Structure Determination of the Gold Atomic Chain on Si(111) by Surface X-Ray Diffraction

Self-assembled metallic chains are attracting interest in a wide range of fields. Regular arrays of metal atomic chains can be fabricated on silicon surfaces by depositing sub-monolayer amounts of metals, offering a rich source of phenomena peculiar to one-dimensional conductors. The Si(111)-5×2-Au surface, the regular array of gold chains on the Si(111) surface, is a representative system discovered about half a century ago, but its complex atomic structure had not been solved. We determined the structure by using surface X-ray diffraction. The structure obtained from the model-free direct methods strongly supports the latest structural model predicted by the theory.

Structure determination is a necessary step for understanding the nature of a system. But, in the case of the regular array of one-dimensional (1D) chains on a surface, the structure determination is not straightforward due to the complexity such as a large unit cell with a low symmetry, a significant 1D reconstruction of the substrate surface that originally has a 2D structure, or an intrinsic incoherence in the chain-chain ordering. The Si(111)-5×2-Au surface is one of the most famous prototypes of a 1D metal on Si, and it and its relatives have been the subject of intensive experimental and theoretical studies [1]. However, the structure of Si(111)-5×2-Au remains controversial, although more than a dozen structure models have been proposed. Recently, two similar promising structure models were proposed from *ab-initio* calculations. One is called the EBH model consisting of three Au rows and the honeycomb chain structure of Si [2]. The other is called the KK model, a modified version of the EBH model [3]. It has an additional Au atom with respect to the EBH model as indicated by the dashed circle in Fig. 1(a). Indeed, the calculations suggest that the KK model is energetically stable, but it is quite difficult for the theory, on its own, to determine which of the two very similar models is correct. Therefore, experimental verification is indispensable to reach a final conclusion.

In order to reveal the structure of Si(111)-5×2-Au, we performed surface X-ray diffraction (SXRD) experiments [4] at beamline 15B2 of the Photon Factory at KEK. The surface was prepared in an ultrahigh vacuum chamber mounted on the 6-circle diffractometer which enabled *in-situ* SXRD experiments on the freshly prepared surfaces. We measured in-plane SXRD data of 1/5-order reflections (37 symmetrically inequivalent reflections) to obtain the 2D structure projected on the surface. For the out-of-plane structure analysis, intensity profiles along two 1/5-order diffraction rods and four integral-order rods (crystal truncation rod) were measured.

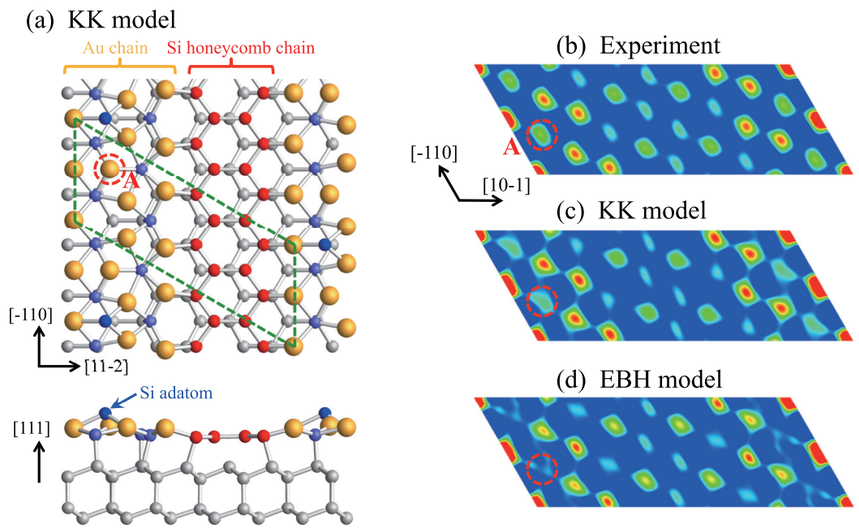

Figure 1: (a) Top and side views of the KK model of the Si(111)-5×2-Au surface [3]. The 5×2 unit cell is outlined by the dashed parallelogram. The larger spheres are Au atoms and the smaller ones are Si where the reconstructed atoms are highlighted. The dashed circle indicates the additional Au atom with respect to the EBH model [3]. (b) 2D Patterson map calculated from the in-plane SXRD data and simulated ones for (c) the KK model and (d) the EBH model. The dashed circle A indicates the peak that becomes stronger by the additional Au atom of the KK model. Note that since the half-order reflections are not included in the calculation [4], the essential unit cell of the Patterson map is 5×1 and the ×2-modulated structure is folded into the 5×1 unit cell.

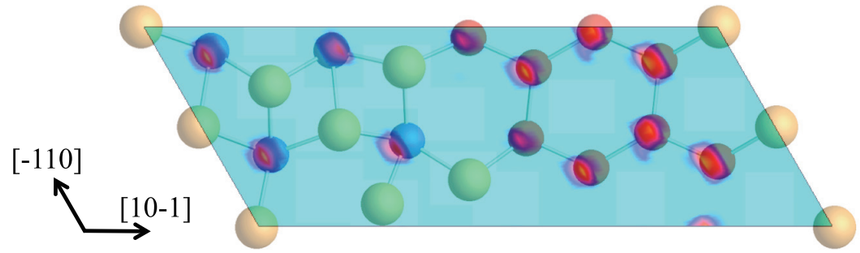

Figure 2: 2D holographic reconstruction of the surface Si atoms. The KK model is overlaid on the image. The arrangement of Au atoms, obtained from the Patterson map of Fig. 1(b), was used as the reference structure to image out the surface Si atoms. The space-inverted twin images and values of less than 35% with respect to the maximum value are omitted for clarity.

A promising way to solve such a complex structure without ambiguity is to derive structural information directly from measured diffraction data. First, we calculated the 2D Patterson map of the surface by Fourier transforming the in-plane reflection intensity data. 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 their electron densities. In the present case, since the electron density of Au is more than five times greater than that of Si, the Patterson map is dominated by the arrangement of Au atoms. Comparing the experimental Patterson map [Fig. 1(b)] to the simulated ones for the KK model [Fig. 1(c)] and EBH model [Fig. 1(d)], one can see that the KK model reproduces the experimental map very well, whereas the EBH model fails to reproduce the peak A indicated by the dashed circle, due to the lack of the additional Au atom.

Now, the arrangement of Au atoms is obtained from the Patterson map, but the positions of Si atoms cannot be solved due to their minor contribution. The arrangement of Si was imaged out directly from the in-plane SXRD data by using a holographic method [5]. The principle 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 Au atoms obtained from the Patterson map is a good reference structure. Figure 2 shows the reconstructed image overlaid with the KK model. All the peaks agree well with the Si atoms of the KK model. Therefore, the direct structure analyses of the in-plane SXRD data support the KK model without ambiguity. Moreover, the atomic positions along the height direction determined from the out-of-plane SXRD data also agree with the KK model [4]. The experimental evidence strongly suggests that the properties of the Si(111)-5×2-Au surface should be reexamined in light of the KK model.

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