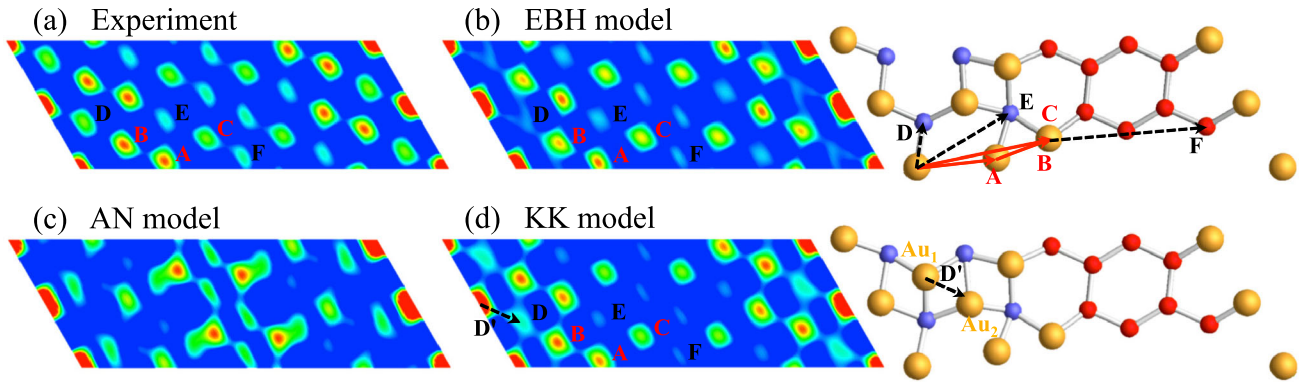

FIG. 2 (color online). 2D Patterson maps for the Si(111)-(5 × 2)-Au structures. (a) Experimental map calculated from the measured intensity for 74 (37 inequivalent) in-plane fractional-order reflections and the simulated maps for (b) the EBH model, (c) AN model, and (d) KK model. Since the half-order reflections are not included in the calculation the essential periodicity of the Patterson maps is 5 × 1, and the 5 × 2 structure is folded into the 5 × 1 unit cell. In (a), (b), and (d), the maps consist of peaks *A*–*F*, and other peaks are their space inversion images. In (b), Au-Au (solid lines) and Au-Si (dashed lines) interatomic vectors are indicated in the structure model. In (d), vector D' is the averaged interatomic vector between Au_1 and Au_2 rows of the 5 × 1-folded structure, which makes the intensity of peak *D* stronger compared with that of the EBH model map (b).

Si, and topmost bilayer of the substrate were used for the simulation. We confirmed that the deeper atoms do not change the essential features of the maps. In the EBH and KK models, the Si adatoms (see Fig. 1) were omitted because of their random population [11,24]. The simulated maps were constructed from the same reciprocal space range as the experimental data set.

The Patterson map is the autocorrelation function of the electron density. Therefore, the position of a peak corresponds to an interatomic vector between two atoms, and its intensity corresponds to the product of the electron densities of the two atoms. The experimental map consists of six peaks A–F as indicated in Fig. 2(a). Other peaks are their space inversion images. Clearly, the AN model does not reproduce the experiment [Fig. 2(c)]. Thus, the AN model is excluded from the candidates. Possibly the disagreement between the SXRD and RHEED results stems from the multiple scattering in RHEED, which violates the single scattering approximation for the Patterson map construction.

Both the EBH and KK models well reproduce all the peak positions. In the EBH Patterson map, the strong peaks A, B, and C correspond to the Au-Au interatomic vectors and the weaker peaks D, E, and F correspond to the Au-Si interatomic vectors, as indicated in the structure model of Fig. 2(b). These features are common to the KK model [Fig. 2(d)]. A clear drawback of the EBH model is that the intensity of peak D is much weaker than that of the experimental map. The additional Au atom in the KK model overcomes the drawback. In the 5×1-folded KK model, Au_1 and Au_2 rows produce the averaged interatomic vector D' as shown in Fig. 2(d). The additional Au-Au interatomic vector makes peak D stronger, in agreement with the experimental map. Thus, the 2D Patterson map clearly prefers the KK model over the EBH model.

