TWO-DIMENSIONAL SMALL ANGLE SCATTERING FROM SUBMONOLAYER ISLANDS

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ABSTRACT

Motivated by surface x-ray scattering experiments on homoepitaxially grown Ag(001), scattering models for surfaces having submonolayer coverages are discussed in the context of small angle scattering. It is shown that the surface diffuse line shapes can be interpreted in terms of intra-island and inter-island scattering. The connection between these models and other surface experiments is also discussed.

INTRODUCTION

There has been considerable interest in understanding the morphology of a growing crystal surface$^1$ and diffraction as well as scanning-probe (SPM) techniques have been used for surface characterization. SPM techniques provide images in real space and the spatial specificity of SPM is particularly valuable for investigating mechanistic behavior on a local scale. However, scattering methods remain as indispensable tools because of their unique suitability for in situ studies where the temperature or other conditions must be changed and for their natural ability to reveal spatial correlations. Scattering tools used for surfaces include electron, atom, and x-ray scattering.

X-ray scattering, in particular, is kinematic and is well suited for quantitative experiments. However, it is often difficult to work backwards to a specific structural configuration from the correlation functions observed in scattering experiments. Thus, it would be useful to improve the ability to extract information on the surface morphology from the experimental scattering data. Models have been developed which describe surfaces in terms of terrace size distributions$^{2,3}$, although, these models have been largely one-dimensional in nature and do not fully allow for the correlations that will be present on the surface. Even in the submonolayer regime, where there are only two crystalline height levels present, the interpretation of experiments can be problematic$^4$.

In this paper, we discuss the two level problems in surface scattering (two dimensions), which is analogous to small angle scattering$^5$ in three dimensions. Connection will be made to experimental studies of Ag(001) that have taken rather different approaches to the analysis of the data$^{4,6,7,8}$.
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Figure 1. Transverse scans through the (110) in-plane position, as described in the text, for different coverages of Ag on Ag(001) at 250 K. The diffuse line shape is different at half-integer coverage than for whole-integer coverage.

EXPERIMENTAL

Experiments were performed in an ultra-high vacuum chamber (ambient = low $10^{-10}$ Torr) located on the SUNY X3B2 beamline at the National Synchrotron Light Source using a wavelength of $\lambda = 1.0207$ Å. The Ag(001) crystal was prepared, in situ, by repeated Ar ion sputtering and annealing (>700 C) cycles – the experiments are essentially performed on a collection of naturally formed (001) facets which have a typical dimension of ~ 5000 Å. Ag was deposited onto the crystal at a rate of approximately 0.1 monolayer (ML) per minute, in situ, from a thermal oven. The scattering measurements were performed in a grazing incidence geometry where the incoming and outgoing beams made equal angles (~0.3 degrees) with the surface. The scattering vector was essentially located in the surface plane near the (110) anti-Bragg position (“out-of-phase” beam) and the scans were performed by rotating the sample about the surface normal. This yields a scan through (110) along an arc in the plane of the surface, approximately along [1-10]; in Fig. 1, $q$ is the distance in reciprocal space from (110) along this direction.

Figure 1 shows the scans for three coverages deposited at 250 K. Each exhibits a two component line shape: a narrow, resolution-limited, central peak having an intensity attenuated by the rms surface roughness; and a broad diffuse scattering. Because Ag(001) exhibits near layer-by-layer
growth, the narrow central peak has low intensity at half-monolayer coverages due to the presence of islands but its intensity recovers for the smoother surface at whole-monolayers. This cycle of intensity oscillation is found\textsuperscript{9} to repeat with a period of one ML, although the intensity tends to slowly decay over many layers due to the non-ideal layer-by-layer growth. This is the same phenomenon that is often observed in reflection high-energy electron diffraction (RHEED).

Here, we focus on the diffuse scattering, which has a shape that is also found\textsuperscript{8} to oscillate with ML period. The half-ML coverages exhibit lobes of intensity that have maxima at \( q \neq 0 \) whereas the whole-ML coverages have intensity that is peaked at \( q=0 \) and the integrated intensity is larger. The trend of the data in Fig. 1 essentially continues upon further coverage due to the layer-by-layer nature of the growth and a similar evolution has also been observed by van der Vegt et. al\textsuperscript{6}. A full presentation of our experiments will appear elsewhere\textsuperscript{8}; here, we shall concentrate on a discussion of submonolayer scattering models.

