

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

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Introduction

An accurate determination of their atomic-scale structure enables insight into the 2-D physics of surface-phase transitions, dynamics, and kinetics. One example is the 1/3 monolayer (ML) Sn on the Ge(111) surface. At room temperature (RT), it forms a $(\sqrt{3} \times \sqrt{3})R30^\circ$ (hereinafter called $\sqrt{3}$) reconstruction and is typically modeled with a single Sn atom occupying T_4 -adsorption sites (i.e., T_4 -sites) in the $\sqrt{3}$ unit cell (see Fig. 1). When it cools from the critical temperature T_C of ~ 210 K to near 100K, the surface reconstruction completes a gradual and reversible transition to a (3×3) phase [1]. Scanning tunneling microscopy (STM) images show that one of the T_4 -site Sn atomic protrusions in the (3×3) unit cell appears to be different than the other two [2]. Despite several investigations of this system, the structure and nature of this transition are still unresolved [1, 3]. The main controversies are whether the Sn atoms (and underlying Ge atoms) possess a rippled topography at both RT and low temperature (LT) and whether the topography is “one up and two down” or “two up and one down.”

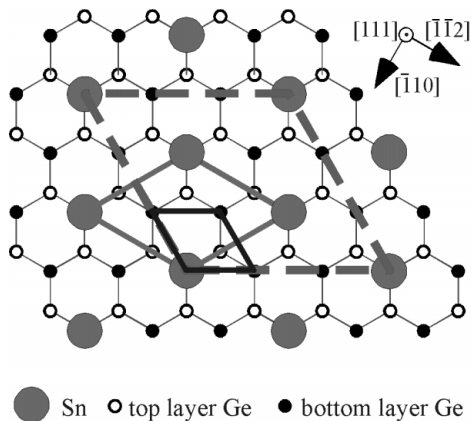


FIG. 1. Top view of the 1/3 ML Sn/Ge(111) surface showing the Sn adatoms in T_4 -sites and the top Ge bilayer. The (1×1) , $\sqrt{3}$, and (3×3) surface unit cells are shown as black, gray, and dashed lines, respectively.

Methods and Materials

We present a new approach for determining the locations of adsorbates on crystalline surfaces. This x-ray standing wave (XSW) direct-space imaging procedure is based on the inversion of the XSW-measured Fourier coefficients (amplitude f_H and phase P_H) for the Sn distribution. The first step in the analysis is to create an atomic density map with low resolution (0.5 \AA). The second stage uses conventional XSW analysis and a model based on the image to determine the Sn adatom position with high resolution (0.04 \AA).

Because the XSW is generated by dynamical Bragg diffraction from the bulk Ge crystal, it does not require long-range ordering of Sn atoms to sense their vertical distribution. XSW results are element-specific and model-independent and provide the projected positions of the Sn atoms within the 3-D primitive unit cell of the bulk Ge crystal. With measurements at both RT and LT, the time-averaged vertical distributions for Sn can be compared. In a phase transition where Sn atoms are displaced from a single height at RT to a corrugated Sn structure at LT, the XSW results would differ for RT and LT. An XSW finding of an unchanged vertical distribution, however, would support an order-disorder transition, where the long-range order in the Sn vertical distribution at LT is lost at RT due to rapid, correlated fluctuations in the Sn heights [4].

The sample preparation and measurements were performed in an ultrahigh vacuum chamber coupled to a six-circle diffractometer located at DND-CAT undulator beamline station 5-ID-C at the APS. The base pressure for the chamber was 2×10^{-10} torr. The Ge(111) surface was argon ion sputter-cleaned and annealed until low-energy electron diffraction (LEED) showed a well-ordered $c(2 \times 8)$ reconstruction (c means centered). Sn was evaporated onto the clean surface at RT, and the sample was annealed to 473K to obtain a sharp $\sqrt{3}$ LEED pattern. Upon cooling of the sample to 115K, the surface displayed a (3×3) reconstruction. The coverage of Sn on the surface was determined to be 0.29 ± 0.03 ML by *ex situ* Rutherford backscattering spectroscopy.

During the XSW measurements, the Ge single-crystal substrate was scanned in angle through a selected hkl Bragg peak, and the induced modulation in the Sn L-shell

x-ray fluorescence yield was measured by using a solid-state Ge detector. The incident beam energy was set at $E\gamma = 7.00$ keV by the Si(111) high-heat-load beamline 5-ID monochromator and horizontally focussed with a pair of glass mirrors. The beam was further conditioned with a pair of nondispersive, Si channel-cut (two-bounce) post-monochromators that were tuned to produce a strongly modulating XSW in the Ge. For each hkl reflection from the Ge substrate, the corresponding hkl reflection was selected for the Si post-monochromators to minimize dispersion. Two Bragg reflections normal to the surface, (111) and (333), and two off-normal reflections, $(11\bar{1})$ and $(33\bar{3})$, were measured at RT and LT.

