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Electron in a Box and Ultrathin Metallic Films as Probed by ARUPS

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Ultrathin metallic films may act as quantum boxes when some conditions are met. Here, we discuss these conditions for the simplest case of one-dimensional confinement and we review some of the properties that emerge from the reduced dimensionality of the films. We emphasize the difference between extremely thin layers of up to several monolayers thickness and thicker ultrathin films. Taking the Ag/V(100) system as a case study, we show the most prominent features of the electronic structure of the films, as revealed by the angular resolved ultraviolet photoemission spectroscopy (ARUPS).

Key words: ultrathin metallic film, electron-phonon coupling constant, angular resolved photo emission spectroscopy.

INTRODUCTION

Recently, manipulation of individual atoms and molecules has become reality. It is a matter of immediate future to turn these achievements into technologies. This trend is already under way and an ever increasing number of laboratories turn towards nano-oriented research. The term nano encompasses anything between an atom and structures of sub-micron dimensions. The reduced dimensionality on these scales may significantly change the properties of a material when compared to those of the bulk analogue. The dimensions on the nano-scale are so small that quantum effects prevail.

The first experimental observations of the so-called quantum size effect (QSE) were made in semiconductors where many different structures have been produced and studied, like quantum dots, quantum wires, *etc*. In the

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case of metallic systems, the first experimental observations of the quantum size effects were made in thin metallic films when the interference effects were observed in the reflection of low-energy electrons from thin gold films.[1] The effect was ascribed to the interference of electrons reflected at the substrate-film interface and the vacuum-film interface and it was observed for all thicknesses smaller than 100 Å.

It should be noted, however, that ultrathin metallic films are reduced in dimensionality only in the direction perpendicular to the film surface. The other two dimensions are usually very large and are measured in cm. As a consequence, the results of various kinds of measurements are dependent on the direction along which the experiment is performed. This is particularly transparent in the photoemission spectroscopy measurements, which in turn present the core of this paper. It will be shown that a metallic film may represent a quantum well whereas the electrons are confined within the film and between a symmetry band gap on the film-substrate side and the potential step at the vacuum side of the film. These electrons form stationary states (standing waves) and are often called quantum well states (QWS).

The idea of standing wave formation due to the QSE was pursued by Jaklevic[2,3] to explain oscillations observed in electron tunneling through thin metallic films of Mg, Pb, Au and Ag. The effect was observable up to a thickness of 500 Å.

Further experimental work on the QSE on the reflectivity and transmission of electrons normally incident to the epitaxially grown thin metallic films (of Cu and Ag on a W(110)) was done by Jonker *et al.*,[4–6] Park *et al.*,[7,8] Zhu *et al.*[9] and Zdyb *et al.*[10] for Cu/Ni(001), Ag/Cu(111), Ag and Cu on Si(111)7×7 systems.

In these early works, the experiments probed only the unoccupied QW states. The first measurements of the occupied states were performed by measuring electric conductivity of Sn and In ultrathin films during deposition[11] and resistivity of Pt films in a wide thickness range of 30–3000 Å.[12] Fischer *et al.*[13–15] made an effort to produce clear experimental evidence for the existence of QSE in Pt very thin films. Jalochowski *et al.*[16–18] further documented the importance of QSE in resistivity measurements.

Once the existence of QW states and their importance for transport properties of thin metallic films had been established beyond any doubt, a large number of different oscillatory phenomena in thin films were explained within this, quantum well states, picture. Probably the best known phenomena are those connected to magnetic multi-layered structures and super-lattices. An excellent review of this field has been recently given by Himpsel *et al.*[19] and we refer the reader to it when looking for magnetism related papers. The quantum size effects in thin films were observed also in the Helium atom scattering (HAS) experiments,[20–23] in the Hall effect measurements,[24] in the Second harmonic generation (SHG) studies,[25,26] in the Work function measurements[27] and in the diamagnetic optical response of metallic (Ni, Al) ultra-thin films.[28,29]

BASIC DESCRIPTION OF THE QW STATES IN METALLIC FILMS

The simplest way of describing the problem of electron confinement within a metallic film of atomic thickness is to start with a one-dimensional quantum well with finite walls. The bottom of such a well is flat and the walls may or may not be of the same height. If we consider the case of a film that has a substrate on one side and vacuum on the other, we talk about an asymmetric quantum well. By solving the Schroedinger equation for this system with a specific film thickness and a system-specific effective potential as parameters, one can get the energies of the corresponding quantum well states. This description is not expected to yield exact solutions for the following reasons: a) the model uses the step potential on the vacuum side instead of an image potential of the $1/z$ type (z is distance from the surface into the vacuum); b) the step potential on the substrate side is not a realistic potential of the interface; c) the bottom of the well is not flat in reality. Still, this simple description may give us an insight into the states' wave functions and it has been successfully applied to the problem of photon energy dependence of QW states, as will be discussed later in the text.