The Patterson map is very sensitive to the atomic arrangement of Au. However, all the Si-Si interatomic vectors overlap with Au-Au or Au-Si interatomic vectors, and thus, the arrangement of the reconstructed Si can not be uniquely determined from the map. To image out the Si atoms directly from the experimental data, we applied a holographic method [34] to the 2D imaging. The basic idea of this method is that the measured diffraction wave is regarded as the interference between the reference wave from a known structure with a major scattering contribution and the object wave from the unknown one with a minor contribution. In the present case, the arrangement of the Au atoms of the KK model can be a good reference structure because the scattering intensity of Au is about 30 times greater than that of Si. The 2D hologram function at a given point $hk0$ in reciprocal space is defined as

$$\frac{I^{\mathrm{exp}} - |F^{\mathrm{Au}}|^2}{F^{\mathrm{Au}*}} = F^{\mathrm{Si}} + \frac{F^{\mathrm{Au}}}{F^{\mathrm{Au}*}} F^{\mathrm{Si}} + \frac{|F^{\mathrm{Si}}|^2}{F^{\mathrm{Au}*}},$$

where I^{exp} is the measured diffraction intensity at $hk0$ and F^{Au} and F^{Si} are the scattering amplitudes from the Au atoms and the reconstructed Si atoms, respectively. By Fourier transforming, the first term gives the electron density map of the Si atoms. The second term, the conjugate twin image, can be suppressed by taking the real part of the Fourier transform, and the third term is negligible because $F^{\mathrm{Au}} \gg F^{\mathrm{Si}}$. The image of the reconstructed Si atoms is shown in Fig. 3. Clearly, all the peaks reproduce the KK model. We confirmed that the difference Fourier map also produces a similar image.

Finally, the out-of-plane structure of the 5×2 reconstruction was determined by a least-squares fit to the out-of-plane data. The KK model was used as the starting structure; the in-plane atomic positions of Au were those determined by the Patterson map, and all the Si positions were assumed to be the same as in the EBH model. The 5×2 structure was folded into the 5×1 unit cell, and the atomic positions along the out-of-plane direction were averaged over the respective doubled atoms. The fitting parameters were the heights of all the Au atoms and the positional variations along the in-plane and out-of-plane directions (which were treated in the form of Debye-Waller factors) for the Au atoms, the reconstructed Si atoms, and the topmost bilayer of the Si substrate. The Si adatom was omitted due to its random population and its negligible contribution to the diffraction intensities. The resulting structure parameters are given in the Supplemental Material [35]. The positional variations are relatively large, 0.2–0.3 Å, which would be due to the inherent imperfections of the 5×2 structure such as the incoherence in the chain-chain arrangement and the random distribution of the Si adatom that causes the local structural modification [31]. The structure model satisfactorily reproduces the experimental data with a reasonable χ^2 value of 2.5, as shown in Fig. 4. We note that the EBH model also reproduces the out-of-plane data with $\chi^2 = 2.5$. The probable reason the out-of-plane data fail to distinguish the two similar models is because of the surface imperfections that would affect the out-of-plane data at a high-l region rather than the in-plane data. In light of the obvious

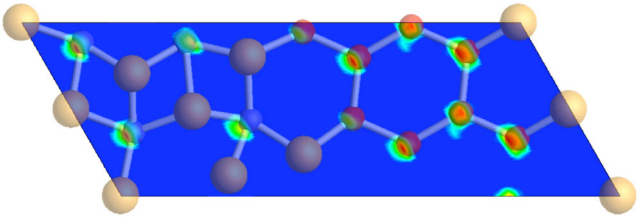

FIG. 3 (color online). 2D holographic reconstruction of the Si adlayer of the Si(111)-(5×2)-Au surface. The Au arrangement of the KK model obtained from the Patterson map [Fig. 2(a)] is used as the reference structure, and the Si adlayer is imaged out. The space-inverted twin images are omitted for clarity. Values less than 35% with respect to the maximum value are omitted.

