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Authors

Yinnon, AT
Lidar, DA
Gerber, RB
[et al.](#)

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Structure Determination of Disordered Metallic Sub-Monolayers by Helium Scattering: A Theoretical and Experimental Study

A.T. Yinnon,^a D.A. Lidar (Hamburger),^{a,b} R.B. Gerber,^{a,c} P. Zeppenfeld,^d M.A. Krzyzowski,^d and G. Comsa^d

^a*Department of Physical Chemistry and The Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

^b*Department of Chemistry, University of California - Berkeley, Berkeley, CA 94720, USA*

^c*Department of Chemistry, University of California - Irvine, Irvine, CA 92697, USA*

^d*Institut für Grenzflächenforschung und Vakuumphysik, Forschungszentrum Jülich, Postfach 1913, D-52425 Jülich, Germany*

An approach based on He scattering is used to develop an atomic-level structural model for an epitaxially grown disordered sub-monolayer of Ag on Pt(111) at 38K. Quantum scattering calculations are used to fit structural models to the measured angular intensity distribution of He atoms scattered from this system. The structure obtained corresponds to narrowly size-dispersed compact clusters with modest translational disorder, and not to fractals which might be expected due to the low surface temperature. The clusters have up to two layers in height, the lower one having few defects only. The relations between specific features of the angular scattering distribution, and properties such as the cluster sizes and shapes, the inter-cluster distance distribution etc., are discussed. The results demonstrate the usefulness of He scattering as a tool for unraveling new complex surface phases.

I. INTRODUCTION

The physical and chemical properties of heteroepitaxial metallic sub-monolayers depend on their structure, and the determination of the latter is therefore of considerable technological and scientific importance. Scanning tunneling microscopy (STM) and scattering techniques have proved to be powerful methods for determining adlayer structure [1–8]. The STM technique, for instance, has many advantages but is inherently local and therefore the statistical characterization of disordered surfaces requires averaging over many surface patches. In contrast, a single atomic beam scattered from a surface can cover an entire adlayer at once. Thermal He scattering enjoys several additional advantages over other methods for identifying adlayer structure. (i) The wavelength of a thermal He atom matches the size of metal surface unit cells. (ii) Interference due to the quantum nature of the He particles results in a high sensitivity to surface details. (iii) The He atoms do not perturb the surface significantly. Finally, in contrast to x-rays and neutrons which penetrate the bulk, He atoms solely probe the topmost surface layer.

So far, little is known on the relation between different kinds of adlayer disorder and the corresponding scattering patterns, which is clearly necessary for the determination of structural properties from experiment. Studies in this field include the case of defects at very low concentration [9–12], models of translationally random small compact clusters [13,14] and fractal surfaces [15,16]. In this letter, we report a detailed atomic-level structure determination based exclusively on He scattering. We studied He scattering data for an epitaxially grown disordered Ag sub-monolayer on a Pt(111) surface at 38K. Using quantum scattering calculations, various models of surface disorder were compared to the experimental data. The sensitivity of the scattering distributions to

the structural features of the surface allowed us to progressively narrow down the class of disorder, until a satisfactory fit was obtained. A first step in this direction was taken in Ref. [17], where we showed that the broad classes of (a) isolated, translationally random adatoms and (b) fractal structures can be ruled out as plausible models of the surface structure. On the other hand a qualitative agreement was found with scattering intensities resulting from a model of translationally random, narrow size-dispersed compact clusters. Here we report new results revealing significant quantitative agreement between He scattering simulations and the same experimental data, from which a clear picture of the surface structure emerges. While the resulting fit between scattering intensities is not unique, the procedure introduced here for the analysis of He scattering data is at least capable of ruling out several plausible models of surface disorder. The structure identified in this procedure represents, in our view, a new metastable phase in the sense that it is composed of compact clusters with modest translational disorder, similar to that seen, e.g., in detailed STM experiments, mainly for Pt/Pt(111) [7].

II. EXPERIMENTAL PROCEDURE

The thermal He scattering experiments were performed in an ultrahigh vacuum (UHV) system. The Pt(111) sample was cleaned and characterized in situ and a sub-monolayer of Ag was evaporated onto the 38K Pt(111) surface by means of a Knudsen cell. The scattering apparatus was equipped with a time-of-flight (TOF) spectrometer, allowing to separate the elastic from the inelastic He scattering intensity. The scattered He atoms were recorded as a function of the wavevector transfer ΔK parallel to the surface. The outgoing He atoms were measured in the incidence plane. Thus

$\Delta K = k_i(\sin \theta_f - \sin \theta_i)$, where k_i is the incident wavevector, and θ_i, θ_f are the incident and outgoing scattering angles, respectively. The total scattering angle was held constant: $\theta_i + \theta_f = 90^\circ$.

