Surface Science Letters

Probing step decoration by grazing-incidence helium scattering

Martial Blanc *, Klaus Kuhnke, Vittorio Marsico, Klaus Kern

Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Abstract

We describe a method for the in situ study of step decoration modes in vapor-phase epitaxial growth. It is based on the large cross-section of thermal energy He atoms for diffuse scattering exhibited by surface defects. In grazing-incidence scattering geometry, this sensitivity can be used to monitor ordering and growth processes at step edges. We illustrate the method with results for Ag and Pt deposition at the {111} steps on the vicinal Pt(997) surface. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Atom–solid scattering and diffraction – elastic; Growth; Platinum; Silver; Surface defects

Steps are the most abundant defects at crystalline surfaces and are known to influence strongly surface processes such as sticking, chemical reaction, epitaxial growth, etc. The eminent importance of steps for crystal growth was recognized by Kossel 70 years ago [1]. Binding energies for adatoms are in general larger at steps (and in particular at kink sites in the steps) than on terrace sites as a result of the increased coordination. As a consequence, a new crystal layer is built by adding atoms to the step sites if the average adatom diffusion length is larger than the terrace width [2–4]. Today, this growth mode is usually called step-flow growth. It is the dominant growth scenario at high substrate temperature and low supersaturation, where thermodynamics dominates kinetics. Step decoration in heteroepitaxial systems can be exploited to grow quasi one-dimensional structures like quantum wires. Here the substrate step arrays act as a template [5,6].

Indirect demonstrations of preferential adsorption at step sites have been obtained by thermal desorption spectroscopy [7] or photoelectron spectroscopy [8]. The in situ observation of step decoration, however, is a challenging experimental task. The technique to be employed has to be both sensitive to minute amounts of coverage and selective to the population of step sites. The most powerful tool to study defects at surfaces is the scanning tunneling microscope. It provides direct, real-space images of the surface topography on the atomic scale. In some cases (in particular close-packed metal surfaces) however, it is not easy to obtain atomic resolution in the immediate vicinity of steps. Among the available scattering techniques, thermal energy He atom scattering (TEAS) is particularly sensitive to the presence of adatoms and defects as a result of its very large cross-section for diffuse scattering [9]. This unusual sensitivity has been widely exploited to study the

* Corresponding author. Fax: +41 21 6933604;
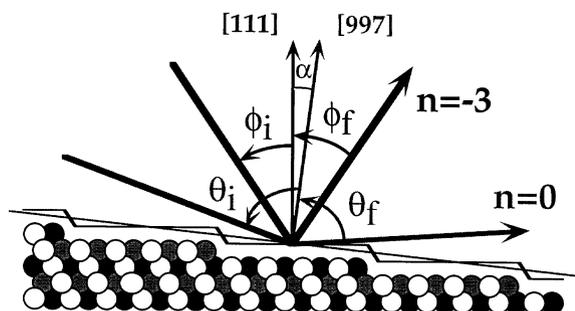e-mail: martial.blanc@ipe.dp.epfl.ch

Fig. 1. Side view of the bare vicinal Pt(997) surface (miscut angle $\alpha = 6.45°$) and the experimental scattering geometries used. The $n=0$ order reflection is specular to the (997) macroscopic surface ($\theta_i = \theta_f$). The higher diffraction orders (e.g. $n = -3$) are always chosen to be specular to the (111) terraces ($\phi_i = \phi_f$). This implies that only $n=0$ is accessible, even in extremely grazing geometry.

lateral distribution and order of adsorbates and defects at surfaces. Moreover, grazing He scattering can selectively monitor adsorbates at the steps of vicinal surfaces [10].

We have recently shown that specular thermal energy helium scattering in grazing scattering geometry can also be employed for the in situ study of ordering and growth processes at step edges [11]. Here we demonstrate and discuss in which way this sensitivity is connected with the scattering geometry, and how the geometry can be used to enhance different features.