**SCATTERING MODEL AND DISCUSSION**

The scattering, which peaks at \( q \neq 0 \), is similar to *inter*-particle correlations in conventional (3D) small-angle scattering. Similarly, the presence of diffuse scattering peaked at \( q=0 \) suggests *intra*-particle scattering. This observation motivates an analysis in terms of 2D small angle scattering from the surface where we will consider only two atomic layer heights because of the relatively smooth surface, even when several monolayers have been deposited. This interpretation has also been discussed by Bardotti et. al\textsuperscript{4}.

The differential scattering cross section is given by a sum over all atomic positions \( \vec{r} \) parallel to the surface\textsuperscript{11}:

\[
\frac{d\sigma}{d\Omega} = P(Q)b^2(Q) \left| \sum_{\vec{r}} e^{i\vec{q} \cdot \vec{r}} e^{iQ_z c m(\vec{r})} \right|^2 = P(Q)b^2(Q) \left| A(\vec{q}, \phi) \right|^2 \left| 1 - e^{i\phi} \right|^2
\]

where \( Q_z \) and \( \vec{q} \) are the momentum transfer perpendicular and parallel to the surface, respectively. \( P(Q) \) is the polarization factor and \( b(Q) \) is the atomic scattering length (for x-rays, this is the atomic form factor times the classical electron radius). \( N \) is the total number of atomic sites across the surface, and \( cm(\vec{r}) \) is the height of the surface at position \( \vec{r} \) where \( c \) is the lattice spacing perpendicular to the surface and \( m \) is an integer. The scattering amplitude \( A \) contains all of the information about the surface correlations and the denominator is the so-called “crystal truncation rod” factor that is necessary for the case of x-ray scattering. \( \phi = Q_z c \) is a phase and is equal to \( \pi \) for the data in Fig. 1 (anti-Bragg or out-of-phase condition).
Considering only two height levels,

\[ A(q, \varphi) = \sum_{\tilde{r}} e^{i\tilde{q} \cdot \tilde{r}} (1 - \theta(\tilde{r})) + e^{i\varphi} \sum_{\tilde{r}} e^{i\tilde{q} \cdot \tilde{r}} \theta(\tilde{r}) \]

\[ \equiv A_T + e^{i\varphi} A_I \]

where \( A_T \) is a scattering amplitude for the lower level (the terraces) and \( A_I \) is the amplitude for the upper level (the islands). \( \theta(\tilde{r}) \) is 0 or 1 for the absence or presence of an island, respectively, at the position \( \tilde{r} \). It can be seen from equation (2) that \( |A|^2 \) for a surface with islands is indistinguishable from a surface with holes. Using the fact that phase information is lost at the lateral sample boundaries,

\[ |A|^2 = (2\pi)^2 n_a N \left[ 1 - 2\Theta J (1 - \cos \phi) \right] \delta^{(2)}(q) + 2(1 - \cos \phi) A_I \]

where \( n_a \) is the number of atomic sites per area and \( \delta^{(2)}(q) \) is a two-dimensional delta-function. Due to the equivalence of scattering from islands or holes, \( A_I \) is either \( A_T \) or \( A_I \) and \( \Theta_J \) is either \( \Theta \) or \( 1 - \Theta \), respectively, where \( \Theta \) is the coverage. Without loss of generality, we will consider the case of islands, below.

The 2D small angle scattering approach represents the position within an island in terms of a position of the island, \( \tilde{R} \), and a position, \( \tilde{u} \), relative to \( \tilde{R} \) such that \( \tilde{r} = \tilde{R} + \tilde{u} \). Then,

\[ A_I = \sum_{R} e^{i\tilde{q} \cdot \tilde{R}} f_R(q) \quad \text{where} \quad f_R(q) = \sum_{\tilde{u}} e^{i\tilde{q} \cdot \tilde{u}} \theta(\tilde{R} + \tilde{u}) \]

where \( f_R(q) \) is the “form factor” of an island located at \( \tilde{R} \) and \( N_I \) is the number of islands. This will work as long as one can identify island positions. If the upper level is connected continuously across the sample surface then one can describe the holes (the terrace level) instead of islands, as it is unlikely that both the islands and terraces connect continuously across the sample surface.

