X-ray Standing Wave Analysis of the 1/3 ML Sn/Si(111) Surface

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Introduction

The atomic scale structure of the 1/3 monolayer (ML) Sn/Si(111)-(√3x√3)R30° surface has recently attracted attention because of its structural and electronic similarities to the 1/3 ML Sn on Ge(111) surface, which also forms a √3 structure at room temperature (RT). It is generally accepted that the main feature of this atomic configuration is the adsorption of 1/3 ML of Sn at the T_4-adsorption sites, as depicted in Figure 1. While scanning tunneling microscopy (STM) images show that all the Sn adatoms at the T_4 sites appear equivalent at RT, the Sn/Ge(111) surface changes to a (3 x 3) reconstruction when cooled below its transition temperature of ~210 K [1]. However, despite the similarities between Ge and Si, the Sn/Si(111) surface maintains the same √3 superstructure at low temperature (≥6K) [2]. The phase transition in Sn/Ge(111) has been attributed to a number of phenomena, yet there is little agreement on the dominant driving force for the low temperature (LT) (3 x 3) reconstruction. It is the unresolved nature of this phase transition on Sn/Ge(111) and its apparent absence in the case of Sn/Si(111) that has motivated our recent attempt to determine the structural details of the Sn/Si(111) surface at RT.

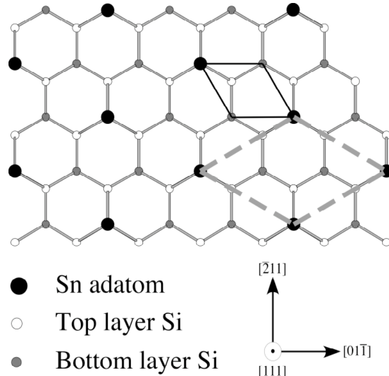

Fig. 1. Ball-and-stick diagram of the 1/3 ML Sn/Si(111) surface. The (1x1) and the (√3 x √3)-R30 surface unit cells are inscribed in solid black and dashed grey lines, respectively.

To that end, we have performed in situ Auger electron spectroscopy (AES), LEED, and XSW measurements on 1/3 ML of Sn on Si(111). By a Fourier summation using the XSW measured Fourier amplitudes and phases, we are able to generate a model-independent image of the Sn time-averaged atomic distribution. While this direct-space image confirms Sn is located at the T_4-adsorption site, it is unable to sufficiently resolve whether there are one or two types of Sn on the surface. However, applying a conventional XSW analysis approach demonstrates that our XSW results are not compatible with a flat √3 structure. For a second surface prepared under slightly different conditions, we will also demonstrate a case of a certain fraction of Sn atoms substituting for Si atoms within the subsurface Si layer. This surface proves to be an effective demonstration of the model-independent direct-space imaging approach.

Methods and Materials

The model-independent direct-space imaging approach takes advantage of the fact that the XSW-measured coherent fractions (f_H) and coherent positions (P_H) are the directly measured amplitudes and phases of the *hkl* Fourier components of the Sn distribution. Therefore, the collected XSW reciprocal-space data can be Fourier inverted according to the following equation [3]:

$$\rho(\boldsymbol{r}) = \sum_{H} f_H \exp\left[-2\pi i(\boldsymbol{H}\cdot\boldsymbol{r} - P_H)\right] = 1 + 2\sum_{H\neq -H\neq 0} f_H \cos\left[2\pi(P_H - \boldsymbol{H}\cdot\boldsymbol{r})\right]$$

The result of this Fourier sum is an element-specific, direct space atomic-density map. Since the photoelectric effect cross-section (in the dipole-approximation) is proportional to the E-field intensity at the center of the atom, the resultant 3D atomic-density map is for the time-averaged locations of the atomic centers. This elemental distribution is generated independently from any presupposed structural constraints, unlike conventional XSW analysis that relies on the comparison of experimental and model-calculated XSW parameters. Since this summation includes only the hkl Fourier coefficients that arise from the allowed bulk Bragg reflections, the calculated adsorbate atomic density is necessarily projected into the primitive unit cell of the substrate. This XSW Fourier reconstruction method has been very recently developed and used to generate one-dimensional impurity atom distributions in bulk crystals [3] and to produce three-dimensional density profiles of adatoms on single crystal surfaces [4-6].

