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# Reflection high-energy positron diffraction study on the first surface layer

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**Abstract**. Reflection high-energy positron diffraction (RHEPD) is a powerful tool for studying surface structure. In particular, the topmost surface layer can be observed, facilitated by the characteristic of total reflection for positrons. A previous RHEPD study on a Si(111)-√21×√21-Ag surface, using a $^{22}$Na-based beam, is revisited and the analysis detailed.

## 1. Introduction

The structure of the surface of a crystal is, in general, different from that of the bulk. A typical example is a 7×7 reconstructed structure on a clean Si(111) surface [1]. Crystal surfaces can exhibit electronic and magnetic properties which may significantly change with slight displacements of atomic position in the first surface layer. Therefore, a precise knowledge of the atomic arrangement of this layer is needed to fully understand surface properties.

Reflection high-energy positron diffraction (RHEPD) is a powerful method used to investigate the structure of the first surface layer [2,3]. When the glancing angle of a positron beam directed onto a surface is below a particular value, positrons are totally reflected from the material, as depicted in Fig. 1, due to the positive crystal potential. This critical angle is given by $\theta_c = \arcsin(eV/E)^{1/2}$, where $eV$ and $E$ denote the mean potential energy of the positron in the crystal and the energy of the incident positron beam [2]. For example, for a beam of energy $E$ = 10 keV incident on Si for which $eV$ = 12 eV, $\theta_c$ is 2.0°. Under the total reflection condition, the intensities of the diffraction spots are very sensitive to the structures and thermal vibration of the first surface layers. A RHEPD apparatus using a $^{22}$Na positron source was developed in 1998 [3,4] and used in surface structure investigations [5] until recently. In this paper, we describe details of the study of a √21×√21 superstructure made with this apparatus as an example of surface structure analysis using RHEPD.

## 2. Structure analysis by RHEPD

### *2.1. Si(111)-√21×√21 surface*

Adsorption of one monolayer (ML) of Ag atoms on a clean Si(111)-7×7 surface leads to the formation of a √3×√3-Ag structure. The basic framework of the Si(111)-√3×√3-Ag structure was deduced by pioneering work using surface x-ray diffraction [6]. Subsequently, using low-temperature scanning tunneling microscopy and first-principles calculations, the ground-state structure was confirmed to be an inequivalent triangle (IET) structure [7]. In 1994, it was discovered that a √21×√21 superstructure

having a large unit cell appeared when a small amount of Au atoms were deposited onto the √3×√3-Ag surface [8, 9]. Moreover, it was found that adsorption of other noble and alkali metal atoms also led to the formation of a √21×√21 superstructure, accompanied by a significant increase of surface electrical conductivity [10].

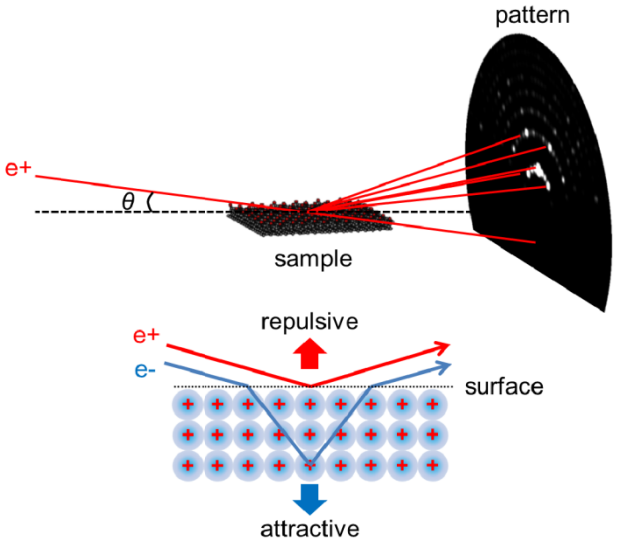


**Figure 1.** Experimental setup of RHEPD (top) and schematic drawings of positron and electron incidences on a crystal surface (bottom). When the positron beam is incident on the surface, the positron is repelled by the positive crystal potential and is totally reflected when the glancing angle is below a certain critical angle.

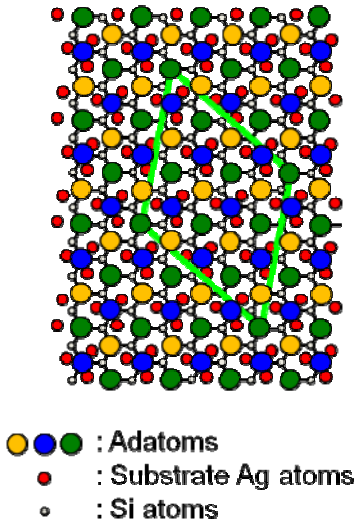


**Figure 2.** The twenty-one possible adatom adsorption sites of the √21×√21 superstructure: the centers of seven large Ag triangles, the centers of seven small Ag triangles, and the centers of seven Si trimers are denoted by orange, blue, and green circles, respectively. Red and open circles denote the substrate Ag and Si atoms. The rhombus indicates a √21×√21 unit cell.

