

Thickness-dependent interference structure in the 0–15-eV electron transmission spectra of rare-gas films

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We report electron transmission spectra for thin films of Ar, Kr, and Xe physisorbed on platinum. The curves show characteristic features related to the number of monolayers in the film. These structures are interpreted in terms of interference effects due to the reflectivity at the vacuum-film and film-substrate interfaces. Evidence of layer-by-layer physisorption on Pt suggests the use of this kind of experiment to study complete and incomplete wetting of substrates.

I. INTRODUCTION

Low-energy (0–20 eV) electron transmission spectroscopy (LEETS) has recently emerged as a valuable tool in studying both elastic and inelastic electron interactions in thin polycrystalline films of gases physisorbed on metallic substrates.^{1–4} Elastic or “quasielastic” scattering in such films was found to be sensitive to crystal order^{1–4} and electronic band structure,⁴ the latter being responsible for minima in the transmitted current whenever the incident electron energy coincides with that of a gap. More generally, the features appearing in the elastic part of transmission curves were found to be related to the structural order of the films via the energy dependence of a structure factor.^{2–4} In condensed xenon films, the effects of both thermal and positional structural disorder on low energy electron transmission spectra could be identified.² All “elastic” features were found for film thicknesses varying from about 20 Å to hundreds of angströms. In this range, their shapes and energies remained practically unchanged as a function of thickness and only their intensities varied. We report here LEET spectra for thinner films (one to three monolayers) of Ar, Kr, and Xe, where we can observe structures whose energies vary with film thickness. These features do not appear related to the band structure of the film and are shown to arise from a completely different mechanism.

In Sec. II, we briefly describe the spectrometer and the procedure utilized to obtain precision layer-by-layer deposition of the rare gases. The results are given in Sec. III with some emphasis on the differentiation between the two types of spectral features in the elastic scattering region of LEET spectra: the ones whose energies and line shapes depend on the number of monolayers in the film and those which appear to grow with increasing film thickness without other significant changes. In Sec. IV, we derive a simple model to explain the occurrence of the thickness-dependent spectral features. It presumes that the films are well-ordered within the coherence area of the

incident beam. The model leads to an interpretation in terms of interference phenomena due to reflections of the electron wave between the film-vacuum and film-substrate interfaces. It is capable of predicting the relative energies of the thickness-dependent spectral features. This provides evidence that these films are well ordered with a good wetting of the substrate. Finally, we mention in the conclusion (Sec. V) the interest of such experiments to study complete and incomplete wetting of substrates.

II. EXPERIMENT

The apparatus consists of a high-resolution electron transmission spectrometer of the type described by Sanche⁵ and Bader *et al.*³ The spectrometer is housed in an ion- and titanium-pumped ultrahigh-vacuum system reaching a base pressure of 5×10^{-11} Torr. The main components include a trochoidal monochromator, a pair of deflector plates, and a closed-cycle refrigerated cryostat of variable temperature (10–300 K). The magnetically collimated electrons leaving the monochromator are deflected by the plates and impinge at normal incidence on a film condensed on a metallic substrate attached to the cold end of the cryostat. We measure the current transmitted through the film as a function of primary electron energy. The metal substrate (i.e., the electron collector) consists of a polycrystalline platinum ribbon 1.0×0.5 cm and 0.008 mm thick. It is electrically isolated from the cryostat by a sapphire sheet. The temperature of the substrate is maintained constant and monitored by a thermocouple (Au–0.07 at. % Fe versus Chromel copper) secured to the copper block of the cryostat. A difference of 2 K between the temperature of the copper block and that of the metal substrate was deduced from vapor pressure versus temperature data.⁶

The trochoidal monochromator has been previously described in detail.⁷ In the present experiment, the incident current is $\approx 3 \times 10^{-9}$ Å and the resolution 0.04 eV full width at half maximum. As previously explained,⁵ deflector plates between the monochromator and the tar-

get can prevent any electrons reflected once from the target from returning to it again. This configuration thus allows measurements of the absolute value of the transmitted current.