If the island size is uncorrelated with the size of neighboring islands, and if the island sizes are uncorrelated with the separation distance between islands, then one can write:

\[ |A_I|^2 = N_I \left\{ \langle |f|^2 \rangle + \langle |f| \rangle^2 \int d^2 \tilde{r} \rho(\tilde{r}) e^{-i\tilde{q} \cdot \tilde{r}} \right\} \]

where \( <> \) indicates an average over the surface and \( \rho(\tilde{r}) \) is the number density of islands at \( \tilde{r} \) when there is an island located at \( r=0 \). Because at an infinite distance away \( \rho(\infty) \) saturates to a constant value, eq.(5) will also contribute a delta component so that the final result becomes:
The delta (resolution-limited) component contains information on the uncorrelated roughness of the surface and should vanish for half coverage when $\phi = \pi$. In Fig.1, a residual delta component is found for nominal half-ML coverage, which is probably due to a slight inaccuracy in the coverage. A small third-layer occupancy or inaccuracy in $\phi$ would also have a similar effect.

The first term of the diffuse scattering represents the intra-island scattering whereas the second term contains the inter-island correlations. Since the form factor for the islands is peaked at $q=0$, the double-lobe shape of the diffuse scattering comes only from inter-island correlations with $\rho(r)$ having a maximum at some finite distance.

We now use these ideas to discuss the results in Fig. 1. For whole-ML coverage, the spatial correlation between islands is evidently insignificant. Clearly the correlated part of the diffuse scattering will be weak since the islands (or holes, which are equally likely in this case) cover a small fraction of the surface. Also, as will be shown below, the depletion around an existing island plays an important role in defining the correlation – with a long depletion region at low coverage, the correlation between islands will be poorly defined. Finally, island sizes that are small relative to their separation permit large island-size fluctuations so that $A_{\text{diff}}^2 >> A_{\text{delta}}^2$.

Thus, the intra-island scattering dominates the diffuse intensity near whole-ML coverage.

For fractional coverages that are not small enough to fall within this regime, the islands occupy a larger portion of the surface and the island size fluctuations will be smaller. Moreover, the depletion around an island is more effective in defining the island separation, as will be shown below. Thus, the lobes in Fig.1 arise from the inter-island scattering.

In a recent electron scattering study of Cu/Cu(001) by Dürr et. al.\textsuperscript{12}, two components of diffuse scattering were observed simultaneously: a two-lobe feature was found along with a much weaker and broader central diffuse peak. By studying the coverage dependence, they attributed the latter to the island size. From the discussion of eq. (6), it is clear these are the two diffuse contributions associated with inter-island and intra-island scattering, respectively.

The diffuse lobes appear to be a convenient method to extract the average island separation. However, kinetic Monte Carlo (KMC) simulations\textsuperscript{4} have empirically demonstrated a coverage-dependent polynomial correction to the island separation obtained from the diffuse intensity when the island density is constant. We can show this effect analytically from the model in eq. (6) where the peak positions are biased by the form factor of the islands which has a maximum at $q=0$. Assuming a Gaussian for the island form factor (without loss in generality for small island size, since this gives the correct curvature at $q=0$) and a Lorentzian for the inter-island correlations (which is close to the experimental line shapes), the intensity is:

$$|A|^2 = |A_{\text{delta}}|^2 + |A_{\text{diff}}|^2$$

$$|A_{\text{delta}}|^2 = (2\pi)^2 n_a N \{1 - 2(1 - \cos \phi)\Theta(1 - \Theta)\} \delta^{(2)}(\vec{q})$$

$$|A_{\text{diff}}|^2 = 2(1 - \cos \phi) N_1 \{\langle |f|^2 \rangle + \langle f \rangle^2 \} d^2 \vec{r} [\rho(\vec{r}) - \rho(\infty)] e^{-i\vec{q} \cdot \vec{r}}$$

The delta (resolution-limited) component contains information on the uncorrelated roughness of the surface and should vanish for half coverage when $\phi = \pi$. In Fig.1, a residual delta component is found for nominal half-ML coverage, which is probably due to a slight inaccuracy in the coverage. A small third-layer occupancy or inaccuracy in $\phi$ would also have a similar effect.
\[
e^{-q^2D^2} \frac{\kappa^2 + (q \pm k_0)^2}{\kappa^2 + (q \pm k_0)^2},
\]

where \(D\) is assumed to be the island diameter, \(k_0 = \frac{2\pi}{S}\) where \(S\) is the island separation, and \(\kappa\) is the width of the diffuse lobes. The maximum of the diffuse lobe will shift to a value smaller than \(k_0\), according to

\[
|q_{\text{max}}| = k_0 \left\{ 1 + \frac{1}{2D^2k_0^2} \left[ -\left(1 + D^2\kappa^2\right) + \sqrt{\left(1 + D^2\kappa^2\right)^2 - 4D^4\kappa^2k_0^2} \right] \right\}.
\]

