X-ray standing wave imaging of the $\frac{1}{3}$ monolayer Sn/Ge(111) surface

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X-ray standing waves (XSW) are used to measure the structure of the ($\sqrt{3}\times\sqrt{3}$)R30° to (3×3) low-temperature phase transition for the $\frac{1}{3}$ monolayer Sn/Ge(111) surface. A three-dimensional direct-space imaging approach, based on the summation of several hkl XSW-measured Fourier coefficients, is demonstrated. At room temperature, the Sn atoms are found to occupy the $T_d$-adsorption sites with one-third of the Sn atoms 0.45 Å higher than the remaining two-thirds. The (3×3) phase has no significant change in the XSW-measured structural parameters. This is consistent with an order-disorder-type phase transition.

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Insight into the two-dimensional (2D) physics of surface phase transitions, dynamics, and kinetics often requires an accurate atomic-scale description. For example, at room temperature (RT), the $\frac{1}{3}$ ML (monolayer) Sn on Ge(111) surface forms a ($\sqrt{3}\times\sqrt{3}$)R30° (to be called $\sqrt{3}$) reconstruction and is typically modeled with a single Sn atom occupying one of three $T_d$-adsorption sites in the $\sqrt{3}$ unit cell (see Fig. 1). When cooling from the critical temperature ($T_c$~210 K) to near 100 K, the surface reconstruction completes a gradual and reversible transition to a (3×3) phase. Scanning tunneling microscopy (STM) images show one of the $T_d$-site Sn atomic protrusions in the (3×3) unit cell appearing different than the other two. Despite numerous investigations into this system, the structure and nature of this transition are still unresolved. To study this apparent broken symmetry in this system, the structure and nature of this transition are still unresolved.

The leading models for this phase transition generally fall into either a displacive or an order-disorder transition. In the former, one model is that Ge atoms replace Sn atoms on the surface to form substitutional point defects. At RT the Sn atoms nearest to the Ge defects appear as small regions of (3×3) phase that increase in area as the temperature is lowered. Petersen et al. proposed that the Ge defects locally freeze in a soft phonon mode for the (3×3) phase. In an order-disorder explanation of the transition, Avila et al. used molecular dynamics to show that the vertical distribution of Sn atoms is attributed to dynamical fluctuations where the Sn atoms fluctuate between the two heights and spend little time in transition between the two positions. At low temperature (LT), the three Sn atoms in the unit cell are locked into a “one up and two down” configuration with long-range order and form the ground-state (3×3) phase. As the temperature increases, the long-range order in the vertical distribution of the Sn atoms is lost because the Sn atoms undergo correlated, rapid fluctuations between the two heights. At RT STM and diffraction observe the smaller $\sqrt{3}$ unit cell because all of the Sn atoms appear equivalent due to time averaging of the rapid interchanging of their heights.

To better understand this phase transition, the atomic-scale structures for the phases need to be accurately quantified. Several surface x-ray-diffraction (SXRD) experiments have been completed for this system but have come to somewhat different conclusions. The main controversies are whether the Sn atoms (and underlying Ge atoms) possess a rippled topography at both RT and LT, and whether the topography is one up and two down or “two up and one down.”

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, model-independent, and provide the projected positions of the Sn atoms within the 3D 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. A model with displacement of Sn atoms would predict that the XSW results would differ between the RT and LT, while the XSW finding of an unchanged vertical distribution would support an order-disorder transition.

Typically, to determine the adsorption site with the XSW technique, the positions of the atoms are triangulated using two measurements, one normal to the surface and the other off-normal to the surface. A top view of the $\frac{1}{3}$ ML Sn/Ge(111) surface showing the top Ge bilayer (two layers separated by $d_{111}/4$) and Sn adatoms in one-third of the $T_d$ sites. The (1×1), $\sqrt{3}$, and (3×3) surface unit cells are drawn in black, gray, and dashed lines, respectively.