Before condensing Ar, Kr, and Xe on the metallic substrate, the latter was cleaned by resistive heating at ~ 1500 K and by argon sputtering followed by annealing at high temperature. After repeated annealing cycles, the Pt ribbon crystallized with a preferential (111) orientation of the surface. This had been previously verified⁸ by observing, near the threshold energy of emergence of the first diffracted peak, interference structure characteristic of the Pt(111) surface.⁹ It will be seen in Sec. III that our spectra are characteristic of well-ordered films.

The gas was admitted in the vacuum through a leak valve connected to a tube whose opening was located in front of the collector. Most of the molecules ($>98\%$) leaving the tube condensed on the cryostat. The actual number deposited on the collector was estimated from geometrical considerations and gas kinetic theory (i.e., expansion of a known volume of gas at a given pressure and temperature into vacuum),^{3,10,11} assuming a sticking coefficient of unity. The number of monolayers condensed on the collector could be estimated by calibrating the amount of gas injected to produce a monolayer. The thickness of the film was then increased in steps of one monolayer using the calibrated values and assuming no change in sticking coefficient with film growth. Matheson research-grade gases ($>99.995\%$ pure) were used without further purification.

It was possible to precisely condense a single monolayer of rare gas on the platinum substrate by allowing a small leak of the gas to flow out of the admission tube while keeping the substrate temperature above the bulk sublimation temperature of the solid but below the evaporation point of the first monolayer. For example, in the case of xenon this temperature lies around 60 K⁶ when the background pressure of the gas is 10^{-10} Torr. Thus, at this temperature only one monolayer of Xe is supposed to physisorb on the substrate. This was verified in the following manner. First, we calculated the number of molecules and the leak time required (with a given opening of the leak valve) to completely cover the substrate with one monolayer. Then, we constantly recorded LEET spectra at a fast rate while the gas was being condensed on the substrate. We noticed that during the "one-monolayer leak time" the transmission spectra changed drastically whereas afterwards they remained the same no matter how long we continued to expose the substrate to the gas source. We therefore concluded that the modifications of the spectral shapes during the "one-monolayer leak time" were produced by changes in electron scattering intensities due to gas adsorption and that beyond that time the sticking coefficient was zero. When we lowered the temperature below the bulk sublimation temperature the spectral line shapes continue to change for much longer times indicating multilayer formation. The transmission spectra reported herein were recorded at different thicknesses for temperatures of 15 to 45 K but the "one-monolayer leak time" was established in the temperature range previously mentioned. The results which follow indicate that film

growth occurred by successive layers (i.e., complete wetting) approaching bulk phase asymptotically with increasing thickness.