Generating a direct-space atomic density map $\rho(r)$ from XSW-measured Fourier coefficients is simple and straightforward. One needs only to accurately measure a set of Fourier coefficients over a sufficient range of reciprocal space, apply certain symmetry rules¹ and sum up the Fourier terms, as shown below:

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{\mathbf{H}} \mathbf{F}_{\mathbf{H}} \exp[-2\pi i(\mathbf{H} \cdot \mathbf{r})] \\ &= 1 + 2 \sum_{\mathbf{H} \neq -\mathbf{H} \neq 0} f_{\mathbf{H}} \cos[2\pi(P_{\mathbf{H}} - \mathbf{H} \cdot \mathbf{r})]\end{aligned}$$

Results and Discussion

The results from the XSW measurements are summarized in Table 1. At both 300 and 115K, the measured $P_{\mathbf{H}}$'s are the same within experimental error. The reduction in $f_{\mathbf{H}}$ at LT is caused by Sn interacting over time with adsorbed gases. During the XSW experiments, the normal (111) reflection was measured several times to monitor the decrease of f_{111} (P_{111} remained constant). The fraction of randomly distributed Sn ($1 - C$) increased by 10% over a 24-hour period. Just before and after the sample was cooled to 115K, identical results were obtained for P_{111} and f_{111} at both RT and LT.

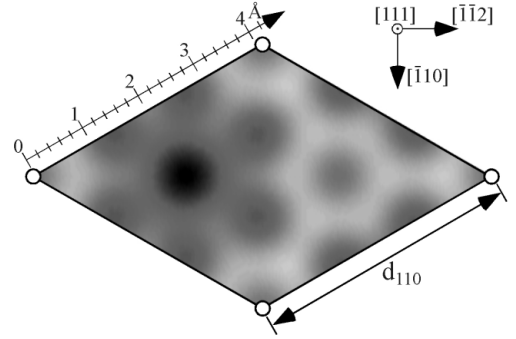
TABLE 1. Summary of the XSW results for a 0.29 ± 0.03 ML Sn/Ge(111) surface. The origin ($P_{\mathbf{H}} = 0$) is centered on the bulk-like Ge site in the top of the bilayer.

(hkl)	RT, $\sqrt{3}$, 300K		LT, (3×3) , 115 K	
	$P_{\mathbf{H}}$	$f_{\mathbf{H}}$	$P_{\mathbf{H}}$	$f_{\mathbf{H}}$
(111)	0.63 (1)	0.73 (1)	0.64 (1)	0.63 (1)
$(11\bar{1})$	0.54 (2)	0.75 (2)	0.53 (2)	0.64 (2)
(333)	0.77 (2)	0.33 (2)	0.82 (3)	0.22 (3)
$(33\bar{3})$	0.62 (2)	0.52 (2)	-	-

¹ In general, for XSW measurements, $P_{\mathbf{H}} = -P_{\bar{\mathbf{H}}}$ and $f_{\mathbf{H}} = f_{\bar{\mathbf{H}}}$. The Ge(111) threefold surface normal axis yields equivalent results for $(hk\bar{l})$, $(\bar{h}kl)$, and $(h\bar{k}l)$.

The XSW-measured Fourier coefficients for the sample at RT are used to create the direct space density map in Fig. 2. The top view is a cross-sectional cut through the 3-D image at 2.0 Å above the surface, and the side view is through the long diagonal of the (1×1) unit cell. In these images, the dark spots, representing the Sn atom maximum density, are located in the T_4 -site and are centered ~ 2.0 Å above the top of the bulk-like bilayer. The density oscillations appearing in the image are the result of unmeasured Fourier coefficients that abruptly truncate the summation. Since the XSW is generated by the Ge substrate, the atomic distribution is projected into the primitive unit cell of the Ge crystal. Thus, if there are two distinct heights in the 2-D superlattice, their projections will superimpose to form a combined distribution. The resolution of this method along the $[111]$ direction corresponds to one-half of the smallest

Top view along $[111]$ at height of 2.0 Å



Side view along $[\bar{1}10]$ and at the diagonal

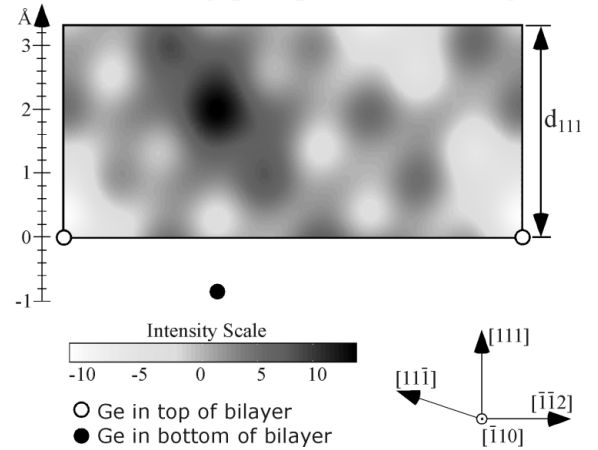


FIG. 2. XSW direct space atomic density maps for the $1/3$ ML Sn/Ge(111) surface at RT. The XSW measurements project the extended structure into the primitive unit cell of the bulk crystal. The top view corresponds to a (1×1) 2-D unit cell. The circles added to the image represent the bulk-like top bilayer Ge atomic sites.