Sample preparation and characterization were conducted in an ultra-high vacuum (UHV) chamber (base pressure ~1.5 x 10^{-10} Torr) located at the 12ID-D undulator BESSRC-CAT experimental station at the Advanced Photon Source. The single-crystal Si(111) samples were degassed for 6 to 8 hours at 873 K, and then annealed for 15 min. at 1113 K to remove the chemically grown protective oxide. The high-temperature anneal produced a clean, well-ordered Si(111)-(7x7) surface, on which a total of 0.33(3) ML of Sn was evaporated onto the clean, RT Si(111) surface using an effusion cell. The coverage of Sn was determined in UHV by comparing the intensity of the Sn Lα x-ray fluorescence to that of a Sn-implanted Si(111) standard calibrated by RBS. The samples were annealed for 4 min. at 913 K, and then allowed to slowly cool to RT (at a rate of ~1 K/s). This process resulted in a reduction in the Sn coverage to 0.23(3) ML and a sharp √3 LEED pattern. In a separate set of XSW measurements, a second Si(111) substrate was annealed at 933K for 2 minutes after depositing 0.45 ML of Sn, producing a sharp √3 LEED pattern and a final Sn coverage of 0.33(4) ML.

For the case of the lower-coverage 0.23 ML sample, the XSW measurements were conducted by scanning the sample in angle through the allowed Si (*hhh*) Bragg reflections (h = 1, 3, 4, 5) and simultaneously collecting the diffracted beam intensity and x-ray fluorescence spectra (using an in vacuo photodiode and energy-dispersive Si(Li) detector, respectively) at each angular step. Three additional off-normal XSW measurements were collected in the same manner utilizing the Si ($\bar{1}11$), ($\bar{3}33$), and ($5\bar{1}\bar{1}$) Bragg reflections in order to determine the in-plane Sn distribution. The {111}, {333}, and ($5\bar{1}\bar{1}$) XSW measurements were collected using 6.9 keV x-rays that were

conditioned by the high-heat-load 12ID Si(111) monochromator. For the {111} XSW measurements, a pair of detuned non-dispersive Si(111) channel-cut crystals was used to condition the incident beam; in all other cases, a single d-spacing-matched Si(hhh) channel cut was used. Because of the particulars of the experimental setup, the higher-order Si(hhh) measurements required the use of higher-energy x-rays (h = 4, 9.4 keV; h = 5, 11.2 keV). In the case of the higher-coverage, 0.33 ML Sn/Si sample, a separate set of *hkl* XSW measurements was collected. In all cases, fitting the normalized reflectivity and Sn Lα fluorescence yield with dynamical diffraction theory produced the coherent position (P_H) and coherent fraction (f_H) for the adsorbed Sn atoms.

Results and Discussion

The results from the set of XSW measurements are summarized in Table I, while the direct-space Sn density distribution generated from the results from the 0.23 ML Sn/Si surface is shown in Figure 2. The resolution limit of this method corresponds to one-half of the smallest d-spacing measured, which in this case is $d_{555}/2$ = 0.31 Å. The top view shown in Fig. 2(a) shows the Sn density variations at a height of 1.80 Å above the Si(111) surface (where the origin is chosen to be the top atom of the bulk-like Si(111) bilayer). This view demonstrates the maximum Sn atom density is centered at the T_4 adsorption site, as expected. This is confirmed by the XSW coherent position measurements of the 0.23 ML Sn/Si surface agreeing with the relationships $P_{\bar{1}11} = (P_{111}+1)/3$ and $P_{\bar{3}33} = (P_{333}+1)/3$, which are the geometrical symmetry conditions for the occupation of T_4-adsorption sites on the Si(111) surface.

Table 1: A partial summary of the XSW results for the two types of Sn/Si(111) surfaces. The origin (P_H = 0) is centered on the bulk-like Ge site in the top of the bilayer.

	0.23 ML Sn		0.33 ML Sn	
(hkl)	P_H	f_H	P_H	f_H
(111)	0.61(1)	0.76(2)	0.71(1)	0.54(1)
(11$\bar{1}$)	0.49(1)	0.89(5)	-	-
(333)	0.75(2)	0.44(2)	0.71(3)	0.17(3)
(33$\bar{3}$)	0.58(2)	0.36(3)	-	-
(022)	-	-	0.09(1)	0.51(3)
($\bar{1}$33)	-	-	0.74(4)	0.15(5)
(444)	0.37(3)	0.20(7)	-	-
(555)	0.92(4)	0.27(8)	-	-

The side view shown in Fig 2(b) is a cross-sectional cut through the Sn density distribution containing the long diagonal of the (1x1) surface unit cell. While this view also shows the Sn occupies the T_4-adsorption site, there is no obvious vertical asymmetry or multiple density maxima, as would be expected for Sn adsorbed at multiple heights. This can be interpreted in one of two ways: either the Sn is arranged in a flat, √3 structure as seen in STM images, or the Sn is in a "rippled" configuration, but the height separation between Sn adatoms is less than the 0.31 Å resolution of this XSW direct-space image. In order to distinguish between these two possibilities, a comparison between the measured (*hhh*) coherent positions can be made to obtain a qualitative sense of the vertical distribution of the Sn atoms.