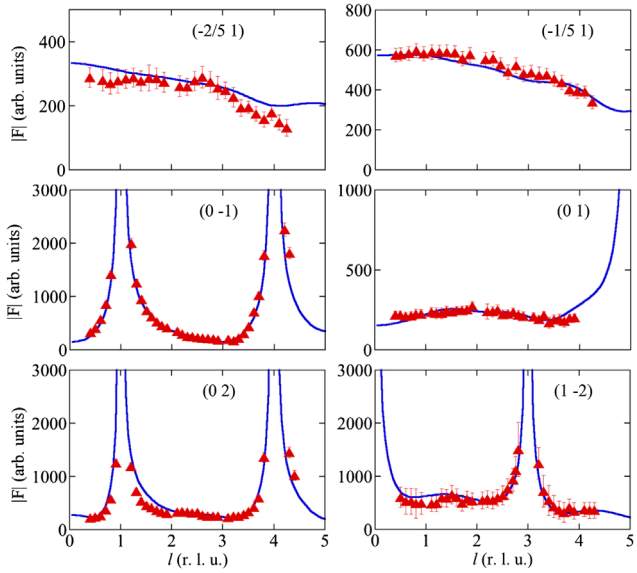

FIG. 4 (color online). Comparison of the measured structure factors $|F|$ along the (hk) rods (solid symbols) and those calculated from the optimized KK model. The χ^2 value is 2.5.

superiority of the KK model for the in-plane data, which is more sensitive to the Au arrangement, we conclude that the KK model is the best structure model.

In summary, the promising two similar structure models of the Si(111)-(5×2)-Au surface, the KK model and EBH model, were examined by SXRD. Both models well reproduce the SXRD data, indicating that the common framework of the structure models is correct. The in-plane SXRD data clearly demonstrate the existence of the one additional Au atom of the KK model, and therefore, we justify the KK model. The experimental support strongly suggests reexamination of properties of the one-dimensional metal in light of the KK model.

We are grateful to S. C. Erwin for providing us atomic coordinates of the 5×2 surface. We thank C. Liu for providing us a recipe for the preparation of the single-domain 5×2 surface. The synchrotron radiation experiments were done at beam line 15B2 of the Photon Factory, KEK, under the approval of the Photon Factory Program Advisory Committee Proposals No. 2005G135 and No. 2008G083.