Theoretical model: Scattering calculations were performed using the Sudden Approximation (SA) [18], which has proven to be very successful in describing scattering from both ordered [19] and disordered surfaces [20], where the very large grids required prevent the use of numerically exact techniques. The SA has been reviewed extensively [21]: it assumes that the momentum transfer parallel to the surface is small compared with that normal to the surface, i.e., $|\Delta K| \ll 2k_z$, where k_z is the wavevector component perpendicular to the surface. On the basis of the experience gained with the SA, including tests against numerically exact calculations [18,19], we estimate that the main predictions of the SA should be reliable for the systems considered here. The He-Pt interaction was modeled using the laterally averaged potential of Ref. [22] which was extracted from experimentally determined surface resonances on Pt(110). We assume that the He/Pt(111) potential is smooth along the surface. Other experimental and theoretical studies of the He/Pt(111) system support this to be an excellent approximation. A further assumption in this work is that the influence of surface vibrations on the elastic angular intensity distribution is small, so they can be neglected. The He/Ag adlayer interactions were represented by a sum of pairwise potentials between He and isolated, adsorbed Ag atoms. Clearly, on clustering of Ag adatoms, some rearrangement of the local electron density is to be expected. Still, we believe a pairwise potential to be a reasonable approximation, especially for small adatom islands. These seem to be present here based also on STM data [23]. The He/Ag adatom interaction was determined by fitting calculated SA single-adatom cross sections to experimental data. Our fitted potential accurately reproduces the experimental cross sections over a large range of incidence energies [17].

III. RESULTS

Our main experimental result is presented in Fig. 1: it shows the purely elastic scattering intensities for a He beam with $k_i = 6.43 \text{ \AA}^{-1} = 21.6 \text{ meV}$ impinging upon a Pt(111) surface covered with 0.5 monolayers of Ag. The orientation of the scattering plane is along the $[11\bar{2}]$ -direction. The main theoretical result is represented by the solid line: the calculated scattering intensities from the structure which we found to produce the best fit with the experimental data. Before going into details we present the central features of this structure: Nearly hexagonal islands with few atomic edge defects, of side-lengths 3-5 unit cells along the $[11\bar{2}]$ -direction, and a height of up to two layers. Such hexagons can accommodate 50-60 atoms and we find the average number of

atomic defects per island to be around 10. At a coverage of 0.5 monolayer about 65 islands are formed per 100^2 unit cells. Whereas our analysis can rule out a third layer, it is not sensitive to the detailed structure of the second layer. The existence of a second layer is corroborated by the dependence of in- and out-of-phase scattering on the incidence energy [24]. The average number of second layer atoms per island can be inferred to be about 30 from the numbers above. The positional distribution of the island centers deviates by no more than three Pt(111) lattice constants per island from a hexagonal superlattice with a lattice constant of 12-13 unit cells. A typical configuration of the first layer is shown in Fig. 2. Our analysis cannot exclude island-shapes differing slightly from hexagonal. However, the existence of compact clusters is supported by STM experiments at low temperatures [23]. The hexagonal shape is the energetically preferred one in such a system, although it must be kept in mind that equilibrium considerations need not necessarily prevail here. The main conclusion of our study is that the Ag layer produced in the experiment has the structure described above. It is remarkable that a *fractal* phase can be ruled out, as one may have expected fractals due to the low adatom mobility at our low surface temperature. A fractal surface would result in a *smooth* decay of the off-specular intensity [17], in complete discrepancy with the observed intensity pattern (Fig. 1). Having stated the structural characteristics of the surface, we turn to a presentation of the analysis which led us to our conclusions, and to a discussion of the sensitivity and uniqueness of our fit.

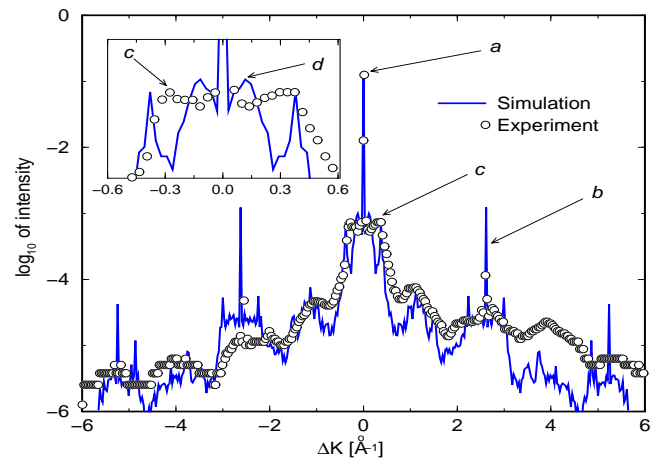


FIG. 1. Normalized, purely elastic scattering along the $[11\bar{2}]$ azimuth recorded from the Ag/Pt(111) system at 50% coverage and a surface temperature of 38K. Intensity normalized to that of incoming beam.