In this paper we study as a model system the growth of Ag on Pt(997) in the submonolayer range in order to characterize the strength of the experimental method. We determine the variation of step sensitivity with incidence angle and compare the observation of the heteroepitaxial system with results for the homoepitaxial Pt/Pt(997) system. The vicinal Pt(997) surface (Fig. 1) is obtained by cutting a Pt single crystal close to the (111) plane with a miscut of $\alpha = 6.45°$ in the $\{11\bar{2}\}$ direction. It is composed of regularly spaced (111) terraces, 20.2 Å wide, separated by monatomic steps of $\{11\bar{1}\}$ microfacets. The surface is characterized by a regular step–terrace ordering, and acts essentially as an echelette grating for He matter waves [12,13]. The position of the He diffraction peaks for such a grating is given by the one-dimensional (1D) Bragg law

$$n\lambda = (h/\sin \alpha)(\sin \theta_f - \sin \theta_i), \quad n = \text{integer}, \qquad (1)$$

where θ_f and θ_i are the angle of incidence and the scattering angle with respect to the macroscopic surface normal, $h = 2.27$ Å is the step height, and α is the angle between the (111) and (997) directions. Note that in order to achieve maximum sensitivity to steps, the measurements were made in step-down incidence, as shown in Fig. 1. All $n < 0$ measurements were performed under in-phase scattering conditions for which Eq. (1) must hold as well as $\theta_i - \alpha = \theta_f + \alpha$. This particular scattering geometry avoids interpretation problems associated with the finite terrace-width distribution of the substrate. However, it defines for a given He wavelength both angles θ_f and θ_i, and thus allows no variation of geometry. The $n = 0$ diffraction peak cannot be observed in this so-called "ideal" condition because specular reflection with respect to the macroscopic (997) surface (i.e. $\theta_i = \theta_f$) is not compatible with an in-phase condition with respect to the terraces.

In order to study the nucleation and growth of silver at the vicinal platinum surface, and in particular the decoration of the steps, we monitor the intensity of the different diffraction peaks during deposition. The intensity variation during deposition provides direct information on the ordering and thus on the growth at the vicinal surface. The experiments were made at a He wavelength of $\lambda = 0.92$ Å with a triple-axis spectrometer described in Ref. [14]. The instrument allows an independent variation of incidence and reflection angle, and gives access to a wide range of scattering geometries (θ_i between 30 and 90°, and total scattering angle $\theta_i + \theta_f$ between 60 and 180°). The Pt(997) crystal was prepared and cleaned in the usual way [12,15]. Silver was evaporated with an MBE Knudsen cell with typical deposition rates of a few 10^{-3} ML s^{-1}.

From STM studies on Ag/Pt(111), it is known that the first Ag layer grows pseudomorphically and its growth mode is of the Stranski–Krastanov type [16]. Around room temperature, up to six monolayers grow in a layer-by-layer fashion before 3D growth sets in. In Fig. 2a we show the intensity
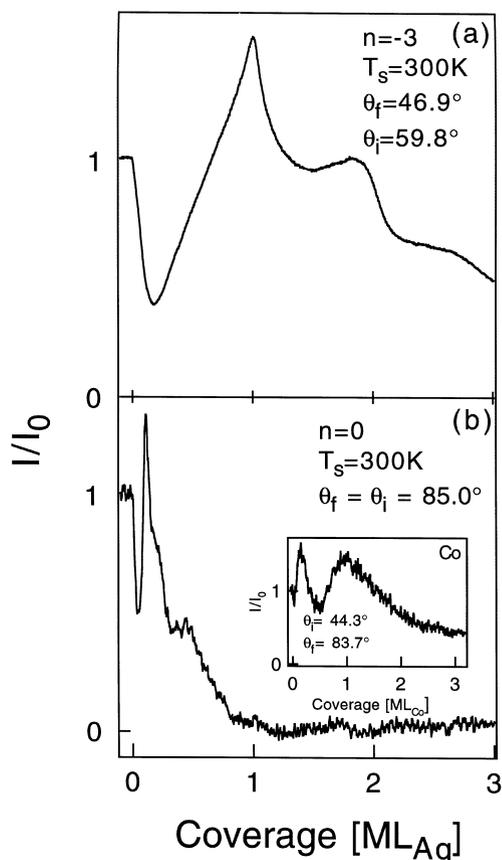
Fig. 2. Normalized He reflectivity as a function of Ag coverage in (a) the $n = -3$ diffraction order, and (b) in grazing scattering geometry in $n = 0$. Inset: reflectivity for Co adsorption on Pt(997) at less grazing incidence and grazing exit ($n = 6$).

