

Atomic Structure of Surfaces and Ultrathin Films

Vesna Mikšić Trontl,^a Ivo Pletikosić,^b Petar Pervan,^b and Milorad Milun^{b,*}

^a*Faculty of Electrical Engineering and Computing, University of Zagreb, Zagreb, Croatia*

^b*Institute of Physics, Zagreb, Croatia*

RECEIVED JANUARY 17, 2006; REVISED MARCH 20, 2006; ACCEPTED MARCH 23, 2006

Keywords
scanning tunneling microscopy
ultraviolet photoemission spectroscopy
ultrathin metallic films
surface structure

Structural and electronic properties of surfaces and ultrathin metallic films are closely connected. Because of their low dimensionality it is of the utmost importance to acquire their structural details at atomic level and their electronic structure resolved in energy and momentum at very high resolution. In this paper, we briefly review several experimental examples that illustrate these requirements and at the same time address some important properties of surfaces and ultrathin films. The examples are restricted to those that used scanning tunneling microscopy to study the structural properties and ultraviolet photoemission spectroscopy to elucidate the electronic structure of the samples.

INTRODUCTION

This paper aims to briefly review some aspects of structural investigations that are rather surface- than bulk-related and to show how structural information obtained with atomic precision and resolution may be combined with modern photoemission studies in order to assess all important factors that influence structural features of surfaces and ultrathin films. Such an approach is extremely important for the emerging nanosciences and nanotechnologies where ultrathin metallic films have a very significant role.

EXPERIMENTAL

Experiments were carried out in an ultra high vacuum chamber with the base pressure in the range of 10^{-8} Pa. The chamber was equipped with a Scanning Tunneling Microscope (STM)¹ and a rear-view Low-Energy Electron Diffractometer (LEED).² For photoemission experiments, we used a

Scienta SES-100 hemispherical analyzer, which simultaneously collects photoelectrons at a range of energies (in our experiments around 5 eV) and angles (around 12°) and a He discharge lamp as the excitation source. The ultimate instrumental resolution of the analyzer is around 5 meV. The binding energies could be read from the photoemission spectrum with an uncertainty of ± 0.01 eV. The angular resolution was around 0.2° . The He I (21.2 eV) photons were used for excitation in photoemission spectroscopy experiments. The polar angle was changed by rotating the sample. The experiments were performed using two sample holders. The one for the photoemission experiments allowed cooling-heating of the sample in the temperature range between 150 K (obtained by a Leybold He cold head) and 1200 K (obtained by resistive, direct heating by thin tantalum wires). The sample holder specially designed for the STM measurements did not allow cooling but only heating (up to 1200 K) and therefore all STM measurements were performed at room temperature. Palladium and copper crystal disks ($\sim 0.5 \text{ cm}^2 \times 0.2 \text{ cm}$) of nominal purity of 99.99 %

* Author to whom correspondence should be addressed. (E-mail: milun@ifs.hr)

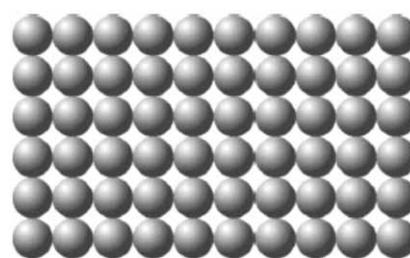
were oriented with the precision of 0.1° and mechanically polished. Further cleaning of the crystals was performed in the UHV chamber. We used the palladium (or copper) single step height to additionally calibrate the STM vertical resolution in the experiments. Silver films were prepared by resistive heating of a tungsten basket filled with pure silver. The deposition rate was adjusted to 0.2–1 ML/min.