Features in the experimental angular intensity distribu-

tion due to *coherent* scattering can be assigned directly, whereas those due to various incoherent scattering mechanisms require comparison to simulation results of scattering from different types of disorder. We consider the following features:

Specular Peak: This feature contains information about island *corrugation* and *size*. The relatively large specular *intensity* (~ 0.1 , Fig. 1, arrow *a*) is typical of He scattering from a surface with large flat patches [25]. This serves as an indication of the smoothness of the Ag adlayer. Furthermore, off-specular scattering from metallic surfaces results mostly from collisions of He with the island-edge region [16]. Thus the large specular peak provides evidence for *compact* Ag islands, several atoms in diameter. In contrast, the *width* of the specular peak is determined by the average diameter d of the islands [17]. The observed width of 0.6\AA^{-1} results in $d \approx 21\text{\AA}$, or 8-9 Pt unit cells along the $[11\bar{2}]$ -direction [the Pt(111) lattice constant being $a=2.77\text{\AA}$], consistent with the above requirement of large islands. The simulation reproduces both the intensity and the width of the specular peak with remarkable accuracy.

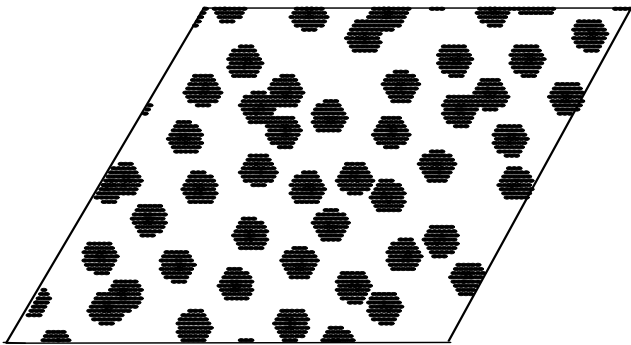


FIG. 2. Typical configuration of Ag islands on Pt(111).

Bragg Peaks: Strong Bragg interference peaks can be observed at $\Delta K = -2.54\text{\AA}^{-1}, 2.60\text{\AA}^{-1}$ (Fig. 1, arrow *b*). Although growth of the first Ag layer on Pt(111) is known to be pseudomorphic in the entire temperature range [24], another interpretation consistent with the data is that the average $|\Delta K| = 2.57\text{\AA}^{-1}$ is the result of an *effective unit cell length* of $4\pi/(2.57\sqrt{3}) = 2.82\text{\AA}$, in between the Pt(111) and Ag(111) values of 2.77\AA and 2.89\AA respectively. Indeed, strain does not permit the Ag islands to relax completely to their natural unit cell size. The absence of Pt(111) Bragg peaks indicates that the atomic corrugation of the island surface is much larger than that of the underlying Pt(111) layer. In our simulations only the island Bragg peaks are reproduced, as the Pt(111) surface is treated as completely flat. The discrepancy in intensities probably indicates that the pairwise additive potential is too repulsive in this case. Assignment of further features requires comparison with simulation.

Interference Maxima at $\Delta K = \pm 0.3\text{\AA}^{-1}$: Indicated by arrow *c* in Fig. 1 and shown enlarged in the insert, this

feature, unlike other interference peaks, is nearly independent of azimuthal direction, but does depend on surface temperature and the adsorption rate. It results from an interference between adjacent island *edges* and can thus be traced to a corresponding average *inter-island center-to-center distance* of $l \sim 30\text{\AA}$. The scattering calculations are extremely sensitive to this distance, along with the average island diameter d . As can be seen in Fig. 1, after extensive fine-tuning of the parameters l and d , the simulation results are compatible with this feature. This fit is one of the main sources of our confidence in the present structural determination, as the combination of l and d poses severe constraints on the allowed geometries at such high coverage. These constraints indicate almost directly an important structural aspect: The *modest* amount of translational disorder.