As pointed out in the Introduction, in order for the electrons within a film to form a QW state, the substrate must have a band gap. In the case of a metallic substrate, there is no true band gap (like in the case of semiconductors and insulators). Still, due to periodicity of the effective potential within metals, the band gaps open at the bulk Brillouine zone (BBZ) boundary, at different energies for different directions and different band symmetries.

One of the simplest ways to think of the QW states is to start from a symmetry band gap, say an sp band of a vanadium monocrystal along the 100 crystallographic direction and look for the electron energy solutions for the gap. Obviously, all Bloch plane waves describing the bulk electronic structure of the sp-electrons must have real values of energy and momentum and as such they necessarily have solutions outside the gap. In order to find the allowed electron energy solutions within the gap, one has to take into account the imaginary momentum values, *i.e.*, those wave functions that exist only at surfaces and exponentially decay into the bulk. When a film is deposited, those sp-electrons (within the film) which have the energy within the band gap may form standing waves (QW states, stationary solutions) by being multiply reflected between the band gap (the substrate potential wall) and the image-like potential at the film-vacuum interface. The allowed QW state energies are determined by the band-gap solutions and the state is formed only when the total phase change for the round trip is:

$$\phi\mathrm{s} + \phi\mathrm{v} + 2\phi_{\mathrm{F}} = 2n\pi \tag{1}$$

where ϕs, and ϕv stand for the phase change upon reflection on the substrate and vacuum side, respectively, ϕ_{F} is the total phase accumulated in traversing the film, $\phi_{\mathrm{F}} = Nkd$, N is the number of monolayers, d is the monolayer thickness, k and n are the QW state quantum numbers. The quantum number n is associated with the number of nodes of the QW state wave function while k has, in the case of thicker ultrathin films, the meaning of the QW state wave vector perpendicular to the film.

This is the so-called »phase accumulation model« that was originally developed[30,31] for describing surface states. A surface state is indeed the solution of equation (1) for the zero film thickness.

By increasing the film thickness, the quantum well gets wider and consequently all QW states get lower in energy. In practice this means that a state just above the Fermi level and a state just above the lower edge of the band gap, for a thickness Nd, will be, for a thickness $(N+1)d$, shifted below the Fermi level (*i.e.*, will be populated) and below the band gap, respectively. In such a way, the photoemission current measured at a constant binding energy, *e.g.* the Fermi level, shows oscillations with increasing film thickness, as the QW states are passing across the band gap. For example, in the Ag/V(100) case, this happens in cycles of 4 monolayers. A particularly nice and didactic experiment of this type is described in reference 32. This density of states (DOS) variation at the Fermi level caused by variation of the film thickness gives rise to the oscillatory phenomena discussed in the Introduction. It is also responsible for the Giant magnetoresistance (GMR) effect in magnetic-nonmagnetic multilayered sandwich systems. It took only ten years from the discovery of the GMR and the first commercial products based on its use.

The space variation of the QW state wave function also depends on the film thickness. At very small thicknesses, the wave function is accurately described by the quantum number n. At larger thicknesses where an effective periodic potential is formed within the film, the wave function space variation is dominated by an additional, slowly varying function, the so-called envelope function. In this paper, we concentrate on the smallest thicknesses only.

PHOTOEMISSION SPECTROSCOPY OF QW STATES IN METALLIC FILMS

Among the large number of experimental methods available, the ultraviolet photoemission spectroscopy, UPS,[33] is particularly suitable for studying quantum well states in metallic films. A lot of photoemission work on metallic QW states has been published in the last ten years. A very recent review may be found in Ref. 34. The UPS probes the valence bands of metals, providing information about the bulk and surface electronic structure and density of states. Information may be acquired by collecting all emitted photoelectrons (the co called angle-integrated mode) or only the photoelectrons along a chosen emission direction (the so-called angular-resolved mode). Since the quantization in the ultrathin films occurs along the direction perpendicular to the film, the photoelectrons emitted perpendicularly to the surface, *i.e.*, in the so-called normal emission, are of particular interest. Further in the paper we show normal photoemission spectra unless otherwise specified.