variation of the $n = -3$ He diffraction peak as a function of Ag coverage. This scattering geometry is far from grazing incidence and specular to the (111) terraces, probing the defect density of the Ag adlayer on these terraces. The observed intensity oscillations demonstrate layer-by-layer growth for Ag on Pt(997) at 350 K up to three monolayers. The oscillations reflect the periodically varying step density of nucleating and successively coalescing islands. The first maximum is employed to calibrate the ML coverage. It can be seen that this growth is imperfect, as indicated by the continuously decreasing intensity of the reflectivity maxima and their increasing shift with respect to integer-layer coverages.

For the zero-order diffraction beam in grazing incidence, the behavior of the reflected He intensity is quite different. Pronounced intensity oscillations are observed in the submonolayer range, whereas the intensity maxima accompanying the completion of the mono- and bilayers are no longer clearly visible (Fig. 2b). The first and most pronounced peak is situated at about 1/8 of a monolayer, and can be assigned to the formation of a complete Ag row at the bottom of the Pt steps [11], which is consistent with the facts that the (111) terraces on the Pt(997) surface have on the average eight rows of atoms, and that the first layer of Ag grows pseudomorphically. The position of the peak does not change with scattering geometry and can thus be attributed to a structure occurring at a defined coverage. The presence of this peak can be explained – by analogy with the oscillations in layer-by-layer growth – by the variation of the defect density at the steps during row formation. When the defect density is at its minimum, which corresponds to row completion, the scattered intensity reaches its maximum. We thus find that for grazing incidence ($\theta_i = 85°$), the reflectivity becomes very sensitive to the ordering at the step. The fact that the intensity of the first-row peak maximum is higher than the initial intensity does not necessarily indicate that the ordering at the step is better after decoration with a Ag row. More probably, it is the consequence of the "electronic contrast" between Ag and Pt, which results from the change of the potential felt by the He atoms near the steps.

In the measurement (Fig. 2b) the formation of the second row is not well marked and appears only as a shoulder of the first-row peak. The origin of this low intensity could be (i) a changing interference in the diffraction from the terrace, to which the $n = 0$ reflection is sensitive; (ii) a smearing-out of the maximum due to the loss of growth coherence between different terraces;[1] or (iii) a transition to a structure with increased roughness similar to a two-dimensional Stranski–Krastanov growth mode.

---

[1] Terraces receive a number of adsorbates proportional to their width. As all adsorbates migrate to the step, wider terraces complete a given number of rows earlier than narrower terraces.

Two contributions can be responsible for the high sensitivity for row growth demonstrated in Fig. 2b. They correspond to contributions from which step sensitivity arises, which were discussed in the early literature of He scattering from stepped surfaces [12,17]. First, for increasing incidence angle, the terrace moves more and more into the shadow cast by the step. Second, measurements in the zeroth diffraction order of a vicinal surface are themselves sensitive to the step edge. This is due to the fact that the intensity envelope for reflection from a flat terrace provides little intensity in the zeroth diffraction order. The main intensity comes from the bending of the repulsive He surface potential at the step. Experiments performed on row growth under less grazing incidence and grazing exit angle have also shown a substantial step sensitivity, as illustrated in the inset to Fig. 2b, which shows Co adsorption. We can thus conclude that the grazing exit angle is essential for the step sensitivity, while the grazing incidence improves the illumination of the steps by the He beam. The $n=0$ condition takes advantage of both contributions.