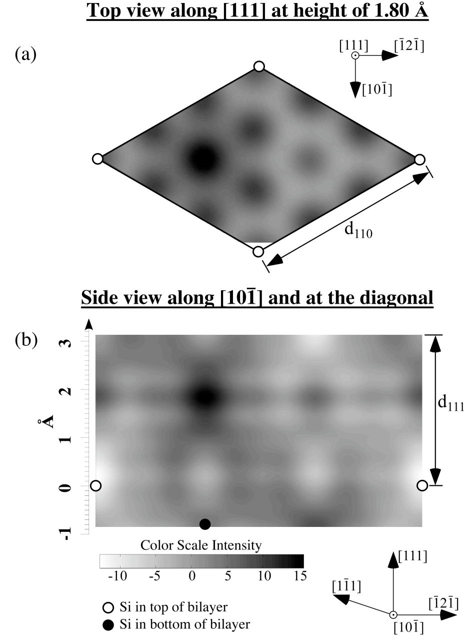

Fig. 2. 2D cuts through the 3D XSW direct space Sn atomic density maps for the 1/3 ML Sn/Si(111) surface. The superstructure is projected into the primitive unit cell of the bulk crystal. The atomic density scale is shown as a color bar, which represents the region of maximum Sn atomic density as dark spots. (a) Top view of the (1 x 1) surface unit cell. (b) Side view of the (1 x 1) surface unit cell. The subsidiary maxima surrounding the T_4 site are artifacts due to the termination of the Fourier sum.

If the equilibrium state of the √3 surface is composed of Sn atoms at a single height, it would be expected that the measured P_{111} and P_{333} would follow the relationship: $P_{333} = \mathrm{Mod}_1[3P_{111}]$. This relationship will hold if the time-averaged distribution of Sn, as projected along the [111] direction, is symmetric. However, if one compares the results from the (111) and (333) XSW measurements, it can be seen that our measured value for P_{333} = 0.75 is less than $\mathrm{Mod}_1[3P_{111}]$ = 3(0.61)-1 = 0.83, which demonstrates the Sn atomic distribution is not consistent with the single height model developed by earlier structural studies. In fact, relating the measured (111) and (333) coherent positions demonstrates the time-averaged projected Sn distribution is asymmetric and furthermore bottom-heavy. While the additional (*hhh*) XSW parameters will help refine the details of this asymmetric configuration, this simple comparison of two measurements immediately addresses the primary question concerning the 1/3 ML Sn/Si(111) surface structure: whether or not the RT Sn vertical distribution is flat or asymmetric. However, in order to precisely determine the structural details of this asymmetric Sn distribution, an appropriate model for the Sn/Si(111) surface can be used to interpret the XSW results. In the model chosen for this study, the following constraints are employed: 1) one-third of the ordered Sn is located at a height h_A and the remaining two-third are at a height h_B, 2) the rms vibrational amplitudes $\langle u^2 \rangle^{1/2}$ along the [111] direction for all Sn atoms are identical, and 3) some fraction of Sn (1 - C) is randomly distributed, while the remaining fraction C of Sn is located at T_4 sites. As the direct-space images in the previous section show, the assumption that Sn adsorbs at some height above the T_4 sites is a valid one.

In order to relate the measured amplitude *(f_H)* and phase *(P_H)* of the Hth Fourier coefficient (F_H) to the model parameters, the following equation is used:

$$F_m = f_m exp(2\pi i P_m) = C[(1/3)exp(2\pi i m h_A/d_{111}) + (2/3)exp(2\pi i m h_B/d_{111})] \times exp(-2\pi^2 m^2 < u^2 > /d_{111}^2)$$

In this equation, m refers to the order of the (hhh) reflection of interest (m = 1, 3, 4, 5). A global chi-squared minimization routine was used to integrate the four sets of XSW data, account for the relative errors for each individual XSW measurement, and calculate a set of model parameters. The fitting routine resulted in a structural model with a "one up, two down" configuration, with the up position at h_A = 2.04(5) Å above the top of the Si bulk-like layer and the down position at h_B = 1.78(3) Å. The vibrational amplitude for the Sn atoms in the [111] direction was calculated to be $<u^2>^{1/2}$ = 0.13(3) Å, while the Sn ordered fraction was C = 0.81(2). The reduced chi-squared value for this fit was 1.98.