Figure 1 shows a set of UP spectra, each taken with different excitation (photon) energy, of a thick silver film deposited on a V(100) surface. The electron energy is referred to the Fermi level of the sample (the so-called binding energy). By increasing the photon energy, the sp valence band peak (Δ_1) shifts away from the Fermi level and eventually mixes with the 4d silver bands.

This behaviour is a consequence of the film electronic structure shown in Figure 2b in the reduced zone scheme for the fcc silver in the 100 direction. The sp valence band is denoted as Δ_1. The Δ_1 peaks in Figure 1 correspond to direct (optical) transitions between the lower and upper branches of the band. The band crosses the Fermi level and reaches the bulk Brillouin zone at the $X_{4'}$ point. The Δ_1 band of the vanadium surface (shown in Figure 2a) has a gap ± 2 eV around the Fermi level. When a thin silver film is deposited on a V(100) surface, the sp electrons of the film that have energies lying within the Δ_1 band gap of V(100) see the band gap as a potential wall. These electrons form stationary (quantum well) states whose wave functions are located within the film with the tails extending across both interfaces. These stationary states are seen in UP spectra as peaks of characteristic energy, intensity and width.

Figure 3 shows the UP spectra of the QW states of Ag films in the thickness range of 1–7 monolayers (ML) deposited on the V(100) surface, except for the 3 ML film which has no occupied QW state. Detailed description of the growth modes, structure and electronic properties of this system may be found in Refs. 35 and 36. Note that the Δ_1 band gap of V(100) extends to 2 eV below the Fermi level, *i.e.*, the peaks in Figure 3 positioned between 0 to 2 eV binding energy are true QW states. Obviously, each film is character-

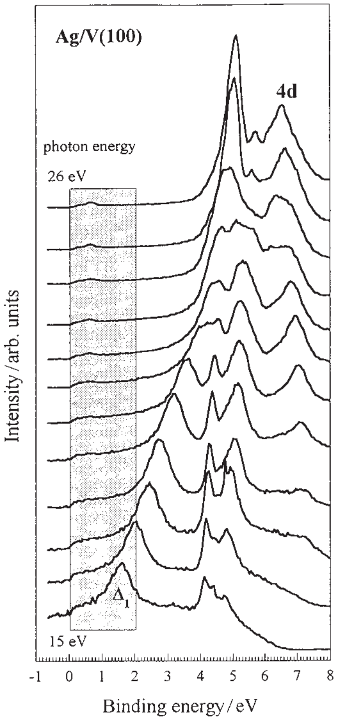

Figure 1. Normal emission photoemission spectra of a thick Ag layer on a V(100) surface taken with photon energies of 15 to 26 eV in steps of 1 eV. Note the strong dispersion of the sp silver band (Δ_1). Shaded area indicates the extension of the V sp-band gap.

ized by one single QW state. Each spectrum was taken at a photon energy that, if the film were thick, would not allow the Δ_1 direct transitions within the band gap energy window (compare Figure 1).

The intensity of QW states appears to be very sensitive to the presence of defects within the film. Defects may arise from irregular film growth, poor substrate surface conditions, large lattice mismatch between the substrate and overlayer, *etc*. The most perfect conditions in this respect were achieved for the Ag/Fe(100) system: the substrate surface was an Fe whisker (100) perfect plane of micron dimensions and the lattice mismatch of Ag and Fe was below 1%. These conditions combined with a very careful deposition process enabled the growth of perfect silver films up to 120 ML thickness, still showing characteristic QW states.[37]

Surfaces of macroscopic monocrystals are far from being perfect on the micron scale. Figure 4 shows an STM image of the V(100) surface used in this study.[38] There are a number of many relatively large (several thou-

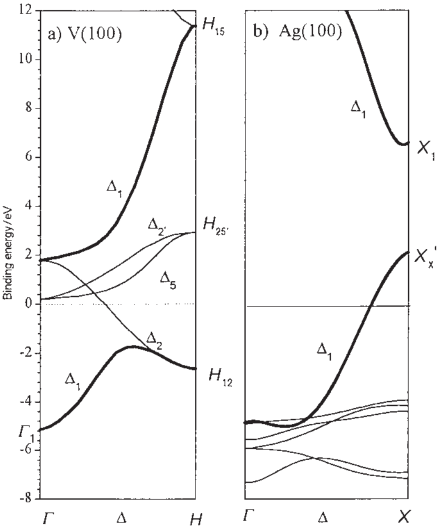

Figure 2. The energy bands of vanadium[50] (a) and silver[51] (b) along the Γ-Δ-H (X) direction of the bulk Brillouin zone, corresponding to the normal emission from (100) surface. The sp-bands are drawn as thick lines to emphasize the coincidence of the Ag Δ_1 band with the Δ_1 band gap of vanadium.