d-spacing measured: in this case, $d_{333}/2 = 0.5 \text{ \AA}$. Within this resolution, the Sn distribution is elongated in the [111] direction but does not show two distinct positions in the direct space image. Rather, the two positions are smeared together and result in a bottom-heavy ovoid shape in the direction normal to the surface.

While the XSW direct-space imaging technique is useful for determining the position of the adsorbate *a priori*, the XSW results can also be used to precisely determine the positions of the Sn atoms with respect to a model that is suggested by this XSW direct-space image and other techniques. By using the normal (111) and (333) XSW measurements, the vertical distribution for the Sn atoms can be determined by using a model with the following constraints: (1) a fraction C of Sn atoms are at T_4 -sites; (2) the remaining fraction $(1 - C)$ are randomly distributed; (3) for Sn at the T_4 -sites, $1/3$ are at height h_A and $2/3$ are at height h_B ; and (4) the rms vibrational amplitudes $\langle u^2 \rangle^{1/2}$ for all Sn atoms are identical and isotropic. The $1/3$ and $2/3$ weightings are based on the 1:2 Sn arrangement observed with STM at LT [2].

These model constraints permit a single adsorption height and do not necessarily assume either a one up and two down or two up and one down configuration. The fact that P_{333} is measured to be less than $3P_{111}$ modulo-1 (i.e., $0.77 < 0.89$) indicates a bottom-heavy, asymmetric distribution that is consistent with one up and two down. If the time-averaged up:down occupation ratio was even, P_{333} would equal $3P_{111}$ modulo-1; and if it was 2:1, P_{333} would be greater than $3P_{111}$ modulo-1. A Fourier coefficient in the [111] direction and its measured amplitude f_H and measured phase P_H are related to the four parameters of the model as follows:

$$\begin{aligned} F_H &= f_H \exp(2\pi i P_H) \\ &= C \exp\left(\frac{-2\pi^2 m^2 \langle u^2 \rangle}{d_{111}^2}\right) \times \\ &\quad \left[\frac{1}{3} \exp\left(\frac{2\pi i m h_A}{d_{111}}\right) + \frac{2}{3} \exp\left(\frac{2\pi i m h_B}{d_{111}}\right) \right] \end{aligned}$$

For the 111 reflection $m = 1$, and for the 333 reflection $m = 3$. By using the (111) and (333) measured values of P_H and f_H in Table 1, the four unknown model parameters can be determined. At RT, the Sn atoms have a one up and two down configuration, where $h_A = 2.32 \pm 0.05 \text{ \AA}$ and $h_B = 1.87 \pm 0.05 \text{ \AA}$. The vibrational amplitude for the Sn atoms was determined to be $\langle u^2 \rangle^{1/2} = 0.08 \pm 0.04 \text{ \AA}$, and the Sn random fraction $(1 - C)$ for this sample was 0.18 ± 0.04 .

Although the T_4 -site assignment is in agreement with the SXRD results [1, 3], the XSW-measured vertical distribution of Sn atoms is different. At RT, Bunk et al.

[3] determined a single position for the T_4 -site Sn atom and refined the height to be 1.84 \AA above the surface. While their structure at LT has a similar Sn distribution (one up and two down), their model has a smaller vertical separation in height (0.26 \AA). The model proposed by Avila et al. has a comparable vertical split in height (0.49 \AA), at both RT and LT. However, their distribution showed the opposite asymmetry (two up and one down) [1].

In conclusion, the measured Sn XSW Fourier coefficients for a select set of hkl Ge Bragg reflections are combined to produce a 3-D-direct space image of the Sn atom distribution within the Ge primitive unit cell. For the $\sqrt{3}$ phase at RT, these XSW measurements show that Sn adatoms are at the T_4 -site, with two-thirds of the Sn at 1.87 \AA above the top of the bulk-like Ge bilayer and one-third of the Sn at 2.32 \AA (i.e., one up and two down). The time-averaged Sn distribution, when projected into the (1×1) unit cell, shows no significant change when going through the phase transition. This agrees with an order-disorder transition in which Sn atoms are “frozen” below T_C and undergo correlated fluctuations above T_C , with little time spent in transition between the two heights [5].

Acknowledgments

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