BULK VERSUS SURFACE

When discussing properties of various materials, in most cases it is done in terms of their bulk characteristics. Indeed, most of the properties, being mechanical, electric, magnetic, heat transport, and many others, are dominantly a consequence of the existence of bulk. As most materials are (poly)crystals, a number of methods have been developed to describe and predict properties of bulk periodic systems.³ In principle, »bulk« means periodicity in all directions and without boundaries. Although, fortunately, no such ideal crystal exists, it appears that these methods may fairly be used to assess the properties of real systems, ranging from very small (micron) to very large pieces of a material. For simplicity, let us consider a metallic system. It is best described as an ionic crystal lattice immersed in a sea of electrons. These electrons form electron bands whose charge may be mostly located near the cores or distributed across the whole crystal interior. Note, however, that a real crystal has surfaces. Here the periodicity abruptly stops and our rather simple models based on infinite periodicity cease to be adequate. Surface atoms differ from those in the bulk primarily in the number of neighbors: their coordination number is smaller, at least one of atomic orbitals dangles free and, as a consequence, surface atoms have higher potential energy, enhanced chemical reactivity and are exposed to various species from the surroundings. In order to minimize the energy, the surface layer relaxes in the direction perpendicular to the surface. This relaxation affects at least two topmost layers and its magnitude depends very much on the atomic structure of the respective surface. For example, relaxation effects are larger for fcc(110) surfaces where atoms have fewer neighbors than in the case of fcc(111) surfaces (Table I).

TABLE I. Relaxation effects on various surfaces as measured by LEED. Change of the bond length perpendicular to the surface plane is expressed in % with respect to the bulk value.

Surface	Material (bond length change)
fcc(111)	Al, Co, Ni, Cu, Ag, Pt, Au (all < 1 %)
fcc(100)	Al, Co, Ni, Cu, Rh, Ag, Pt (all < 1 %)
bcc(110)	Na, W, Fe (all < 1 %)
bcc(100)	Fe (1.5 %), Mo (4 %), W (2–4 %)
fcc(110)	Ag (1.5 %), Al (1.5 %), Ni (1.5 %), Cu (1.5 %)



Pt(100)

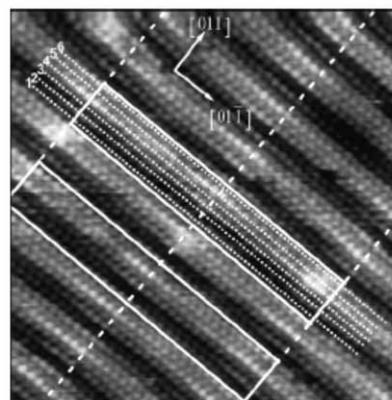


Figure 1. Model of an idealized Pt(100) surface layer and a STM image of a real Pt(100) surface.⁵ The solid rectangle shows the unit cell of the superstructure.

In many cases, surfaces reduce their potential energy by severe reconstruction of one or more surface layers, thus producing completely new structures. One of the most famous cases is the reconstruction of Si(111) into Si(111) 7×7 surface.⁴ Figure 1 shows a dramatic case of Pt(100) reconstruction:⁵ the upper panel shows an idealized Pt(100) surface layer and below it is an STM image of the real Pt(100) surface. In the STM image, each bright spot corresponds to one Pt atom. Obviously, the reconstructed surface has little, if at all, resemblance with the idealized (100) surface.

In some cases, the reconstruction process may be triggered by adsorbates. For example, the V(100) surface is very stable and does not reconstruct even at very high temperatures.⁶ However, if a small amount of oxygen is allowed to adsorb on it, this surface undergoes 5×1 reconstruction.⁷ Interestingly enough, heating of silver films deposited on the reconstructed surface lifts off the reconstruction completely. The smallest amount of silver required is only half of the monolayer.⁸

EXPERIMENTAL METHODS FOR THE ASSESSMENT OF SURFACE STRUCTURES AT ATOMIC RESOLUTION

X-ray diffraction probes the interior of a sample while surface information presents only a negligible part of the overall information. To study surfaces, one has to use

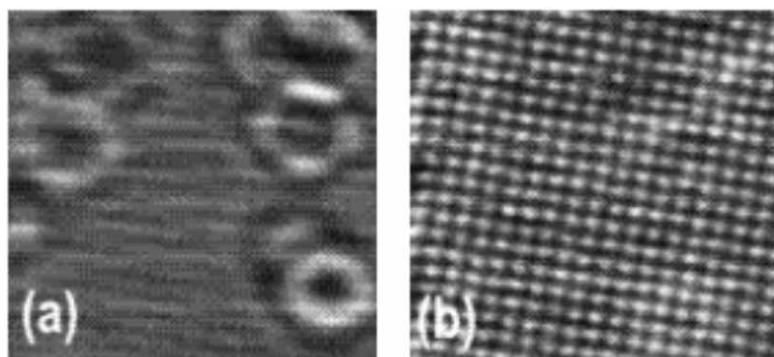


Figure 2. Constant current STM images of a 5 ML thick Ag film on V(100).¹¹ a) Standing wave patterns of point-defects derived surface electrons visible at bias voltage: $U_B = 222$ mV. b) Atomic resolution STM image of the same surface as in a) obtained at different bias voltage: $U_B = 24$ mV.