In order to demonstrate this latter dependence we performed reflectivity measurements in $n=0$ diffraction order for different angles of incidence. In Fig. 3 the reflectivity is plotted as a function of Ag coverage for angles of incidence varying from 72.8 to 87.5°. We can clearly see the transition from the rather terrace-sensitive, more normal incidence (curves d and c) to the step-sensitive grazing incidence (curves a and b). The relative intensity of the first-row peak decreases slowly with the angle of incidence, while the monolayer peak becomes more prominent. It should also be noticed that the second-row peak, which was only a shoulder in Fig. 2b, can be well resolved at extremely grazing incidence (87.5°). This series of measurements demonstrates nicely the crucial importance of the scattering geometry on the step sensitivity. In addition to the choice of the diffraction order, it is the grazing scattering geometry which contributes to the extreme step sensitivity. While this general rule holds, we note that for certain systems, a first-row maximum can be observed even in higher-order ($n\neq0$) reflections. These maxima (or shoulders) are, however, broad
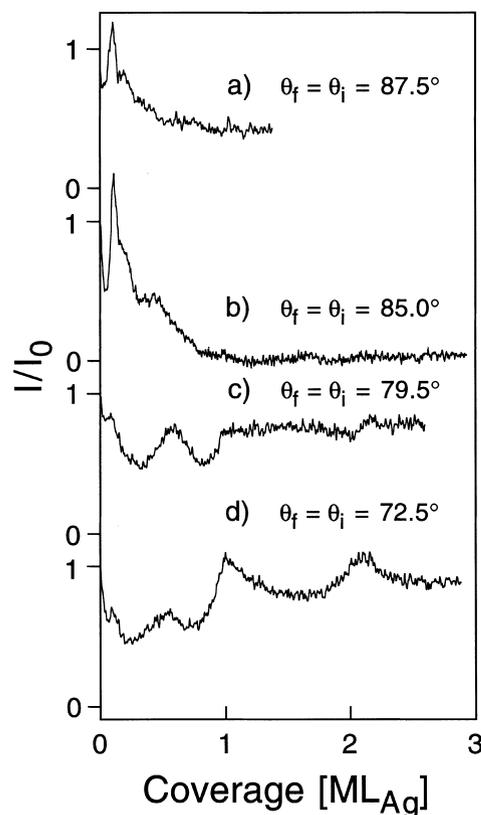

Fig. 3. Normalized He reflectivity in $n=0$ diffraction order as a function of Ag coverage for different exit angles. Note the transition from step sensitivity for grazing geometry (a and b), to terrace-sensitivity for more normal geometry (c and d).

and not nearly as well defined as in the zeroth diffraction order.

Similar results have been obtained for a variety of adsorbates on Pt(997), including the rare gases xenon and krypton [11,18] and the metals Cu and Co [19]. In the case of xenon, a row-by-row growth until the second row was observed, whereas only the first row was observed for krypton, as for Co and Cu. These results demonstrate that the initial row growth of adsorbates at steps is a widespread phenomenon. Thermal He scattering in grazing-incidence geometry is a method which is well adapted to the study of this special type of step decoration, and holds promising prospectives for studying order–disorder phenomena at steps in general.
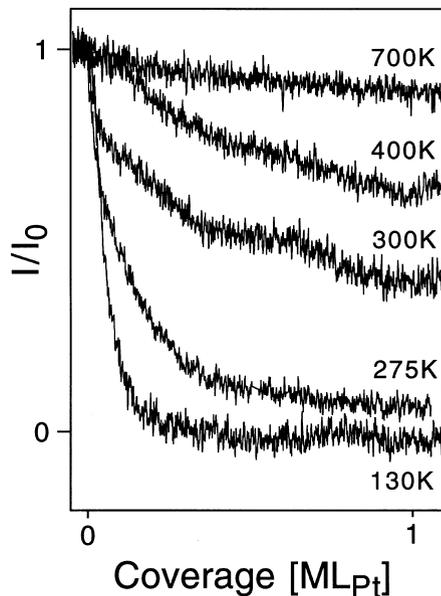
Fig. 4. Normalized He reflectivity in $n=0$ diffraction order ($\theta_i = \theta_f = 80°$) as a function of Pt coverage for different adsorption temperatures.

