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Quantum size effect in the photoemission intensity emitted from thin metal films

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Abstract

Photoemission spectra are calculated for thin films of Ag on Au(111) using the method of Green's function matching. For very low photon energies ($\omega \lesssim 10$ eV) the peak intensities of the thin film states oscillate with the film thickness. These oscillations are caused by the relaxation of the k_{\perp} -conservation of the optical excitation in photoemission.

Keywords: Gold; Green's function methods; Metallic films; Photoelectron emission; Semi-empirical models and model calculations; Silver

The atomic-scale confinement of valence electrons in low-dimensional structures may give rise to discrete states, which may be observed by photoemission. In particular, the study of epitaxially grown metallic overlayer systems is a field of increasing interest [1–12]. The overlayer states appear for energies within a local band gap of the substrate. They are considered to be precursors of the bands of the thin film material, which partially overlap the local band gap of the substrate. This physical picture is well substantiated by a simple nearly-free-electron model (NFE) for sp-bands, whereas the electronic structure of the composite system is formulated by means of phase rules [1–6,9,10,12] or of Green's function matching [7,8].

Relative to the peak position analysis, there are

only a few investigations in the literature concerning photoemission intensities arising from quantum well states. Most of these studies on peak characteristics are concerned with the morphology and thickness distribution of the ultrathin overlayers [9–11]. However, even if thickness inhomogeneities and local photon field effects are neglected, intensity modulations occur as a consequence of indirect optical transitions in thin layers [9]. Recently, Miller et al. [12] reported on quantum well like resonances in Ag films on Ni(111), which in addition to a peculiar dispersion show an oscillatory behaviour in their intensities as a function of photon energy.

The present work considers peak intensity modulations of the photoemission from thin film states as a function of film thickness ($D = Nd$). This oscillatory behaviour is well developed for low photon energies for which the period of oscillation δN exceeds the width of the area distribution of

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thickness. Furthermore, the escape depth L must be at least of the order of δN . For final state energies slightly above the emission threshold [1,2], L is of the order of some tens of Å. In fact, the intensity oscillations are revealed in the normal emission spectra from Cs/Cu(111) (Ref. [2], peak B in Fig. 1) and from Ag/Cu(111) (Ref. [4], even for an excitation energy of 10 eV) but have not been interpreted in these papers. The calculations of photoemission intensities by Miller et al. [12] of Ag/Ni(111) are based on the assumption of diffuse scattering at the Ag-Ni interface because of large lattice misfit. From the lack of k_{\parallel} conservation the truncation of the dipole matrix element is concluded. The present paper considers lattice-matched systems where the truncation of the matrix element is explained by a sufficient localization of the initial state within the layer.

To explain the intensity oscillations, the dipole matrix element is considered first. For a simple illustration, emission in normal direction is considered, with local fields and interface roughness being neglected. The final state is approximated by a single Bloch wave of wave vector k_f , i.e. the reflection of photoelectrons at the inner interface is neglected. The main contribution to the optical matrix element arises from an outgoing Bloch wave of wave vector k_x which, together with the reversed wave of $-k_x$, forms the initial state, i.e. the thin film state labelled α . Summing up the atomic layer contributions, the optical matrix element yields

$$M = \frac{1 - e^{i(k_f - k_x)Nd}}{1 - e^{i(k_f - k_x)d}} M_0, \quad (1)$$

where M_0 belongs to the first monolayer of the film. Owing to the boundary conditions, k_x fulfills the phase quantization rule

$$[2k_x D + \phi_0 + \phi_1](2\pi)^{-1} = \alpha, \quad \alpha = \text{integer}, \quad (2)$$

where ϕ_0 and ϕ_1 are the phases of reflection at the surface and the inner interface, respectively.

k_f is determined by the final state energy $E_x + \omega$ via band dispersion. Consequently, there is no k_{\perp} -conserving optical excitation, except that $k_f = k_x$ is accidentally fulfilled if a suitable photon energy ω is chosen. As a consequence of Eq. (2), the energy of the thin-film states depends on the film thickness,

and so do k_f and the phases via the energy conservation. For a large thickness, M strongly peaks at $\Delta k = k_f - k_x = 0$ which implies a direct optical transition. Although this direct optical transition occurs for a certain photon energy (if α is fixed), the initial states are close together for a large thickness so that for an arbitrary photon energy there is state α of energy E_x available fulfilling $\Delta k = 0$. The failure of these direct transitions in very thin films was substantiated by Jalochoowski et al. [9].