Various models for the √21×√21 superstructure were proposed by a number of researchers [8,9,11,12], however, it could not be ascertained which one was correct. As depicted in Fig. 2, there are 21 possible adsorption sites on the Si(111)-√3×√3-Ag surface [13]: (i) the centers of seven large Ag triangles, (ii) the centers of seven small Ag triangles, and (iii) the centers of seven Si trimers. Since seven equivalent sites exist for each of these candidates in the √21×√21 unit cell, the number of possible structure models is ${}_{21}C_3 = 1330$ when the number of adatoms is three (~0.14 ML coverage). To determine the surface structure, we performed a screening analysis of this structure using RHEPD rocking curves and intensity profiles of the diffraction spots [14].

### 2.2. *Determination of the vertical components of atomic positions*

A RHEPD rocking curve is a plot of the intensity of a certain diffraction spot versus glancing angle. Figure 3 illustrates two different incident directions used in the analysis. Figure 3(a) shows a view along the $[11\bar{2}]$ direction, neglecting the small glancing angle, where periodicity of the atomic distribution along the perpendicular directions of [111] and $[1\bar{1}0]$ is seen. This incidence condition is called the many-beam condition [15]. Figure 3(b) shows a view from 7.5° off the $[11\bar{2}]$ direction, where the atoms appear to be randomly distributed in plane and only the periodicity along [111], i.e., the direction perpendicular to the surface, is seen. This is called the one-beam condition [16]. The

rocking curve analysis is conducted in two steps. First, by analyzing the rocking curve in the one-beam condition, we determine the vertical components of the atomic positions ignoring the accurate in-plane configurations but taking only the atomic density in the plane into account. Second, we determine the in-plane components by analyzing the rocking curves in the many-beam condition with fixed vertical components determined by the analysis in the one-beam condition.

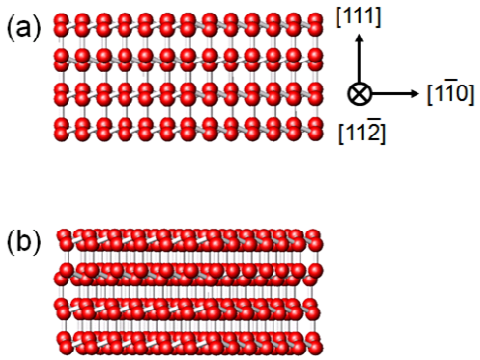


**Figure 3.** Diamond structures when viewed (a) along the [ 11$\bar{2}$ ] direction (many-beam condition) and (b) along 7.5° off the [ 11$\bar{2}$ ] direction (one-beam condition).

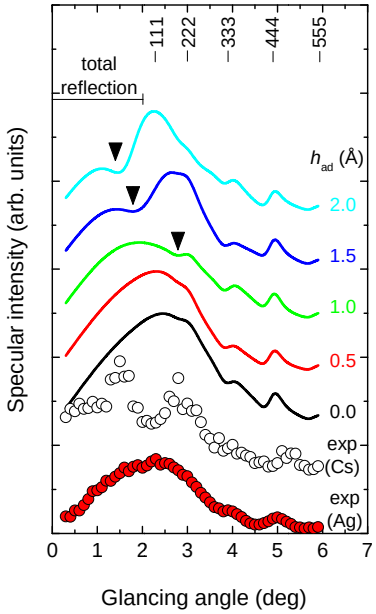


**Figure 4.** RHEPD rocking curves from the Si(111)-√21×√21 super-structures under the one-beam condition. Red closed circles show the experimental curves from Si(111)-√21×√21-Ag. For compare-son, the open circles show those from a Si(111)-√21×√21-(Ag,Cs) surface. Solid lines indicate the rocking curves calculated with various adatom heights ($h_{ad}$) up to 2.0 Å.

Red filled circles in Fig. 4 show a measured RHEPD rocking curve of the specular reflection spot for a Si(111)-√21×√21-Ag surface at 7.5° off the [ 11$\bar{2}$ ] direction (one-beam condition [16]). The solid lines show RHEPD rocking curves at various Ag adatom heights ($h_{ad}$) from the substrate Ag layer calculated using dynamical diffraction theory [15]. The parameters used in the calculations are described in reference [14]. From the curve fitting procedure using the reliability factor (*R*-factor) defined in reference [17], the adatom height for the Si(111)-√21×√21-Ag surface was determined to be 0.53 Å [14].

In order to illustrate the sensitivity of the rocking curve in the one-beam condition, Fig. 4 includes the calculations for a range of values of $h_{ad}$ which illustrate that the shape of the rocking curve varies with $h_{ad}$. As $h_{ad}$ increases from zero, the broad peak rising in the total-reflection region shifts towards lower glancing angles. This is due to the decrease in the critical angle of total reflection caused by a

reduction in the crystal potential at the surface because of less overlap between the adatoms and the substrate Ag atoms. At higher $h_{ad}$, a dip structure appears in the broad peak, as shown by the arrowheads. The position of the dip gradually shifts towards lower glancing angles with increasing $h_{ad}$. The tendency of the shift can be explained by the interference of the positron waves reflected from the adatom and the substrate Ag layers [18]. The value of $h_{ad}$ for the Si(111)-√21×√21-Ag surface is small so there is no significant dip structure observed. For comparison, the rocking curve measured from the Cs atoms adsorbed √21×√21 superstructure (Si(111)-√21×√21-(Ag,Cs)) [19] is also plotted in Fig. 4. In this case, a distinct dip structure is seen because of the large atomic radius of the Cs atoms.