surface sensitive methods. A surface analogue of the classic structural probes is the Low-Energy Electron Diffraction⁹ (LEED), which provides structural information in the reciprocal space. It is used to study periodic structures of topmost surface layers and adsorbed films. Information is integrated over a millimeter scale. It does not provide atomically resolved information like the Scanning Tunneling Microscopy (STM) does.¹⁰ STM provides atomically resolved images of a selected surface part in real space, on a nanometer scale. It may operate in air, liquid or vacuum. In principle, an STM apparatus is very simple: it consists of a very sharp metallic tip that ends with a single atom and a sample. Bias voltage is applied between the tip and the sample. For a given bias and the tip-sample distance, a particular current of tunneling electrons is detected. By changing the lateral position of the tip, the current will change according to the topography of the surface. If the tip is close enough to the surface (within ≈ 300 – 500 pm), an atomically real-space image of that surface will be obtained. In Figure 1, we have shown an atomically resolved image of the Pt(100) reconstructed surface. There the white spots correspond to higher tunneling currents and may be directly connected with the position of Pt atoms.

However, high density of electronic states (DOS) should not necessarily be connected with surface atom positions. They may as well originate from multi-body electronic excitations, as shown in Figure 2 for the case

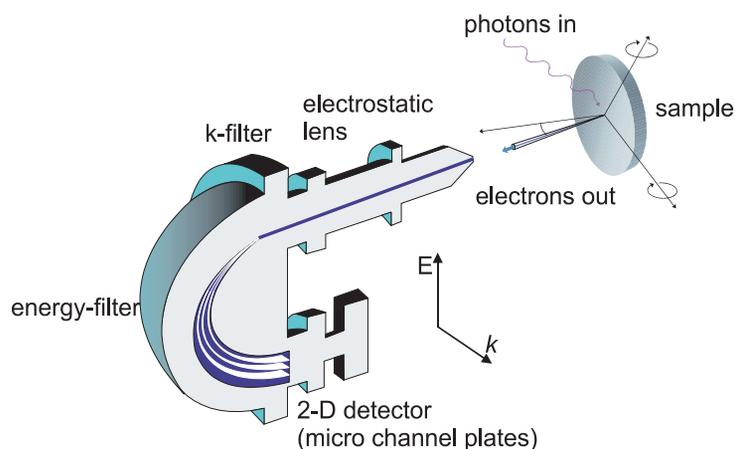
of surface electrons of an adsorbed silver film. The figure shows an STM image of a 5 ML thick silver film on V(100) surface at room temperature. The circular features in Figure 2a are standing waves obtained by scattering of the surface electrons on the defects present at the surface.¹¹ Detection of the standing waves depends solely on the bias voltage in the STM experiment: a small change in tunneling conditions brings back the atomically resolved Ag/V(100) image,¹¹ as shown in Figure 2b.

A whole set of methods have been developed based on the STM. Among them and from the point of view of atomically resolved studies of surfaces, the most important one is the Atomic Force Microscopy (AFM). It measures the force acting between a sharp tip and the surface and is usually used when the sample is not conductive. In this paper, however, we concentrate on the use of STM.

EXPERIMENTAL METHODS FOR THE ASSESSMENT OF ELECTRONIC STRUCTURE OF SURFACES

A large number of methods have been developed to probe surface properties. They use various excitation sources (electromagnetic radiation, ions, neutrals) and measure the surface response.¹² The most powerful method to study the electronic structure of surfaces and adsorbed layers

Figure 3. Schematic presentation of the high-resolution Scienta SES-100 analyzer. Basic operation principles are presented. Due to the 2-D multi-channel detector, simultaneous angle (k) and energy resolution of photoelectrons emerging from the sample surface to the detector entrance is possible.