The period of oscillations of the photoemission peak intensity arising from thin film states is estimated from the change of the phase in Eq. (1) with thickness. The result is

$$\delta N = 2\pi \left[\Delta k \cdot d + N \cdot d \cdot \frac{dE_x}{dN} \left(\frac{1}{|v_x|} + \frac{1}{|v_f|} \right) \right]^{-1}, \quad (3)$$

ω fixed,

where v_x and v_f are the velocities of the corresponding waves.

Although the optical matrix element explains the modulation of the intensity, a quantitative calculation of the emitted current requires both the matrix elements and the density of the states available to be included. The technique employed for the calculations is based on the Green's function matching method [13]. Its application to photoemission has been demonstrated in detail for a single surface [14]. For nearly free electron models, the method enables the direct calculation of the photoelectron intensity by means of the Fourier transform, analogous to the calculation of the Green's function (in layer representation) itself. Therefore, no separate calculation of M from the wave functions is required. The Bloch waves of the initial and the final state are selected by the poles corresponding to the contour of the k_{\perp} -integration, whereas matching equations provide the correct asymptotic behaviour of the Green's function. For technical details, the reader is referred to Ref. [14]. The generalization of method to quantum wells with lattice-matched interfaces is obvious, although the calculations are more extensive. Unlike the assumptions leading to Eq. (1), the reflection of the Bloch waves at the interface contributes ingoing and reflected waves to both the initial and the final state. Furthermore, the binding energy is not

restricted to the region where Eq. (2) is valid, i.e. bound states as well as resonances are considered in the calculation. In comparison with the single surface case [14], here the projected objects (e.g. the projected Green's function) are 2×2 matrices because of two interfaces. The following approximations are made to simplify the calculations: (i) the range of integration extends over the layer thickness instead of the half space, i.e. emissions from the substrate metal as well as from the surface potential region are neglected; (ii) field effects are neglected; (iii) the energy dependence of the transmission of the photoelectrons through the surface is neglected. Approximation (i) is based on the assumption that the initial states are predominantly localized within the layer. This is the case except for weak resonance states, which correspond to a strong coupling to the bulk states of the substrate material. Because of assumption (ii), the finite escape depth L is solely obtained from complex k_{\perp} for the initial and final states according to the optical potential. Assumption (iii) implies the neglect of final state resonances since they are surely weak, compared to the assumptions about initial states. The assumptions underlying approximations (i) and (iii) are different from the investigations of Miller et al. [12] of weak resonance states, for which lifetime broadening of the corresponding peaks can be neglected in comparison to the broadening by coupling to continuum states.

To be specific, Ag films on Au(111) are considered here. Nearly-free-electron based model calculations yield an excellent agreement with experimental results for both surface state and quantum well binding energies [8]. Unlike the case for Ag/Cu(111) [4] or Ag/Ni(111) [12], the lattice mismatch at the interface Ag/Au(111) is almost vanishing (misfit $< 0.2\%$), according to basic assumptions of the calculation. Unfortunately, no such detailed spectra for intervals of 1-2 monolayers are available from the literature as they are known for Ag/Cu(111) [4]. The band model is exactly the same as described in a previous paper [8]. The NFE model is used for both Ag and Au. The image plane x_i is arranged slightly (0.17 \AA) outside the geometrical surface x_0 (half a monolayer outside the outermost atomic layer) in order to adjust the surface state energy. A constant

potential ($V_1 = -9.8 \text{ eV}$ below the vacuum level) is used in the region in between the geometrical surface and the plane of the truncated image potential ($x_1 - x_0 = 0.54 \text{ \AA}$). Fig. 1 shows the energy positions, relative to E_F , of the thin film states. The expression on the left of Eq. (2) is calculated as a function of energy with parameter N . k refers to the Brillouin zone wave vector ($k_{\text{BZ}} = \pi/d$). The function becomes integer at the quantum well energies. Fig. 1b presents these energies as a function of N with α being a parameter. At fixed binding energies, oscillations in photoemission with layer thickness are expected already from the spectral distribution of the initial states, disregarding the matrix element. Maximum intensity arises whenever a peak of state α as a function of N (for fixed ω) passes the fixed energy. Unlike the case of fixed binding energies, oscillations of peak intensities of the energy distribution as a function of N are solely determined by the matrix element, since in this mode the intensity corresponding to state α is followed in its actual positions $E_{\alpha}(N)$.