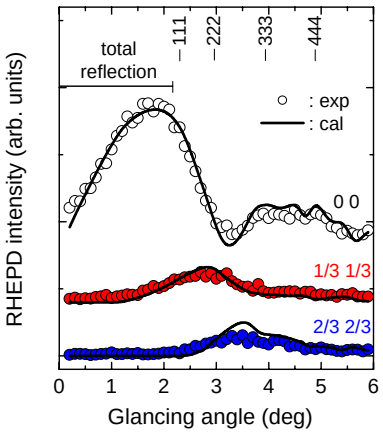


**Figure 5.** RHEPD rocking curves along the [$11\bar{2}$] direction (many-beam condition) for the indicated spots from the Si(111)-√21×√21-Ag surface. Circles show the experimental curves. Solid lines indicate the rocking curves calculated with optimized structure parameters.

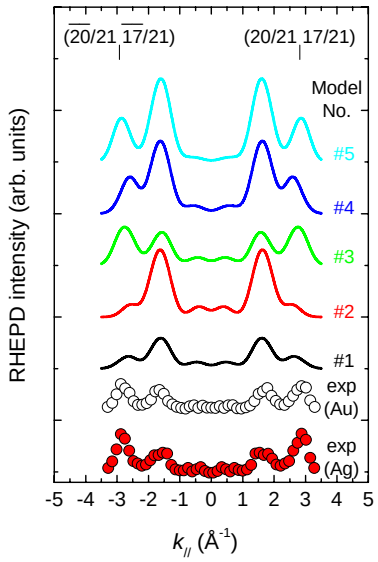


**Figure 6.** Diffraction intensity profiles along the 1/7th Laue zone for the Si(111)-√21×√21 superstructure. $k_{//}$ is the position in the 1/7 Laue zone. Red and open circles indicate the intensity profiles measured from Si(111)-√21×√21-Ag and -(Ag,Au) surfaces, respectively. Solid lines indicate the profiles calculated for the remaining five possible structures.

*2.3. Determination of in-plane components by rocking curve and intensity profiles*

To determine the in-plane components of the atomic positions of the Si(111)-√21×√21-Ag surface, the rocking curves along the [$11\bar{2}$] direction (many-beam condition) were measured. Results obtained are shown by the circles in Fig. 5. The rocking curves for the 00, 1/3 1/3, and 2/3 2/3 spots (spots on the 0th Laue zone) were used in the analysis because the intensities of these spots were greater than those of the higher Laue zones. The solid lines show the best fitted rocking curves. As a result, it was found that all of the three adatoms were located on sites at the center of a large Ag triangle. However, the rocking curves for these spots could not discern which three sites out of the seven were occupied. Nevertheless, the possible structure of Si(111)-√21×√21-Ag was narrowed down by this process to

five (See Fig. 6 of reference [14]), i.e., the possible symmetrically independent distribution of three atoms among the seven possible sites.

The fractional-order spots resulting from the formation of the √21×√21 superstructure carries information about the in-plane distribution of adatoms. However, the intensities of these spots measured with the $^{22}$Na-based slow-positron beam in this study were too weak to give reliable rocking curves. Therefore, the intensity profiles of the spots in the 1/7th Laue zone were used to deduce the correct arrangement out of the five possibilities. The red filled circles in Fig. 6 show the intensity profile extracted from the observed pattern. The solid lines are the profiles calculated for the five possible structures. It is clear that only one graph, #3, matches the intensity profile observed. This is a structure where all the three adatoms are sitting on sites at the center of a large triangle of Ag atoms (orange sites in Fig. 2). More precisely, the occupied sites form a triangle surrounding the Si trimer in the √21×√21 unit cell (#3 in Fig. 6 of reference [14]). It was later shown that the intensity profile from the Au-adsorbed Si(111)-√21×√21 structure (open circles in Fig. 6) resembles that of the Si(111)-√21×√21-Ag surface [20]. This demonstrates that the Si(111)-√21×√21-(Ag,Au) surface has the same atomic consignations as the Si(111)-√21×√21-Ag surface.

## 3. RHEPD with an intense beam and future prospects

Although it was possible to determine the surface structure using the weaker $^{22}$Na-based positron beam at JAEA, Takasaki, owing to the high reflectivity of positrons at surfaces, the RHEPD apparatus was recently moved to the Slow Positron Facility at the Institute of Materials Structure Science, KEK, and connected to a linac-produced, brightness-enhanced intense positron beam [21]. Weak fractional-order spots in the RHEPD pattern from a Si(111)-7×7 surface were successfully observed with this improved apparatus. The intense positron beam makes the structural analysis much more efficient and accurate. A study of a more complex surface structure will be made and even a Pattern function analysis without assuming a possible atomic arrangement will be attempted.

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