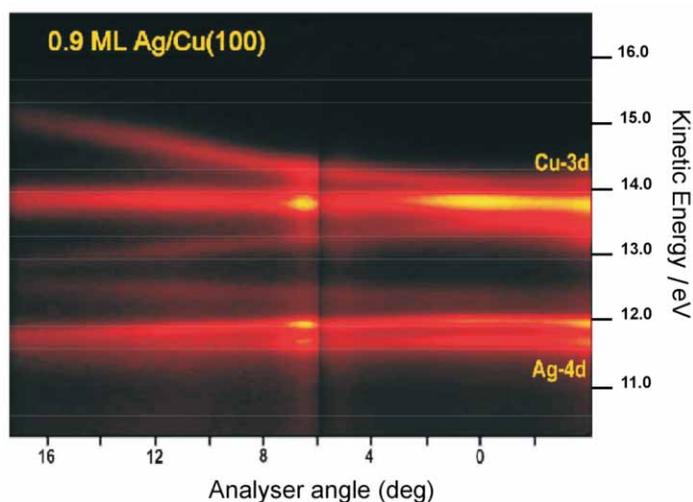


Figure 4. Example of energy vs. momentum (angle) image plot of the photoemission intensity from 0.9 ML Ag/Cu (100). Energy resolution in the experiment was 25 meV and the angular resolution was 0.2° . The Cu 3d and Ag 4d electron bands are clearly discernible in the kinetic energy range of about 16–13 eV and 13–11 eV, respectively.

is certainly the Ultraviolet Photoemission Electron Spectroscopy (UPS),¹³ which in essence is a simple photoemission experiment: photons of precisely defined energy (from a few eV to about 100 eV) excite valence electrons of the sample whereas those with enough energy leave the sample and are analyzed with respect to their kinetic energy, angle of emission, spin, *etc.* Surface sensitivity of the UPS method is very high due to the very short inelastic mean free path (IMFP) of photoemission electrons at these kinetic energies.¹⁴ It may vary between a few angstroms and several nanometers.

Modern analyzers have very high energy resolution (about 1 meV) and very high angle resolution (below 0.2°). In fact, they simultaneously collect information about electron energy and electron momentum within a rather large momentum window. Figure 3 displays schematically the operation principle of such an analyzer.¹⁵ Figure 4 shows an example of the study of 0.9 monolayer (ML)-thick silver islands on Cu(100) surface: the x -axis gives photoelectron momentum k (angle of emission), the y -axis photoelectron kinetic energy E and z -axis contains information about photoemission current intensity at the corresponding E, k point. To obtain a more common presentation of spectra, *i.e.*, those showing photoemission current intensity *versus* electron kinetic energy (the so called electron dispersion curves, EDC), one should take cuts of very narrow k -values, as shown in Figure 5.

ULTRATHIN METALLIC FILMS: GROWTH, STRUCTURE AND ELECTRONIC PROPERTIES

Structural and electronic properties of a particular surface may significantly affect the growth, structure and properties of ultrathin metallic films. Briefly, three major types of film growth are distinguished: a) layer-by-layer or Van der Merwe, which is characterized by the fact that a new layer starts to grow only after completion of the preceding one; b) Volmer-Weber growth, during which atoms of the film agglomerate into clusters and the film is

formed after the clusters become so large as to coalesce; and c) Stranski-Krastanov growth, which starts as a layer-by-layer growth and after completion of this »support« layer, clusters are formed on top of it. Thermodynamically, these growth modes are determined by the