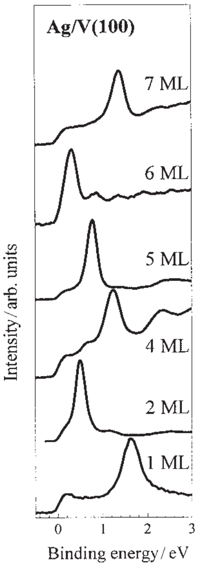

Figure 3. Normal emission photoemission spectra of the QW states characterizing each of the silver films in the thickness range 1–7 monolayers (ML). The energy window was chosen such as to display only the sp-derived QW states. The spectra are taken at indicated photon energies.

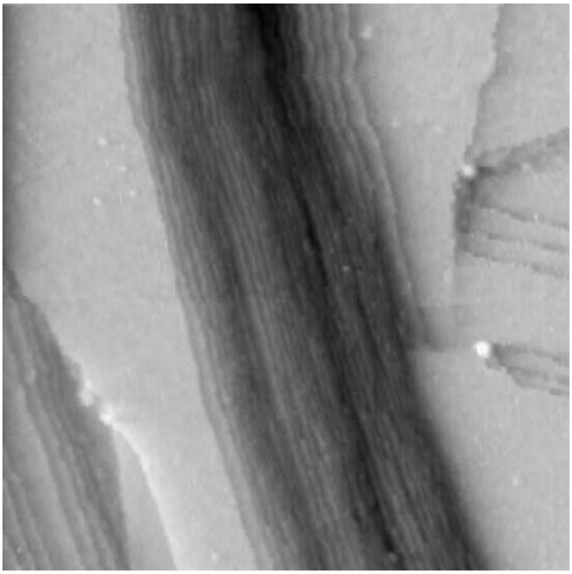

Figure 4. The Scanning Tunneling Microscopy image (200 nm × 200 nm) of a clean and well-annealed V(100) surface. STM bias voltage = 200 mV and current = 6 nA.

sands of nm^2) flat (100) oriented areas that dominate the surface properties. Unfortunately, there are also many (monoatomic) steps (defects) and very narrow terraces where a growth mode might be different. These surface imperfections and the fact that the lattice mismatch between Ag and V is several times larger than in the Ag/Fe case explain why the QW states of the Ag films on V(100) lose significantly their intensity above 8–10 ML thickness and soon become undistinguishable. The lattice mismatch prevents silver films at room temperature to grow in a perfect layer-by-layer mode even on perfect and large areas. The first two layers are stable up to the silver desorption temperature and serve as a substrate for clusters formed after exposing the films to temperatures above the r.t. This mode of growth is known as the Stranski-Krastanov. Therefore, by annealing the films at high temperatures, one can always produce perfect 1 and 2 ML films.[35,39]

The high quality of 1 and 2 ML films is reflected in their QW state spectra, as shown in Figure 5: in both films, the sp-QW state intensity is comparable with the intensity of the d-electron system.[40] These two QW states are the most intense sp-derived states published so far. The topmost spectrum belongs to the 2 ML film that was annealed at 800 K. Since the desorption temperature of the first silver layer on the V(100) surface is 50 K higher than that of the second layer, it is possible to produce intermediate coverages. This is achieved by heating the sample to the onset of the second

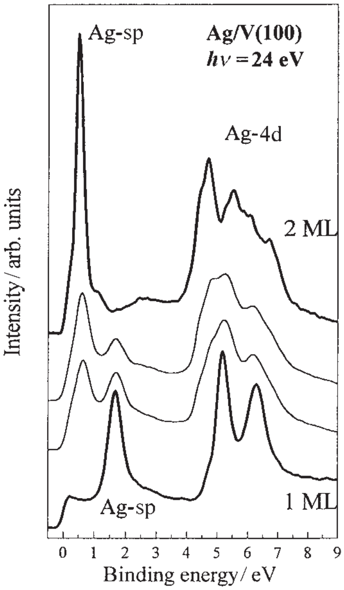

Figure 5. Normal emission photoemission spectra of 1 ML and 2 ML Ag films and two intermediate coverages (thin lines). For details see the text.

layer desorption. The two intermediate coverage film spectra are shown in Figure 5 in between the spectra of the 1 and 2 ML films. Both of them show QW states of 1 and 2 ML films because they are a mixture of patches of both films. After several desorption steps, a complete, perfectly ordered and clean silver monolayer film (bottom spectrum) is obtained.