*sirasawa@issp.u-tokyo.ac.jp

[1] F. J. Himpsel, K. N. Altmann, R. Bennewitz, J. N. Crain, A. Kirakosian, J.-L. Lin, and J. L. McChesney, J. Phys. Condens. Matter **13**, 11097 (2001).
[2] J. Crain and F. Himpsel, Appl. Phys. A **82**, 431 (2006).
[3] N. Oncel, J. Phys. Condens. Matter **20**, 393001 (2008).
[4] S. Hasegawa, J. Phys. Condens. Matter **12**, R463 (2000).
[5] D. E. P. Vanpoucke, J. Phys. Condens. Matter **26**, 133001 (2014).
[6] H. E. Bishop and J. C. Rivire, J. Phys. D **2**, 1635 (1969).
[7] M. Jaochowski, M. Strak, and R. Zdyb, Surf. Sci. **375**, 203 (1997).
[8] J. N. Crain, A. Kirakosian, K. N. Altmann, C. Bromberger, S. C. Erwin, J. L. McChesney, J.-L. Lin, and F. J. Himpsel, Phys. Rev. Lett. **90**, 176805 (2003).
[9] J. N. Crain, J. L. McChesney, F. Zheng, M. C. Gallagher, P. C. Snijders, M. Bissen, C. Gundelach, S. C. Erwin, and F. J. Himpsel, Phys. Rev. B **69**, 125401 (2004).
[10] I. Matsuda, M. Hengsberger, F. Baumberger, T. Greber, H. W. Yeom, and J. Osterwalder, Phys. Rev. B **68**, 195319 (2003).
[11] W. H. Choi, P. G. Kang, K. D. Ryang, and H. W. Yeom, Phys. Rev. Lett. **100**, 126801 (2008).
[12] I. K. Robinson, P. A. Bennett, and F. J. Himpsel, Phys. Rev. Lett. **88**, 096104 (2002).
[13] W. Voegeli, T. Takayama, T. Shirasawa, M. Abe, K. Kubo, T. Takahashi, K. Akimoto, and H. Sugiyama, Phys. Rev. B **82**, 075426 (2010).
[14] G. L. Lay and J. Faurie, Surf. Sci. **69**, 295 (1977).
[15] L. E. Berman, B. W. Batterman, and J. M. Blakely, Phys. Rev. B **38**, 5397 (1988).
[16] T. Hasegawa, K. Takata, S. Hosaka, and S. Hosoki, J. Vac. Sci. Technol. A **8**, 241 (1990).
[17] E. Bauer, Surf. Sci. **250**, L379 (1991).
[18] C. Schamper, W. Moritz, H. Schulz, R. Feidenhans'l, M. Nielsen, F. Grey, and R. L. Johnson, Phys. Rev. B **43**, 12130 (1991).
[19] J. O'Mahony, C. Patterson, J. McGilp, F. Leibsle, P. Weightman, and C. Flipse, Surf. Sci. **277**, L57 (1992).
[20] L. D. Marks and R. Plass, Phys. Rev. Lett. **75**, 2172 (1995).
[21] T. Hasegawa, S. Hosaka, and S. Hosoki, Surf. Sci. **357–358**, 858 (1996).
[22] S. C. Erwin, Phys. Rev. Lett. **91**, 206101 (2003).
[23] S. Riikonen and D. Sánchez-Portal, Phys. Rev. B **71**, 235423 (2005).
[24] H. S. Yoon, J. E. Lee, S. J. Park, I.-W. Lyo, and M.-H. Kang, Phys. Rev. B **72**, 155443 (2005).
[25] C.-Y. Ren, S.-F. Tsay, and F.-C. Chuang, Phys. Rev. B **76**, 075414 (2007).
[26] F.-C. Chuang, C.-H. Hsu, C.-Z. Wang, and K.-M. Ho, Phys. Rev. B **77**, 153409 (2008).
[27] I. Barke, F. Zheng, S. Bockenhauer, K. Sell, V. v. Oeynhausen, K. H. Meiwes-Broer, S. C. Erwin, and F. J. Himpsel, Phys. Rev. B **79**, 155301 (2009).
[28] S. C. Erwin, I. Barke, and F. J. Himpsel, Phys. Rev. B **80**, 155409 (2009).
[29] T. Abukawa and Y. Nishigaya, Phys. Rev. Lett. **110**, 036102 (2013).
[30] C. Hogan, E. Ferraro, N. McAlinden, and J. F. McGilp, Phys. Rev. Lett. **111**, 087401 (2013).
[31] S. G. Kwon and M. H. Kang, Phys. Rev. Lett. **113**, 086101 (2014).
[32] J. Kautz, M. W. Copel, M. S. Gordon, R. M. Tromp, and S. J. van der Molen, Phys. Rev. B **89**, 035416 (2014).
[33] N. McAlinden and J. F. McGilp, Europhys. Lett. **92**, 67008 (2010).
[34] T. Takahashi, K. Sumitani, and S. Kusano, Surf. Sci. **493**, 36 (2001).
[35] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.113.165501 for the determined atomic coordinates.