For calculating the photoelectric current the inverse lifetimes of electrons γ_e and of holes γ_h ($\gamma_e = -2 \text{ Im } \Sigma(E_{\alpha} + \omega)$, $\gamma_h = -2 \text{ Im } \Sigma(E_{\alpha})$) have to be estimated. By analogy with the surface state [14], the peak width of thin film states solely depends on γ_h , provided that the peaks are well separated and the film has a homogeneous thickness, which, in general, is not satisfied. Assuming Lorentzian broadening, the integral peak intensity originating from a localized state is nearly independent of γ_h . It is difficult to determine γ_h with sufficient accuracy in the energy range of interest, i.e. for less than 1 eV below the Fermi energy E_F . The resolution of the analyzer is usually of the same order of magnitude. Since γ_h is insignificant for integrated intensities, the value 0.1 eV is used for it, irrespective of the energy. The electron inverse lifetime is determined by inelastic scattering [15], which strongly depends on the energy in the range of interest ($\omega < 10 \text{ eV}$). For a free electron gas [16,14]

$$\gamma_e = \lambda \left(\sqrt{\frac{E}{E_F}} - 1 \right)^2 \quad (4)$$

was derived. Applying Eq. (4) to Cu [14] yielded

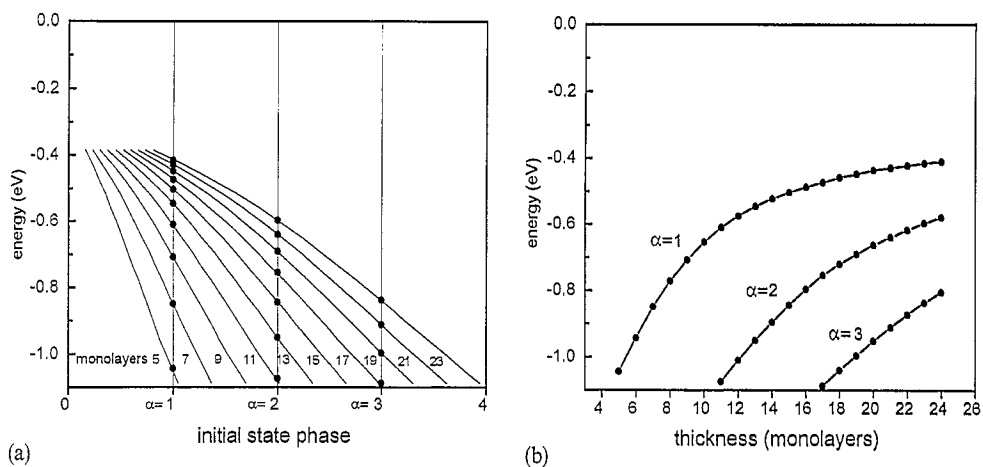


Fig. 1. (a) The normalized phase of the initial state as a function of energy defined by formula (1), calculated for Ag/Au(111). (b) The binding energies of the thin film states as a function of the film thickness.

a reasonable agreement with the photoemission from the (111) face. However, the actual value λ is smaller than for a free electron metal. Similarly, for Ag the estimate from the electron mean free path [15] yields approximately $\lambda=3.2$ eV, which is smaller than $\lambda_0=4.8$ eV obtained after the theory of Quinn and Ferrell [16]. Note that the actual escape depth is slightly smaller than the electron mean free path since the velocities of Bloch waves near the zone boundary are reduced ($L \approx 10$ Å for $\omega=9$ eV, $L \approx 16$ Å for $\omega=6$ eV).