With regard to the higher-coverage, 0.33 ML Sn/Si(111) surface, it was assumed that because the calculated coherent positions do not follow the crystallographic symmetry requirements for T_4-site occupation, the aforementioned structural model could not apply to the higher-coverage Sn surface. However, because of the model-independent nature of the XSW direct-space imaging technique, the XSW measurements collected from the higher-coverage surface can be used to help determine the Sn distribution without relying on a particular model. The XSW direct-space image generated from the XSW parameters in Table 2 is shown in Figure 3. The increased in-plane width of the Sn atomic density distribution is partly due to the lower in-plane sensitivity of the off-normal XSW measurements made for this surface. Above the Si surface, this image is quite similar to the XSW direct-space image from the lower-coverage surface shown in Figure 2, since both indicate a Sn atomic density maximum close to 1.80 Å above the top of the Si bilayer. However, the image in Figure 3 displays an additional Sn maximum that is approximately 25% smaller than the upper maximum and is located 0.35 Å below the top bilayer bulklike Si atoms. The two maxima are separated by 2.15 Å, and therefore are easily distinguished from each other in the XSW direct-space image, which has an expected resolution of 0.52 Å (d_{333}/2). Both atomic density maxima are centered on T_4 adsorption sites; therefore, the image suggests the surface incorporated Sn replaces Si atoms located in the bottom of the surface bilayer.

In order to quantitatively determine the amount and location of the subsurface Sn, the previously discussed structural model can now be implemented after introducing two additional parameters: c_{sub}, the fraction of ordered Sn that has migrated beneath the Si surface, and h_{sub}, the depth below the top of the Si bulk-like bilayer where the Sn has diffused. One constraint imposed on the Sn population is the fraction of ordered Sn located at T_4 sites ($1 - c_{sub}$) is fixed in a 1:2 occupation ratio. The previously described minimization routine can then be applied to the following equation for the *hhh* Fourier components:

$$F_m = f_m exp(2\pi i P_m) = C \times [[(1-c_{sub})/3]exp(2\pi i m h_A/d_{111}) + [2(1-c_{sub})/3]exp(2\pi i m h_B/d_{111}) + (c_{sub})exp(2\pi i m h_{sub}/d_{111})] \times exp(-2\pi^2 m^2 < u^2 > /d_{111})$$

When fitting this revised set of equations to the XSW data, the heights h_A and h_b as well as the thermal vibrational amplitude are fixed at the values determined from the previously discussed calculation (h_A = 2.04 Å, h_B = 1.78 Å, $<u^2>^{1/2}$ = 0.13 Å). After applying these constraints, the least-squares minimization routine returns a best-fit in which 38% (±3%) of the ordered Sn is located 0.37(4) Å below the top of the Si bulk-like surface. The fraction of Sn that is not randomly distributed is C = 0.81(4).

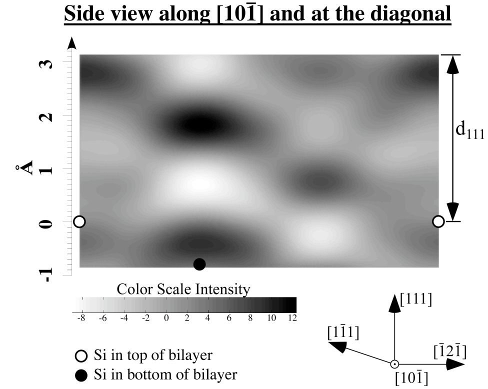

Fig. 3. XSW direct space Sn atomic density image for the Sn/Si(111)-√3 surface. A total of 0.45 ML of Sn was deposited on the Si(111) surface before annealing at 933K. The coverage after annealing was 0.33(4) ML. While the majority of Sn appears adsorbed at the T_4 site, a significant amount appears to occupy a third site directly below the T_4 site within the Si surface.

In conclusion, it has been experimentally determined that Sn adatoms are arranged in a "one up, two down" configuration, with one-third of the Sn at 2.04 Å above the top of the ideal Si bilayer and two-thirds at 1.78 Å. This Sn distribution is similar to the atomic distribution measured by XSW of the √3 phase and (3 x 3) phase of Sn/Ge(111). This similarity supports a dynamical fluctuations model of the Sn/Si(111) surface, in which Sn atoms move in a correlated fashion between two unique adsorption sites. In a separate surface treatment, a higher initial coverage of Sn was deposited on Si(111). The measured Sn XSW Fourier coefficients were used to generate a model-independent 3D direct-space image, which unambiguously shows Sn migrating below the Si(111) surface and substituting for Si in the bottom of the surface bilayer.

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