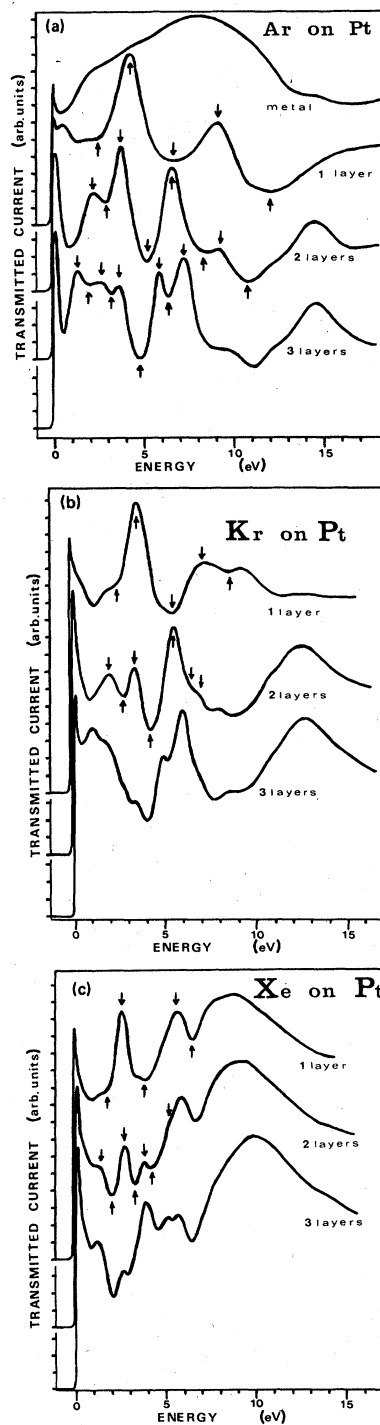


FIG. 1. Electron current transmitted through films of (a) Ar, (b) Kr, and (c) Xe as a function of electron energy. The film thickness is indicated on the right-hand side of each curve. The arrows indicate the position of structures characteristic of the number of monolayers. The current measured on the clean Pt substrate is shown at the top of (a).

III. RESULTS

LEET spectra for one to three monolayers of condensed Ar, Kr, and Xe deposited on Pt are shown in Figs. 1(a)–1(c), respectively. The upper curve in Fig. 1(a) represents the current measured on the bare Pt substrate as a function of electron energy. As may be seen, the presence of just one monolayer of Ar on this substrate can drastically change the characteristics of the current versus energy curve of Pt. In Fig. 1(a), the curves for two and three monolayers may be regarded as composed of a broad maximum between 1–4 eV, other broad maxima around 7 and 15 eV, and a broad minimum extending from 8 to 12 eV. These broad features on which sharp structure is superimposed persist at higher thicknesses. Their mechanism of formation has previously been explained.^{1–4} The other features which modulate these broad undulations change in number and intensity depending on the thickness of the film. They are well defined for one monolayer and become more difficult to observe as the film thickness is increased due to their superposition with features characteristic of thicker films. It is important to note that the structures for one monolayer grow continuously during the formation of this first monolayer. Then the new structures associated with two monolayers emerge only when those for the first layer have reached their maxima. These observations strongly support a layer by layer film growth. A similar behavior is observed in the LEET spectra of Kr and Xe films shown in Figs. 1(b) and 1(c), respectively. In each curve, the vertical arrows identify thickness-dependent features. In all LEET spectra the first peak near 0 eV is due to electron injection in the film.

IV. INTERPRETATION

Low-energy electron diffraction (LEED) experiments performed with rare gases condensed on single and polycrystalline substrates indicate film growth with a surface having the (111) orientation.^{12–17} If we assume that we have well-ordered films of Ar(111), Kr(111), and Xe(111) on our platinum substrate, the only diffracted beam in vacuum in the 0–10 eV range is the specular one. Furthermore, below 8, 10, and 12 eV for Xe, Kr, and Ar, respectively, no electronic transitions are energetically possible and only acoustical phonons¹⁸ contribute to energy losses. These are small due to the weak electron-phonon coupling constant¹⁹ and the short residence time of each electron in the film. Thus, the energy ranges 0–8, 0–10, and 0–12 eV for Xe, Kr, and Ar, respectively, provide wide regions where interference phenomena can be investigated with negligible effects from inelastic events and diffracted-beam emergence. We therefore assume that below the respective excitonic threshold energies, elastic scattering in these molecular films and at their interfaces can be well described by a formalism similar to that employed in LEED to calculate the (0,0) intensity.²⁰

According to Fig. 2 we define (T_f, R_f) , (T_s, R_s) , and (T_v, R_v) as the specular transmission and reflection coefficients of the vacuum-film, film-substrate, and film-vacuum interfaces, respectively. The term arising from propagation through the film is $\Omega = ae^{ikmd}$ where a , the