Fig. 2 presents a series of photoemission spectra for various thicknesses of the Ag overlayer, which is calculated for $\omega=9.0$ eV. The intensity oscillations of the quantum well peaks in dependence on N are well developed, especially for small N . Calculations for higher photon energies yield weaker modulations. For binding energies below the band edge of Au (i.e. $E < -1.1$ eV) there are broad resonances. The intensity increase for large binding energies arises from approaching to the transition $\Delta k=0$, which corresponds to that of the bulk film material. For $N=5$, the surface state is slightly shifted from the silver position [8,11], which agrees with the experimental findings.

Fig. 3 shows the integral peak intensities of the spectra calculated, which result from the residua of the corresponding spectral function [14]. The values are obtained from the true thin film states ($E_x > -1.1$ eV = band edge of gold), since the

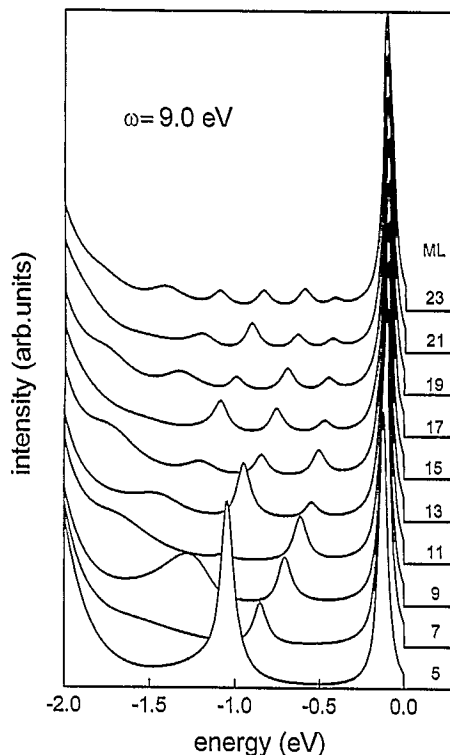


Fig. 2. Photoemission in normal direction calculated for various thicknesses of Ag on Au(111). The strong peak at 0.1 eV below the Fermi energy belongs to the surface state.

above-mentioned approximation (i) is well suited for these states unlike the case for weak resonance states.

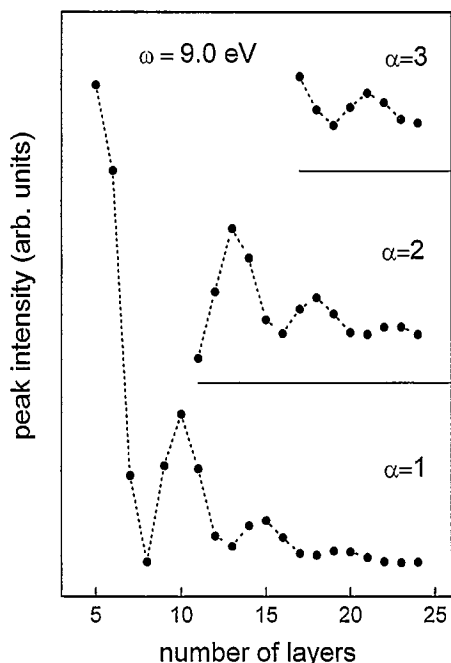


Fig. 3. The relative intensities of the thin film states of Fig. 2.

The period of oscillations δN as a function of photon energy is shown in Fig. 4. The calculation is based on Eq. (3). For large N (i.e. $N > 10$ ML),

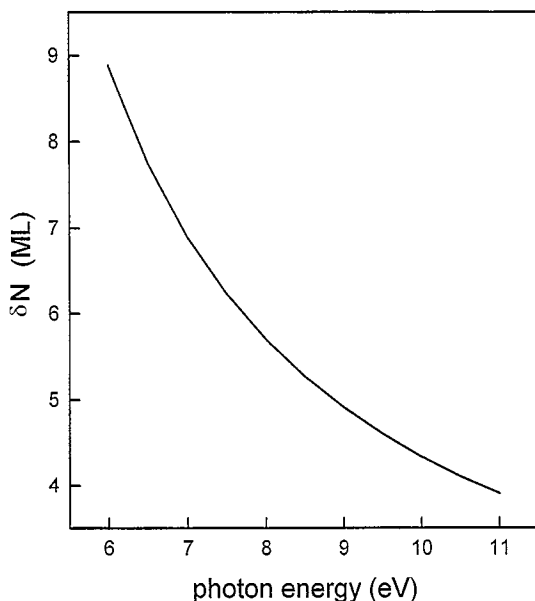


Fig. 4. The oscillation period of the first quantum well state as a function of the photon energy. The calculation refers to $N = 10$ ML.