The d-electrons in these films form stationary states as well.[41,42] Their assignation is not as simple as in the case of the sp-derived states. Three facts make their identification and individual study tedious: 1) There is a large number of states per film because there are five d-QW states per atomic layer in the film. 2) All of them are within a rather narrow energy range. 3) It seems that d-QW states are very sensitive to even a small change in atomic coordination, *i.e.*, film structure.[42] If the film undergoes restructuring, its spectra loose resolution and intensity before the sp-QW states »feel« the change.[42] Therefore, further in the text, we discuss only the sp-derived states.

Photon Energy Dependence

All of the states in Figure 3 are rather intense when compared with the background intensity. It should be pointed out that each spectrum was taken at a different photon energy in order to obtain the maximum in intensity. Namely, all of the states show significant oscillatory dependence of the spectral intensity on the photon energy used for excitation. This is shown in Figure 6 for the photon energy range of 15–100 eV. The spectra displayed in Figure 6 are the so-called CIS, constant initial state, spectra which are measured by sitting on the constant binding energy and changing the photon energy. Such experiments may only be performed using a synchrotron light source.

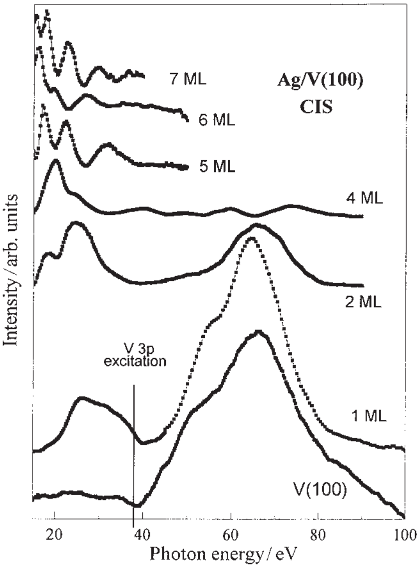

Figure 6. Constant initial state (CIS) spectra of the QW states shown in Figure 3. The spectra above 40 eV photon energy of the films thicker than 4 ML are not discussed here and are consequently not shown. The bottom spectrum shows the data for the clean and well-ordered V(100) surface.

A detailed account of the experiment is given in Ref. 40 along with the theoretical model for the observed oscillatory dependence. The model treats the system as an asymmetric quantum well and relies on Adawi's formalism for one-dimensional photoemission. The crucial feature of the model is that the steep potential walls at the substrate-film and the film-vacuum interfaces are the main sources of the photoemission process whereas the variations of the potential within the film are comparably small and may be neglected. The interference of the two photoelectron sources produces oscillations in the photon energy dependence of the QW states. This model, as may be seen in Ref. 40, fairly reproduces the trends shown in Figure 6 and as such may be considered valid for these, very low thicknesses. With increasing film thickness, the periodic variation of the potential within the film is getting more important while the interference effects from the interfaces are getting smaller. In other words, the thicker the film the more bulk-like electronic structure it has. Eventually, the electronic structure of such a film should be determined by the band energy – band momentum dispersion relation. This in turn means that the photoemission transitions from such bands should be most intense at the photon energies that fit direct (optical) transitions between different branches of the same symmetry (in the reduced BBZ scheme), like in the case of Figure 1.

However, the very thin films may not be subject to these considerations. Firstly, there are just a few monoatomic layers forming the film and one can hardly speak of any periodic potential variations and secondly, the interaction between the substrate and the film extends over several layers (on both sides) and significantly influences the electronic system of the thin film. This is clearly seen in Figure 6: neither of the QW states obey the direct transition predictions. For example, in Figure 1 one sees that for the photon energies of 15–16 eV, the Δ_1 band has direct transition peaks at binding energies within the vanadium Δ_1 band gap. At the same time, the QW states of the 1 and 7 ML films (Figure 3), which have energy within that energy window, do not show intensity maximum at these photon energies, as may be read from Figure 6.