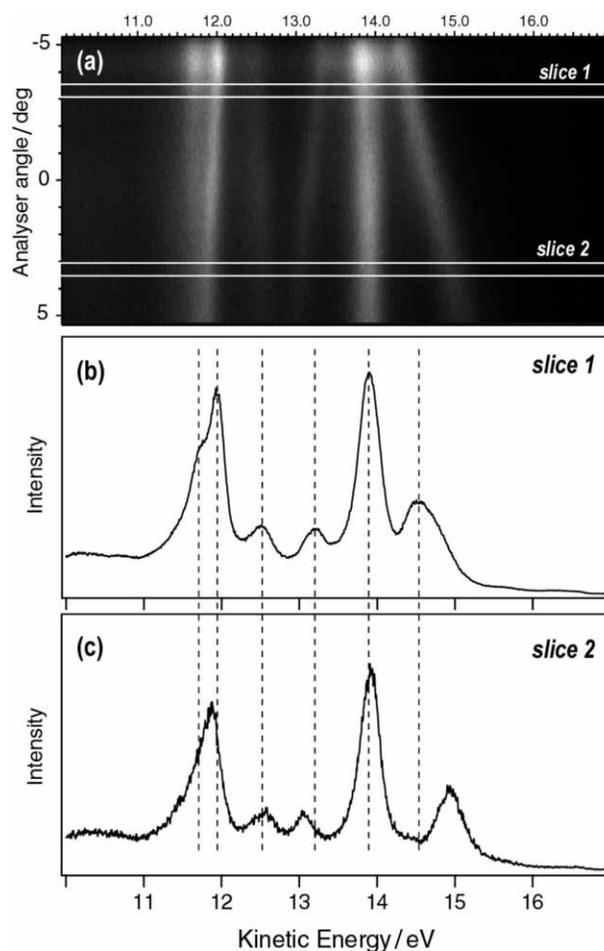


Figure 5. Illustration of the procedure for extraction of the EDC spectra from a SES100 spectrum: a) the same spectrum as in Figure 4 but rotated by 90° ; b) and c) k -space cuts (EDC spectra) taken for two different angles (k -points).

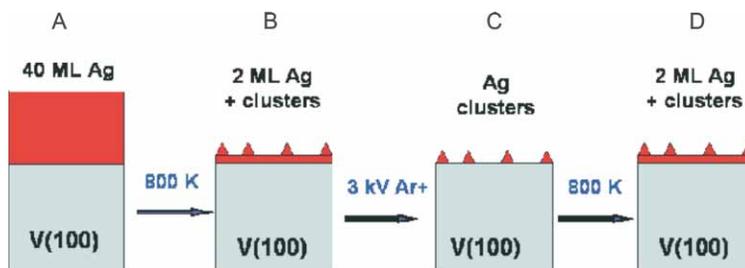


Figure 6. Illustration of the three main types of films using the Ag/V(100) system (see the text). A: Ag deposited at 200 K forms a thick layered film on V(100) – Van der Merwe growth mode. B: Transition to Stranski-Krastanov film caused by heating at r.t. C: Stranski-Krastanov support film was removed after sputtering and only 3-D clusters remained on the surface – Volmer-Weber film. D: Recovery of the Stranski-Krastanov film (2 ML Ag film with clusters) after annealing at 580 K.

difference in surface free energies between the substrate surface and the film, on the one hand, and the strains within the film, on the other hand. Generally, on transition metal surfaces (high surface energy), noble metals (low surface energy) grow layer-by-layer while in the case of deposition of transition metals on noble-metal surfaces, the Volmer-Weber growth prevails.

Naturally, temperature plays a very important role in these processes: at low temperatures at which diffusion of adatoms is frozen, statistical growth is observed. In such a case, 5–7 layers grow simultaneously. At a higher temperature, such a film may become ordered in a layered system and at high temperatures it may reconstruct into a Stranski-Krastanov or Volmer-Weber system.

This is nicely illustrated by the experiment¹⁶ shown schematically in Figure 6. In this experiment, an equivalent of 40 monolayers of silver was deposited on the V(100) surface at 200 K, forming a thick silver film A (Van der Merwe). This film was then heated at room temperature to form a Stranski-Krastanov film B consisting of a 2 ML-thick support with clusters on top. These clusters were 3-dimensional, on the one hand (since they should have accommodated a large quantity of silver), and, on the other hand, their total area, as seen by excitation beams of the spectroscopies used in the study,¹⁶ was rather small compared to the total sample area. The Stranski-Krastanov support film was sputtered off until no silver signal was observed by either Auger spectroscopy or UPS, C. This sample was then annealed at 580 K and as a consequence, both spectroscopies showed recovery of the 2 ML film D. It seems that the long sputtering procedure at r.t. removes the first two silver layers completely, leaving behind only what is left of Ag clusters (Volmer-Weber). Subsequent annealing at 580 K gives enough mobility to Ag atoms to migrate from the clusters and to reproduce the 2 ML support film. This procedure may be repeated as long as there is enough silver preserved in the clusters.