however, δN is almost independent of N and α , hence $N = 10$ ML and $\alpha = 1$ are used. The dispersive term $\propto dE_\alpha/dN$ reduces δN with respect to $2\pi/(\Delta k \cdot d)$. The former has a strong effect on δN for low photon energies where Δk is small. There is a good agreement with values directly obtained from the spectra calculated which verifies the assumption that the finite-size produced modulation is actually related to the optical excitation given by the dipole matrix element (1).

Finally, information concerning intensity oscillations for the band structure determination from experiment is pointed out. The period δN depends on Δk according to Eq. (3). The initial state band $E_\alpha(k_\alpha)$, however, can be obtained from the peak positions $E_\alpha(N)$ [4]. Thus k_f and the final state band, respectively, result from analysing oscillations in photoemission spectra. The term with v_f in Eq. (3) is mostly of little importance since usually $|v_\alpha|^{-1} \gg |v_f|^{-1}$ is valid. Otherwise, for example, the tuning mode of constant binding energy may be used to estimate v_f , yielding intensity oscillations as a function of photon energy. By analogy with Eq. (3), the period

$$\delta\omega = |v_f| \frac{2\pi}{Nd}, \quad N \text{ fixed} \quad (5)$$

is obtained from the change in phase in Eq. (1). Consequently, k_f and v_f are determined from δN and $\delta\omega$, in contrast to the present paper which calculates δN on the basis of the nearly-free-electron band model.

In conclusion, peak intensity oscillations in photoemission of thin film states occur according to a quantum size effect of the optical excitation. This effect can be observed for very low photon energies as calculations in this study have shown.

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References

- [1] S.Å. Lindgren and L. Walldén, Phys. Rev. Lett. 59 (1987) 3003.

- [2] S.Å. Lindgren and L. Walldén, *Phys. Rev. Lett.* 61 (1988) 2894.
- [3] T. Miller, A. Samsavar, G.E. Franklin and T.-C. Chiang, *Phys. Rev. Lett.* 61 (1988) 1404.
- [4] M.A. Mueller, T. Miller and T.-C. Chiang, *Phys. Rev. B* 41 (1990) 5214.
- [5] J.E. Ortega, F.J. Himpsel, G.J. Mankey and R.F. Willis, *Phys. Rev. B* 47 (1993) 1540.
- [6] N.V. Smith, N.B. Brookes, Y. Chang and P.D. Johnson, *Phys. Rev. B* 49 (1994) 332.
- [7] W. Jaskólski, V.R. Velasco and F. Garcia-Moliner, *Phys. Scr.* 43 (1991) 337.
- [8] A. Beckmann, M. Klaua and K. Meinel, *Phys. Rev. B* 48 (1993) 1844.
- [9] M. Jalochoowski, H. Knoppe, G. Lilienkamp and E. Bauer, *Phys. Rev. B* 46 (1992) 4693.
- [10] F. Patthey and W.-D. Schneider, *Phys. Rev. B* 50 (1994) 17560.
- [11] K. Meinel, A. Beckmann, M. Klaua and H. Bethge, *Phys. Status Solidi (a)* 150 (1995) 521.
- [12] T. Miller, A. Samsavar and T.-C. Chiang, *Phys. Rev. B* 50 (1994) 17686.
- [13] F. Garcia-Moliner, *Ann. Phys. (Paris)* 2 (1977) 179.
- [14] A. Beckmann, *Surf. Sci.* 326 (1995) 335.
- [15] D.R. Penn, *Phys. Rev. B* 35 (1987) 482.
- [16] J.J. Quinn and R.A. Ferrell, *Phys. Rev.* 112 (1958) 812.