In addition, while the spectra in Figure 6 show a general trend of decreasing intensity with increasing photon energy, the two thinnest films show different behaviour. The 1 ML film has the highest intensity at a high energy. The overall spectrum lineshape above 40 eV resembles closely the spectrum obtained for the clean V(100) substrate. The two spectra are shown in Figure 6, at the bottom. The photon energy dependence of the clean V(100) is a consequence of the so-called resonant photoemission (RP) process.[43] Namely, the photon energy of 37 eV is just enough to promote a V 3p electron to the Fermi level. The 3p hole left behind may be filled in by an electron from, *e.g.*, the Fermi level while the energy released could be taken by another electron from the Fermi level, which then leaves as a »normal« photoelectron. The two electrons interfere and are responsible for the resonant process. Such a process is available in a wide photon energy range above 37 eV and gives rise to the observed photon energy dependence. In the case of a single atom, this is called Phano resonance.

In the normal, non-resonant photoemission process, the electronic configuration changes as follows (for the case of the vanadium 3d band):

1. absorption of photon: $3s^2 3p^6 3\mathbf{d}^{\mathbf{3}} 4s^2 + h\nu$
2. emission of photoelectron: $3s^2 3p^6 3\mathbf{d}^{\mathbf{2}} 4s^2$ + photoelectron.

In the resonant photoemission process, there are more electrons involved:

1. absorption of photon: $3s^{2}3\mathbf{p}^{6}3d^{3}4s^{2} + h\nu$
2. excitation of 3p electron: $3s^{2}3\mathbf{p}^{5}3\mathbf{d}^{4}4s^{2}$
3. filling of the 3p hole and photoelectron emission: $3s^{2}3\mathbf{p}^{6}3\mathbf{d}^{2}4s^{2}$ + photoelectron.

In real space, this process was believed to be available only for electrons localized on the same atom and was extensively used to distinguish between the valence band features of constituents of alloys. The striking similarity between the QW state photon energy dependence of the silver 1 ML film and the V(100) surface is explained[44] in terms of multi-atom resonant photoemission (MARPE), *i.e.*, both vanadium and silver atoms are involved in the RP process. This is possible because the silver atoms are deeply embedded within the topmost vanadium layer (a detailed structural account of the films is given in Ref. 35). This proximity is crucial: the effect is significantly smaller already in the 2 ML and non-existent in the 4 ML silver film (Figure 6). This MARPE was first reported[45] for discrete atomic levels of some oxides though later, at some conferences, the effect was, at least partly, ascribed to an artifact of the measuring equipment. The Ag/V(100) study[44] discussed here is the first MARPE observed in a metallic system and in the valence band. It was later reported also for transition metal chlorides.[46]

Temperature Dependence and the Electron-phonon Coupling

Another fascinating property of these ultrathin layers is connected with the temperature dependence of the UP spectra of the respective QW states. A typical example is given in Figure 7 where the UP spectra, taken at different temperatures, of the 2 ML film QW state are displayed. Evidently, with increasing temperature, the peak broadens, decreases in intensity and shifts away from the Fermi level. These changes are thoroughly discussed in Refs. 47 and 48 and here we turn our attention to the peak width only. The peaks are nicely fitted with the »Fermi Liquid« lineshape:

$$2\mathrm{Im}\Sigma(\omega) = \Gamma_{0} + 2\,\beta\,\omega^{2} \tag{2}$$

where the left hand side represents the imaginary part of the photo-hole self-energy at energy ω, the energy independent term Γ_{0} is a sum of defect and phonon scattering terms and the quadratic term is the electron – electron contribution. This formula is valid only for two-dimensional and quasi two-dimensional systems, because in such systems the angle-resolved UPS measures directly the photo-hole spectral function, *i.e.*, the UP spectral