Structural similarities between the substrate and the bulk structural characteristics of the film material are often very important for the film structure. It has generally been observed that low-index crystal surfaces promote epitaxial growth of overlayers. In other words, the film

retains the crystallographic direction of the surface upon which it grows. Moreover, if the natural lattice constants of the substrate and the film are very similar, the film grows pseudomorphically, *i.e.*, the structure of the substrate is preserved also in the film. In some cases, the initial steps of the growth may be complicated by formation of a surface alloy. All this is also reflected in the electronic structure of the overlayer.

Figure 7 shows an atomically resolved STM image of a clean and well ordered Cu(100) surface (a), and the same surface after deposition of 0.15 monolayer (ML) of silver. At this coverage, the surface is disordered due to the formation of a surface alloy.¹⁷ At higher Ag coverages, the alloy disintegrates into its constituents and consequently silver forms islands whose atomically resolved image is shown in Figure 7b along with the model of the corresponding $c(10 \times 2)$ ordered film. Obviously, the film structure is rather complex. It is a consequence of the balance between energy minimization through the highest possible coordination of an Ag atom with the surface Cu atoms and the highest coordination of Ag atoms within the film itself. The resulting compression within the silver layer is minimized by buckling of the Ag layer (see the side view of the model). This structure is preserved during further deposition and up to a several layers thick film. The change from surface alloy to $c(10 \times 2)$ system has consequences for the corresponding photoemission spectra, which are shown in Figure 7c where only the Ag 4d part of the spectra is presented: at coverages of 1 ML or smaller, the Ag 4d system is characterized by two peaks, one at 4.92 binding energy (b.e.) and the other at 4.72 eV b.e. at 0.15 ML and shifting to lower b.e. with increasing coverage. The observed increase in splitting of these two peaks is solely due to the discussed structural changes.

Quite a different behavior is seen for silver films deposited on a Pd(111) surface.¹⁸ There the photoemission spectral maxima do not change positions in the low coverage regime (up to 1 ML). This is shown in Figure 8, panel a) together with an atomically resolved image of 1 ML silver film on the Pd(111) surface and of the clean Pd(111) surface, panel b). It clearly shows that the Ag