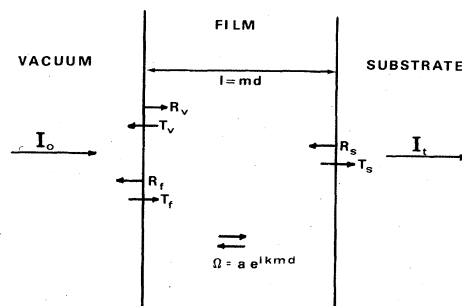


FIG. 2. Schematic representation of the molecular film and substrate with the notations used in the text for reflection and transmission coefficients. I_0 and I_t are the incident and transmitted currents, respectively. Ω is the term arising from propagation through the film, l is the thickness of the film, m the number of monolayers, and d the thickness of one monolayer.

amplitude of Ω , depends on the film thickness and electron energy. The wave vector $k = (E + V_0 + iV_i)^{1/2}$ (in a.u.) where V_0 and V_i are the real and imaginary parts of the optical potential and E the total electron energy in vacuum; m is the number of monolayers and d the thickness of a monolayer. We further define I_0 as the total current incident on the film, I_t as the transmitted current, I_s as the scattered transmitted current, and S as the specularly transmitted amplitude. With these definitions, the transmitted current is given by

$$I_t = I_s + I_0 S^2, \quad (1)$$

where²⁰

$$S = T_f \Omega T_s + T_f \Omega R_s \Omega R_v \Omega T_s. \quad (2)$$

If we let A be the amplitude of $T_f \Omega T_s$ and $(\psi_1 + kmd)$ its phase and B be the amplitude of $R_s R_v \Omega^2$ and $(\psi_2 + 2kmd)$ its phase, where both A and B depend on energy and thickness, then the specularly transmitted amplitude S is given by

$$S = A e^{i(\psi_1 + kmd)} [1 + B e^{i(\psi_2 + 2kmd)}], \quad (3)$$

$$S^2 = A^2 [1 + B^2 + 2B \cos(\psi_2 + 2kmd)]. \quad (4)$$

Substituting (4) into (1), we obtain

$$I_t = I_s + I_0 A^2 [1 + B^2 + 2B \cos(\psi_2 + 2kmd)]. \quad (5)$$

Minima and maxima in I_t occur when

$$\psi_2 + 2kmd = n\pi. \quad (6)$$

If ψ_2 is a slowly varying function of energy and $k \simeq \sqrt{E}$ (in a.u.) in the film, we have

$$\sqrt{E} = \alpha n + \beta, \quad (7)$$

where both $\alpha = \pi/2md$ (in a.u.) and $\beta = (-\psi_2/2md)$ (in a.u.) may be considered constant for a given thickness.

We can verify our results against Eq. (7) by plotting the values of the square root of the energies of maxima and minima in the transmitted current versus n . This is shown in Figs. 3(a)–3(c) for Ar, Kr, and Xe, respectively.