Other Off-Specular Peaks: A detailed theoretical analysis of the off-specular structure was given in Ref. [17]. Some of the peaks can be assigned to either Fraunhofer [9] or rainbow [14] scattering. These, in turn, can be traced back to the “form factor” due to scattering from an *isolated* island. An example is the peak indicated by arrow *d* in the insert of Fig. 1, which is probably a rainbow effect due to a single island. If in reality the electronic density shape depends on cluster size this is expected to be “washed out” in the experiment, as observed here. A great deal can be learned by a trial and error process attempting to assign peaks to islands of different sizes. One parameter which can be determined in this way is the island concentration. For a system consisting of isolated and randomly positioned *identical* islands the intensity of its characteristic off-specular peaks is proportional to the concentration [17]. However, when there is a distribution of island shapes and sizes, as in Fig. 2, each island contributes its own peaks and the simple proportionality is lost. Using the trial and error approach, we arrived at a concentration of 65 islands per 100^2 unit cells. As can be seen in Fig. 1, this yields a quantitative agreement for $\Delta K < 2\text{\AA}^{-1}$ between experiment and simulation, in peak positions, widths and intensities. The agreement is less quantitative for the intensities at $\Delta K > 2\text{\AA}^{-1}$, but a qualitative agreement remains, in that the positions of all minima and maxima are correctly reproduced. It should be mentioned that a basic flaw of the SA, in disagreement with experiment, is that it is symmetric in $\pm\Delta K$, regardless of the incidence angle. The SA inherently assumes small parallel momentum transfer [18], to which the discrepancy for high ΔK can be attributed. Nevertheless, the agreement is noteworthy for all ΔK , and highly sensitive to the parameters of the surface structure.

Uniqueness of the Structural Model: The scope of this letter will not permit us to convey in detail the sensitivity of the fit shown in Fig. 1. Essentially the only parameters of the adlayer that do *not* have a substantial effect on the calculated scattering intensities are the structure of the second layer and the detailed internal struc-

ture of the hexagons. However, all other parameters, and in particular the average island diameter and polydispersity in sizes, average distance and positional distribution, concentration and number of defects, strongly affect the quality of the fit and can be determined with a high degree of confidence by the present trial and error approach. Of course, our search was not entirely random but guided by insight as to which geometric structures can produce a certain feature. To illustrate this and the sensitivity of the intensity distribution to system parameters, consider some features of Fig. 3. Shown there are the calculated intensities for random distributions of non-overlapping perfect hexagons of (a) 91 Ag atoms, (b) 19 Ag atoms, (c) 19 or 91 Ag atoms (equal number of islands), all at 15% coverage. Arrow 1a indicates a peak which is characteristic of the 91-atom hexagons (a), and is absent in the intensity spectrum of the 19-atom hexagons (b). However, it is clearly present in the spectrum of the combined system, as indicated by arrow 1c. Similarly, arrow 2b points at a feature which is present for 19-atom hexagons but not for 91-atom hexagons, yet is present in the spectrum of the combined system, as shown by arrow 2c. The reader will easily recognize additional features in Fig. 3(c) which can be attributed uniquely to only one of the systems. In a manner similar to this we have been able to *resolve* the experimental intensity distribution of Fig. 1 and conclude that its features are due to the structure shown in Fig. 2.

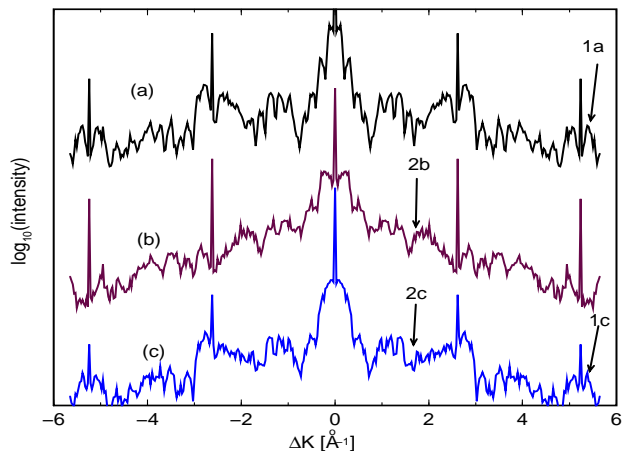


FIG. 3. Calculated He scattering intensities for various test systems of Ag hexagons on Pt(111). (a) 91 Ag atoms per hexagon; (b) 19 Ag atoms; (c) 19 or 91 atoms.

IV. CONCLUSIONS AND OUTLOOK

In conclusion, this study demonstrated that He scattering is capable of performing a “crystallography” of disordered surfaces. We reported one of the first theoretical-experimental detailed atomic-level structure determinations of a disordered surface layer by He scattering: A

well-defined geometry of narrowly size-dispersed, compact hexagonal clusters, with modest translational disorder, is formed by Ag deposited on Pt(111) at 38K. This geometry comes as a surprise, since it has been shown using variable-temperature STM that at 35K individual Ag adatoms do not diffuse on the Pt(111) surface on a time scale of at least two hours [26]. Our results clearly necessitate some mechanism for a significant lowering of the diffusion barrier. How this comes about must be contained in electronic structure considerations, which we do not know at present. Why the high degree of translational order? We speculate that there are long-range forces between large clusters, and these tend to order the clusters. The possible origins of such forces are electrostatic (polarization) interactions, or long-range elastic interactions [27]. A detailed study of these issues will be the subject of future study.

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