Finally, we shed some light on the growth mode from a different point of view. Even though row growth is widespread, so far we have only found this growth mode for heteroepitaxial systems. The adsorption of Pt on Pt(997) does not show intensity oscillations (Fig. 4). In the temperature range 130–700 K, we find a continuous transition from an exponential decay of He reflectivity to a constant reflectivity. This behavior has to be interpreted as a transition between a steadily increasing defect density (growth of rough steps) to a growth mode with constant defect density "kink flow". At intermediate temperatures, the reflectivity decreases initially but appears to approach an equilibrium value which depends on the adsorption temperature. We can speculate that the transition from 1D to 2D growth is governed by changes in the diffusivity at step edges. We emphasize that there is no temperature range for which row growth is observed in this homoepitaxial case. One may ask whether this result has to be attributed to a missing "chemical contrast" for He scattering, or whether it indicates a different growth mechanism. In the case of a substantial "chemical contrast", a kink flow in heteroepitaxy

would lead to an initial change of reflectivity because a substrate kink remains a diffuse scatterer even if adsorbate atoms attach to the kink and continue the growth of the row. If the diffusion of an adsorbate atom along the substrate step is fast, the defect density is expected to stay constant during the completion of the row. In contrast, the oscillating intensity observed in heteroepitaxy indicates that the defect density reaches a sharp maximum at about half row coverage. This strongly suggests that in Pt/Pt(997) homoepitaxy and Ag/Pt(997) heteroepitaxy, different growth modes prevail.

In conclusion, we have shown that grazing-incidence thermal He reflection allows the study of defect densities at steps, and thus accesses step decoration modes. It opens up the possibility to study in detail structures and phase transitions in one dimension. The method can be used for any surface with a sufficiently high step density, and is essentially based on the geometrical enhancement of the step contribution to the reflected He intensity.

References

[1] W. Kossel, Akad. Wiss. Göttingen 1927 (1927) 135.
[2] G.A. Bassett, Philos. Mag. 3 (1958) 1042.
[3] H. Bethge, Surf. Sci. 3 (1964) 33.
[4] H. Röder, H. Brune, J.-P. Bucher, K. Kern, Surf. Sci. 298 (1993) 121.
[5] P.M. Petroff, A.C. Gossard, W. Wiegmann, Appl. Phys. Lett. 45 (1984) 620.
[6] Y.W. Mo, F.J. Himpsel, Phys. Rev. B 50 (1994) 7868.
[7] B. Cathrine, D. Fargues, M. Alnot, J.J. Ehrhardt, Surf. Sci. 259 (1991) 162.
[8] R. Miranda, S. Daiser, K. Wandelt, G. Ertl, Surf. Sci. 131 (1983) 61.
[9] B. Poelsema, G. Comsa, Scattering of Thermal Energy Atoms, Springer, Berlin, 1989.
[10] B. Poelsema, G. Mechtersheimer, G. Comsa, Surf. Sci. 111 (1981) 519.
[11] V.E. Marsico, M. Blanc, K. Kuhnke, K. Kern, Phys. Rev. Lett. 78 (1997) 94.
[12] G. Comsa, G. Mechtersheimer, B. Poelsema, S. Tomoda, Surf. Sci. 89 (1979) 123.
[13] H. Schief, V. Marsico, K. Kuhnke, K. Kern, Surf. Sci. L364 (1996) L631.
[14] H. Schief, PhD thesis, Ecole Polytechnique Fédérale de Lausanne, 1995.

[15] E. Hahn, H. Schief, V.E. Marsico, A. Fricke, K. Kern, Phys. Rev. Lett. 72 (1994) 3378.

[16] H. Brune, H. Röder, C. Boragno, K. Kern, Phys. Rev. B 49 (1994) 2997.

[17] J. Lapujoulade, Y. Lejay, N. Papanicolaou, Surf. Sci. 90 (1979) 133.

[18] V. Pouthier, C. Ramseyer, C. Girardet, K. Kuhnke, V. Marsico, M. Blanc, R. Schuster, K. Kern, Phys. Rev. B 56 (1997) 4211.

[19] M. Blanc, P. Gambardella, K. Kuhnke, K. Kern, paper in preparation.