Note that for \(D \to 0\), \(q_{\text{max}} \to k_0\) as expected. Expanding eq. (8) for small \(D\) we obtain

\[
|q_{\text{max}}| \approx k_0 \left[ 1 - D^2\kappa^2 + \cdots \right].
\]

Using the fact that, at constant island density, the island diameter depends on coverage as, \(D^2 \propto \Theta\), we then expect a polynomial dependence on coverage,

\[
|q_{\text{max}}| \approx k_0 \left[ 1 - a\Theta + b\Theta^2 - \cdots \right].
\]

A similar form was reported by Bardotti et. al.\(^4\) from KMC simulations except that their extrapolation to \(\Theta = 0\) was slightly different than \(k_0\). This might arise from the large coverage considered and that their polynomial was actually a polynomial fit over a limited range of eq. (8). In any case, the experimental island separations will be longer than the actual values due to biasing of the form factor.

Although the above approach gives useful insight, it is probably most useful for small coverage. For larger coverage, there is another way to consider the diffuse scattering. Starting from the definition of \(A_i\) in eq. (2) and using the island-island correlation function, \(\langle \theta(\vec{r} + \vec{r}')\theta(\vec{r}')\rangle_{\vec{r}'}\),

\[
|A_i|^2 = N \sum_{\vec{r}} e^{i\vec{q} \cdot \vec{r}} \langle \theta(\vec{r} + \vec{r}')\theta(\vec{r}')\rangle_{\vec{r}'}
\]

\[
= \Theta N \sum_{\vec{r}} e^{i\vec{q} \cdot \vec{r}} P(\vec{r})
\]

where \(\langle \rangle\) indicates an average over all \(\vec{r}'\). Since the correlation function receives a nonzero contribution only when both \(\vec{r} + \vec{r}'\) and \(\vec{r}'\) have an island, we also introduce \(P(\vec{r})\), which is the probability to find an atom at \(\vec{r}\) to be at the island level if an island exists at \(\vec{r} = 0\). Because \(P(\infty) = \Theta\) is constant, eq. (9) will contribute to the delta intensity and the total delta intensity is the same as given in eq. (6). Explicitly removing the delta contribution, the diffuse intensity becomes,

\[
|A_{\text{diff}}|^2 = 2\Theta(1 - \cos\phi)N \sum_{\vec{r}} e^{i\vec{q} \cdot \vec{r}} \left[ P(\vec{r}) - \Theta \right]
\]
We can now explore the role that depletion of atoms around an island plays in determining the lineshape. The solid curve in Fig. 2 shows a plot of $P(\vec{r})$ for a large coverage. Because there is a high probability that no atoms are at the island level just outside of an island, there is a pronounced minimum in $P(\vec{r})$. This will give a peak at $q \neq 0$ in eq. (10) and two-lobe diffuse scattering will emerge. Alternatively, considering a small coverage in Fig. 2, it can be seen that the depletion plays a much smaller role, since, the probability has a lower bound at 0. Thus, the Fourier transform of a nearly monotonically changing shape will give diffuse scattering peaked at $q=0$ for this case.

![Figure 2. Schematic plot of P(r) for large coverage (solid line) and small coverage (dashed line). At small coverage, P(r) is nearly monotonic whereas oscillation is more pronounced at higher coverage.](image)

**CONCLUDING REMARKS**

It was seen that near whole-ML coverage the scattering is dominated by the intra-island size whereas near half-ML coverage the scattering is dominated by the inter-island correlation length. These features are readily understood from a 2D version of small angle scattering. However, near half-ML coverage, it is clear from Fig. 2 that the depletion region around the island plays a major role in the interference. Here, the inter-island correlation is defined mainly by the contrast between the island and its depletion region. This idea is utilized in a model by Pukite et. al.
where they correlate the island with the depletion region but neglect longer correlations. Van der Vegt et al.\textsuperscript{6} recently applied this model to experiments on Ag(001) where both the island size and separation were extracted. It should be noted that the 2D small-angle scattering approach is equivalent to that of eq. (10), since the former convolutes the island size with the inter-island correlation length.

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