FIG. 1. Top view of the $\frac{1}{3}$ ML Sn/Ge(111) surface showing the top Ge bilayer (two layers separated by $d_{111}/4$) and Sn adatoms in one-third of the $T_d$ sites. The (1×1), $\sqrt{3}$, and (3×3) surface unit cells are drawn in black, gray, and dashed lines, respectively.
the Sn atoms. In the dipole approximation for the photoelectric effect, the normalized XSW fluorescence yield for an atom is

\[ Y(\theta) = 1 + R(\theta) + 2f_H\sqrt{R(\theta)}\cos(\nu(\theta) - 2\pi P_H). \] (1)

The sample preparation and measurements were performed in an ultrahigh-vacuum chamber coupled to a six-circle diffractometer located at the 5ID-C DND-CAT undulator station of the Advanced Photon Source. The base pressure for the chamber was \(2 \times 10^{-10}\) 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. Sn was evaporated onto the clean surface at RT, and the sample was annealed to 473 K to obtain a sharp \(v^3\) LEED pattern. Upon cooling the sample to 115 K, the surface displayed a \((3 \times 3)\) reconstruction. The coverage of Sn on the surface was determined to be 0.29(3) ML by ex situ Rutherford backscattering spectrometry.

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 \(L\) x-ray fluorescence yield was measured 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 5ID monochromator and horizontally focused with a pair of glass mirrors. The beam was further conditioned with a pair of nondispersive, Si channel-cut (two-bounce) postmonochromators that were tuned to produce a strongly modulating XSW in Ge. For each \(hkl\) reflection from the Ge substrate, the corresponding \(hkl\) reflection was selected for the Si postmonochromators 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.

Conventional x-ray-diffraction methods suffer from the so-called “phase problem” because only the amplitude of the diffracted plane wave is detected. Whereas in XSW, the “detector” is the fluorescent atom, located within the interference field, which senses both the amplitude and the phase of the diffracted plane wave. For this reason, the XSW technique determines the amplitudes \(f_H\) as well as the phases \(P_H\) of the measured Fourier coefficients, \(F_H = f_H \exp(2\pi i P_H)\). In the formalism of crystallography, these are the geometrical structure factors (including the Debye-Waller factor) for the individual sublattices of each fluorescent atomic species. Dynamical diffraction theory was used to fit the reflectivity (rocking) curve \(R(\theta)\), and the fluorescence yield \(Y(\theta)\), to obtain the coherent position \(P_H\) and coherent fraction \(f_H\) for the Sn atoms.\(^{20,21}\) In the dipole approximation for the photoelectric effect, the normalized XSW fluorescence yield for an atom is

\[ Y(\theta) = 1 + R(\theta) + 2f_H\sqrt{R(\theta)}\cos(\nu(\theta) - 2\pi P_H). \]

The 180° phase shift in the XSW phase, \(\nu(\theta)\), while scanning in angle \(\theta\) through the Bragg peak causes a modulation in the yield that is sensitive to the atomic positions. To verify that the data collection and analysis procedure were responding correctly, the Ge \(L\) x-ray fluorescence from the substrate was analyzed and found to agree with the Ge bulk crystal structural positions \((P_{111} = 0.88, f_{111} = 0.70)\). The (111) RT results are shown in Fig. 2 as a representative set of XSW data and analysis. In this analysis the origin is centered on the ideal bulklike Ge site in the top of the bilayer. The XSW results for this sample are summarized in Table I. At both 300 K and 115 K the measured \(P_H\) are the same, within experimental error. The reduction in \(f_H\) 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 h period. Just before and after cooling the sample to 115 K, identical results were obtained for \(P_{111}\) and \(f_{111}\) at both RT and LT. In general, \(f_H\) decreases with \(C\) as the separation between atoms approaches \(d_{hkl}/2\).

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 Fou-

\[ \begin{array}{cccccc}
\text{hkl} & P_H & f_H & P_H & f_H \\
(111) & 0.63(1) & 0.73(1) & 0.64(1) & 0.63(1) \\
(11\bar{1}) & 0.54(2) & 0.75(2) & 0.53(2) & 0.64(2) \\
(333) & 0.77(2) & 0.33(2) & 0.82(3) & 0.22(3) \\
(33\bar{3}) & 0.62(2) & 0.52(2) & & &
\end{array} \]
X-RAY STANDING WAVE IMAGING OF THE $\frac{1}{3}$... cell of the Ge crystal. Thus if there are two distinct heights in the 2D 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 $d$ spacing measured, in this case $d_{333}/2=0.5$ Å. 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. Using the normal (111) and (333) XSW measurements, the vertical distribution for the Sn atoms can be determined 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, $\frac{1}{3}$ are at height $h_A$ and $\frac{2}{3}$ are at height $h_B$; (4) the rms vibrational amplitudes $\langle u^2 \rangle^{1/2}$ for all Sn atoms are identical and isotropic. The $\frac{1}{3}$ and $\frac{2}{3}$ weightings are based on the 1:2 Sn arrangement observed with STM at LT.