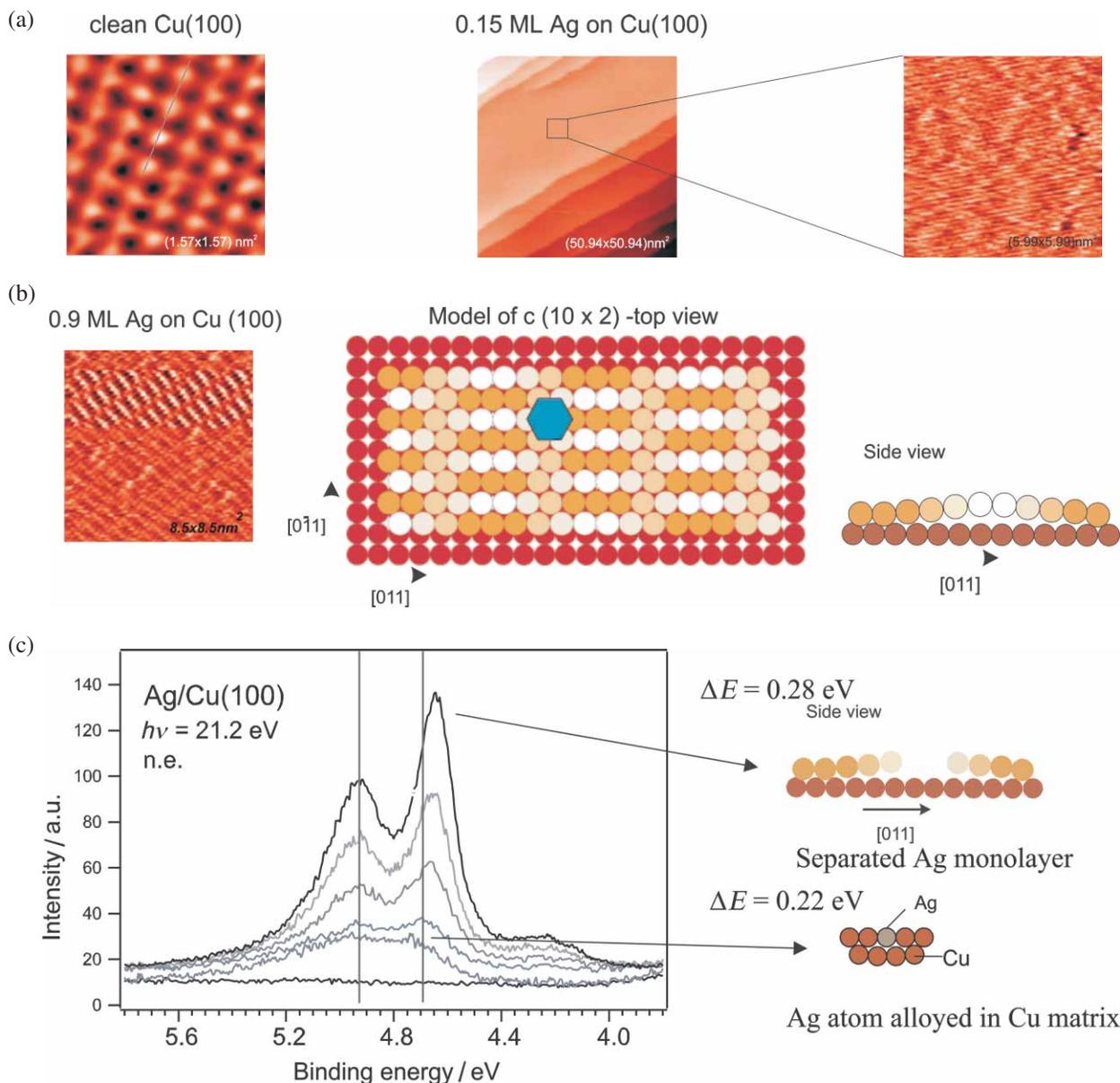


Figure 7. a) Atomic resolution STM image taken at r.t. of clean Cu(100) showing cubic symmetry and STM image for 0.15 ML Ag. Smaller scale STM image showing the region of a Cu terrace containing Ag atoms alloyed in the Cu surface layer (diffuse regions). Due to high mobility of Ag atoms at r.t., no atomic resolution STM image could be obtained. b) Atomic resolution STM image for 0.9 ML Ag taken at r.t. showing the c(10 x 2) structure with slightly deformed hexagonal Ag(111) surface and the associated model are presented. c) Photoemission spectra of Ag 4d region showing the increase of peak splitting when the system changes from individually alloyed Ag atoms in Cu matrix to separated Ag layer on the Cu surface.

films have the same lattice as the Pd substrate, *i.e.*, silver films grow pseudomorphically on this surface (in spite of the fact that the film must be somewhat compressed to accommodate to the Pd lattice).

Generally, lattice mismatch between substrate and film leads to strain (stress) in epitaxial layers. In many cases where the lattice constant tends to adopt its bulk value (causing the formation of superstructure), in order to relieve the strain, some buckling of the film is expected. An example is the Ag c(10 x 2) ordered film on the Cu(100) surface (Figure 7b).

QUANTUM WELL STATES AND STABILITY OF ULTRATHIN FILMS

Ultrathin films are prototype examples of two-dimensional nanosystems. Namely, parallel to the surface their electron bands disperse in the same manner as in the bulk while perpendicular to the surface their electronic system may be quantized and the so-called quantum well (QW) states may be formed^{19,20} providing some basic requirements are fulfilled. The primary condition is that the substrate has an energy gap or a symmetry gap that coincides with the film valence electrons of a given