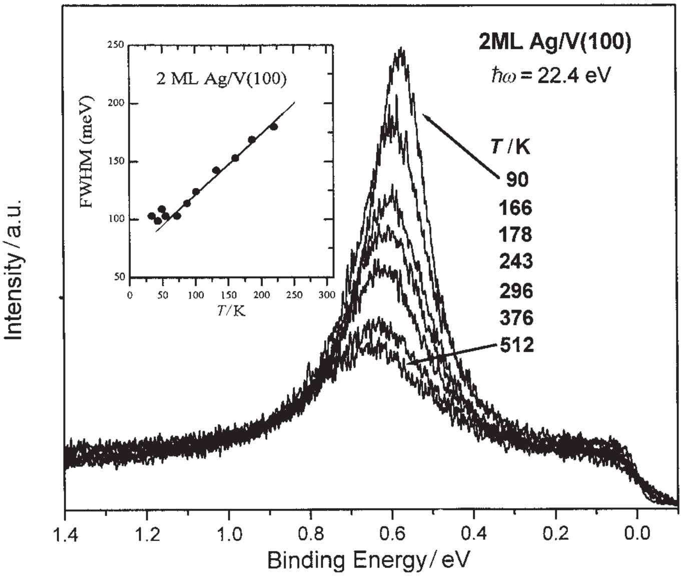

Figure 7. Normal emission photoemission spectra of the 2 ML thick Ag film on V(100) surface taken at indicated temperatures. Inset: Temperature dependence of the 2 ML film QW state with a linear fit to determine the electron-phonon coupling constant.

width is directly proportional to the photo-hole lifetime. Of particular interest here is the phonon scattering term, which irrespective of the other two contributions, can be very precisely extracted. The plot of the peak width *versus* temperature gives a straight line, with a slope that equals $2\pi\lambda k_B$ where λ is the electron (hole) – phonon coupling constant.

A high λ value is a necessary (but not sufficient) condition for an increased superconducting transition temperature and therefore it is important to determine its value experimentally in a quest of tailoring the physical properties of ultrathin films. Figure 7, inset, shows the temperature dependence of the QW state of the 2 ML film. A linear fit of these experimental points gives a λ value of 1.0. It is 5 times higher than the silver bulk value of 0.18–0.22. In this way, values for all films up to 8 ML thickness are determined and the graph of λ *versus* thickness is presented in Figure 8. A striking feature of the graph is the oscillatory behaviour of the electron – phonon coupling value. This is not so for thicker silver films: the ARUPS measurements of Ag films thicker than 10 ML showed a constant λ value (0.22) for films thicker than 12 ML.[49] The oscillatory λ behaviour is explained[47,48] in terms of photo-hole coupling with thermally-induced oscillations of the potential step at the film-vacuum interface.

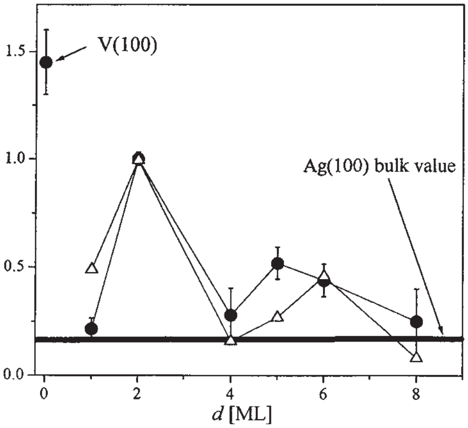

Figure 8. Electron-phonon coupling constant as a function of the Ag film thickness. Experimental points: full circles; model calculations: open triangles.

Within this model, a QW state effective mass enters the calculation. The ARUPS measurements presented in this work make it possible to experimentally determine the effective masses of the QW states with great accuracy.[48] With these masses taken into account, the model almost qualitatively reproduces the experimentally determined values.

CONCLUSIONS

Ultrathin films in the range of up to several monolayers thickness have different electronic properties than thicker ultrathin films. In the angular-resolved photoemission spectroscopy this is manifested in the photon-energy and temperature dependence of the QW states. The oscillatory intensity dependence on photon energy is a result of the one-dimensional photoemission process from the film boundaries and the interference of the two sources. The electron-phonon coupling constant also shows oscillatory behaviour at these small thicknesses. These effects are obviously a result of an extremely reduced dimension perpendicular to the film surface as well as of the electronic rearrangements within the film-substrate interface.

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SAŽETAK

Elektron u kutiji i ultratanki metalni filmovi u ogledalu tehnike kutno razlučene UV fotoemisijske spektrometrije (ARUPS)

Milorad Milun

Ultratanki metalni filmovi ponekad se ponašaju kao kvantne kutije. Prikazani su slučajevi u kojima se dimenzionalnost može smanjiti na samo jednu jedinu dimenziju. Kao modelni sistem uzet je Ag/V (100), a kao alat korištena je tehnika ARUPS kutno razlučena UV fotoemisijska spektrometrija.