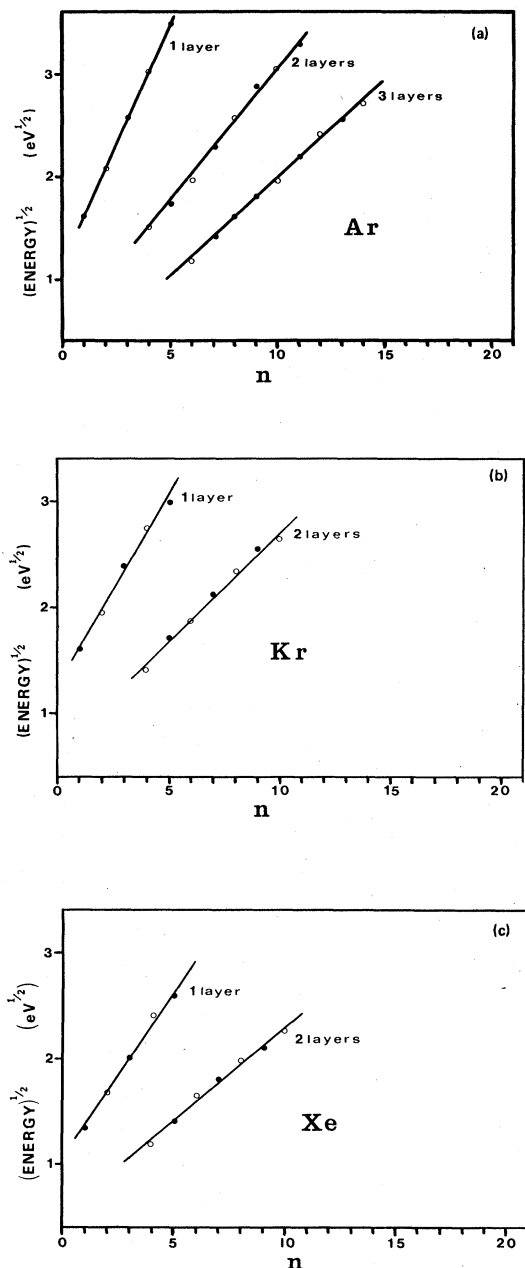


FIG. 3. Plot of $\sqrt{E} = f(n)$, where n is an integer, for physisorbed Ar, Kr, and Xe. The values of the energies correspond to the structures designated in Figs. 1(a)–1(c). Open circles correspond to peaks and full circles to dips.

The maxima (open circles) and minima (full circles) for which \sqrt{E} was computed are indicated by arrows on Fig. 1. The straight lines passing through the points are given by Eq. (7) for one, two, and three monolayers (i.e., $m = 1, 2, 3$) in the case of Ar and one and two monolayers for the results in Kr and Xe. The excellent fit between theory and experiment indicates, in particular, that $\sqrt{E} \approx (E + V_0 + iV_i)^{1/2}$. In fact, for rare gases, V_0 and V_i are known to be weak.^{3,4} We can therefore attribute the linear relationship in Fig. 3 to the phase $2kmd$. Physical-

ly, this represents the phase accumulated by the specular beam between the vacuum-film and the substrate-film interfaces. The relative slope of each curve is inversely proportional to md as given by Eq. (7), but we find a significant difference between the absolute theoretical (α_{th}) and experimental (α_{ex}) values of α . For example, for $m = 1$ and $d = d_{111} = 6$ a.u. in Ar, we have

$$\alpha_{\text{th}} = 0.98 \text{ eV}^{1/2}, \quad \alpha_{\text{ex}} = 0.47 \text{ eV}^{1/2}.$$

The lower experimental value possibly arises from neglecting the energy dependence of the phase change at both interfaces which is included in Ψ_2 [Eq. (6)]. From present LEED theory,²⁰ it appears difficult to quantitate this effect to arrive at a calculated value of α consistent with the experiment.

As expected we find for each curve in Fig. 1 that the maxima and minima correlated with Eq. (7) disappear with growing film thickness. For one and two monolayers, identification of a set of thickness-dependent features is easy and the corresponding $\sqrt{E} = f(n)$ curves show a well-defined linear dependence. For three monolayers, identification was possible for Ar but it is more difficult for Xe and Kr. Three different phenomena may be invoked to explain this behavior. First, for more than three monolayers the shape of the transmitted curves becomes increasingly dominated by the broad "thickness-independent" features characteristic of thicker films. Secondly, the oscillations described by Eq. (5) which are due to changes in reflectivity at the interfaces become weaker (i.e., elastic multiple interlayer and intralayer scattering increases and the contribution arising from interference at the interfaces become weaker). Another reason may be a change in film growth. Beyond three monolayers, it is possible that layer-by-layer growth no longer occurs.

V. CONCLUSIONS

It has been shown that at very small thicknesses, thickness-dependent structures in LEET spectra can be correlated with elastic reflection at the film-vacuum and film-substrate boundaries. We arrived at this conclusion by establishing the relationship $\sqrt{E} = f(n)$ in films of Ar, Kr, and Xe deposited on polycrystalline platinum. This relationship implies that the films are well ordered, at least within a zone comparable to the coherence length of the incident beam. Another implication relates to the wetting properties of the Pt surface. It appears mathematically impossible to obtain the linear behavior described by Eq. (7) without assuming layer-by-layer rare gas deposition. Therefore, it seems that layer-by-layer physisorption occurs on Pt with a good wetting of the surface and that LEETS could be utilized to characterize the wetting properties of metallic and possibly other types of conducting substrates.