These model constraints permit a single absorption height and do not necessarily assume 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-to-down occupation ratio were even, $P_{333}$ would equal $3P_{111}$ modulo 1; and if it were $2:1$, $P_{333}$ 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:

$$F_H = f_H \exp(2\pi i P_H) = C[\frac{1}{3} \exp(2\pi i h_A / d_{111}) + \frac{2}{3} \exp(2\pi i h_B / d_{111})] \exp(-2\pi^2 m^2 (u^2) / d_{111}^2).$$

For the 111 reflection $m=1$ and for the 333 reflection $m=3$. Using the (111) and (333) measured values of $P_H$ and $f_H$ in Table I, the four unknown model parameters are determined. At RT, the Sn atoms have a one up and two down configuration, where $h_A = 2.32(5)$ Å and $h_B = 1.87(5)$ Å. The vibrational amplitude for the Sn atoms was determined to be $\langle u^2 \rangle^{1/2} = 0.08(4)$ Å, and the Sn random fraction (1-$C$) for this sample was 0.18(4).

Although the $T_4$-site assignment is in agreement with the SXRD results, the XSW-measured vertical distribution of Sn atoms is different (see Fig. 2). At RT Bunk et al. determined a single position for the $T_4$-site Sn atom and refined the height to be 1.84 Å 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 Å. The model proposed by Avila et al. has a comparable
vertical split in height, 0.49 Å, at both RT and LT. However, their distribution showed the opposite asymmetry, two up and one down.\textsuperscript{10}

The XSW-determined model parameters appear most similar to those by Petaccia and Floreano \textit{et al.}, who made photoelectron-diffraction (PED) measurements on the (3 × 3) phase and used He diffraction to study the effect of temperature on the local structure of Sn.\textsuperscript{25–27} By analyzing PED from the Sn 4d core level, they determined bond information between Sn and the neighboring Ge atoms and found a one up and two down Sn distribution, however, the difference in heights was 0.3 Å. Their temperature studies found an order-disorder behavior near \(T_C\). The measured XSW values for coherent position and fraction were found to be the same for the normal values for coherent position and fraction were found to be comparable or lower than the barrier height for the transition.\textsuperscript{13}

In a separate set of XSW measurements\textsuperscript{28} on the 1/3 ML Sn/Ge(111) system, the sample was annealed to a higher temperature (573 K) and different values for the Fourier coefficients were found. The analysis of this data indicates an additional, third Sn position, corresponding to Sn substituting for Ge in the bottom of the surface bilayer. This particular 30 min, 573 K thermally activated interfacial diffusion led to 20% of the Sn migrating to this site (compared to less than 5% in the 473 K anneal experiment described above). These results complement STM images that indicate Ge substituting for Sn in the \(T_C\) site.\textsuperscript{14,15}

In conclusion, the measured Sn XSW Fourier coefficients (amplitude and phase) for a selected set of \(h\)\(k\)\(l\) Ge Bragg reflections are combined to produce a 3D direct-space image of the Sn atom distribution within the Ge primitive unit cell. For the \(v3\) phase at RT, these XSW measurements show that Sn adatoms are at the \(T_A\) site with two-thirds of the Sn at 1.87 Å above the top of the bulklike Ge bilayer and one-third of Sn at 2.32 Å, i.e., one up and two down. The time-averaged Sn distribution, when projected into the \((1 \times 1)\) 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” in below \(T_C\) and undergo correlated fluctuations above \(T_C\), with little time spent in transition between the two heights.\textsuperscript{5,11} The magnitude (0.45 Å) of the Sn vertical separation from the XSW results agrees with the soft phonon model\textsuperscript{11} at RT, where the Sn atoms undergo a correlated 0.5 Å switching in their vertical positions.

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23 In general for XSW measurements, \(P_{\mu} = -P_{\bar{\mu}}\) and \(f_{\mu} = f_{\bar{\mu}}\). For the Ge(111) surface the threefold surface normal axis yields equivalent results for \((h\bar{k}l), (h\bar{k}l),\) and \((h\bar{k}l)\).

24 This formulation has also been used to generate 1D distribution functions of bulk impurities in mica. See L. Cheng, P. Fenter, M. J. Bedzyk, and N. C. Sturchio, Phys. Rev. Lett. \textbf{90}, 255503 (2003).