The interference phenomenon reported here is analogous to the one reported by Jonker *et al.*²¹ in metallic films grown on metallic substrates. As in the work of Jonker *et al.*, it may be possible from Fig. 3 to extract some information on V_0 and, from the slope of the $\sqrt{E} = f(n)$ curves, on α , but the positions of the fine

structures are not sufficiently well defined to get precise quantitative information. Above two monolayers, it is obvious that the positions of maxima and minima are affected by other features appearing in thicker films.

Finally, we note that it would be interesting to perform the same kind of experiment on purely monocrystalline

substrates. This should improve ordering of the layers and consequently enhance interference effects due to reflectivity at the film interfaces. It may then be possible to obtain stronger evidence of the ability of LEETS to investigate the wetting properties of substrates, a field of growing interest in recent years.²²

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- ¹L. Sanche, G. Perluzzo, G. Bader, and L. G. Caron, *J. Chem. Phys.* **77**, 6 (1982).
- ²G. Perluzzo, G. Bader, L. G. Caron, and L. Sanche, *Phys. Rev. B* **26**, 3976 (1982).
- ³G. Bader, G. Perluzzo, L. G. Caron, and L. Sanche, *Phys. Rev. B* **26**, 6019 (1982).
- ⁴G. Bader, G. Perluzzo, L. G. Caron, and L. Sanche, *Phys. Rev. B* **30**, 78 (1984).
- ⁵L. Sanche, *J. Chem. Phys.* **71**, 4860 (1979).
- ⁶R. E. Honing and H. O. Hook, *RCA Rev.* **21**, 360 (1960).
- ⁷A. Stamatovic and G. J. Schulz, *Rev. Sci. Instrum.* **41**, 423 (1970).
- ⁸L. Sanche and M. Michaud (unpublished).
- ⁹B. A. Sexton and G. E. Mitchell, *Surf. Sci.* **99**, 539 (1980).
- ¹⁰Y. C. Chang and W. B. Berry, *J. Chem. Phys.* **61**, 2727 (1974).
- ¹¹T. E. Madey, *Surf. Sci.* **33**, 355 (1972).
- ¹²G. Ertl, in *Molecular Processes on Solid Surfaces*, edited by E. Drauglis, R. D. Gretz, and S. B. Jaffee (McGraw-Hill, New York, 1969).
- ¹³H. B. Lyon and G. A. Somorjai, *J. Chem. Phys.* **46**, 2539 (1967).
- ¹⁴S. Y. Tong, T. N. Rhodin, and A. Ignatiev, *Phys. Rev. B* **8**, 906 (1973).
- ¹⁵M. A. Chesters and J. Pritchard, *Surf. Sci.* **28**, 460 (1971).
- ¹⁶K. Christmann and J. E. Demuth, *Surf. Sci.* **291** (1982).
- ¹⁷H. H. Farrell and Myron Strongin, *Phys. Rev. B* **6**, 4711 (1972).
- ¹⁸M. L. Klein and T. R. Koehler, in *Lattice Dynamics of Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1976).
- ¹⁹N. Schwentner, *Phys. Rev. B* **14**, 5490 (1976).
- ²⁰J. B. Pendry, *Low Energy Electron Diffraction* (Academic, New York, 1974).
- ²¹B. T. Jonker, N. C. Bertelt, and R. L. Park, *Surf. Sci.* **127**, 183 (1983).
- ²²For example, see M. Sutton, S. G. J. Mochni, and R. J. Birgeneau, *Phys. Rev. Lett.* **51**, 407 (1983); J. L. Seguin, J. Suzanne, M. Bienfait, J. G. Dash, and J. A. Venables, *ibid.* **51**, 122 (1983); and references cited therein.