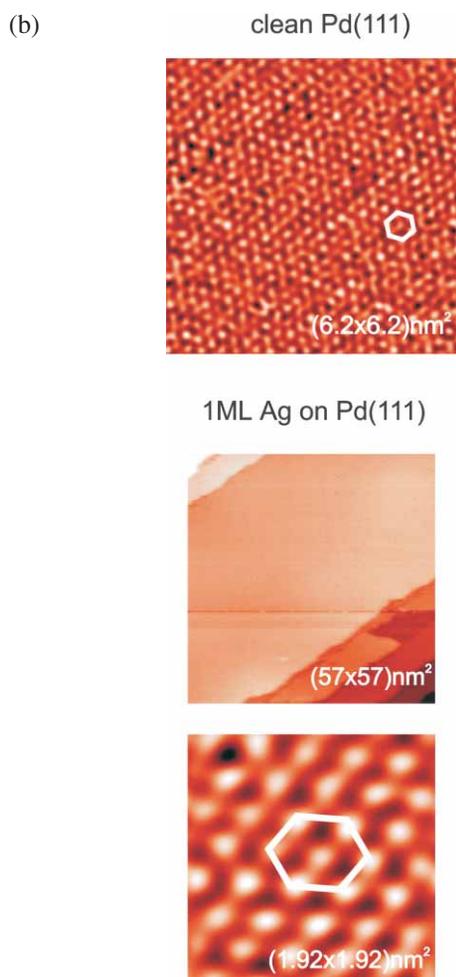
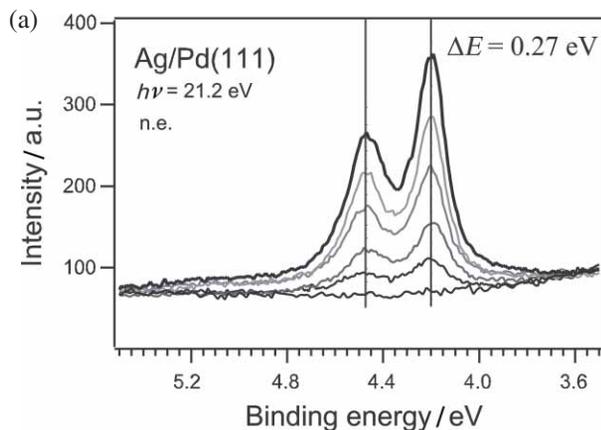


Figure 8. a) Photoemission spectra of the Ag 4d region showing that peak splitting (and positions) remains unchanged in the low coverage regime. b) STM images of nearly saturated Ag monolayer taken at r.t. Smaller scale atomic resolution STM image of Ag monolayer showing hexagonal structure. For comparison, atomic resolution image of clean Pd(111) is given.

symmetry. In such a case, electrons within the film cannot penetrate and hybridize with the substrate electron bands. Instead, they are reflected back into the film and again reflected on the vacuum side by the image potential. Only the electrons that fulfill certain quantization condi-

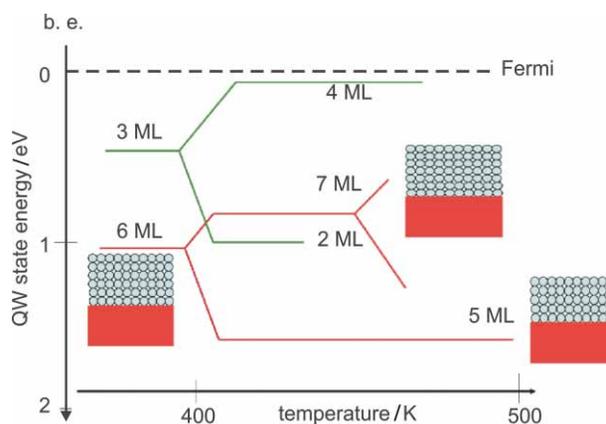


Figure 9. Summary of photoemission experiments for the Ag/Fe(100) system showing the variations in film stability as a function of the corresponding QW state binding energy.²²

tions survive and form standing waves, *i.e.*, QW states. The existence of QW states has enormous influence on many physical properties of the films. These are observed in magnetic properties²¹ (giant magnetoresistance effect), transport properties,²⁰ *etc.* Recently, it has been shown that they may influence the stability of the films themselves. Figure 9 gives a summary of the reported measurements for the Ag/Fe(100) system:²² silver grows layer-by-layer on Fe(100) surface and each integer film thickness is characterized by distinguished sp-derived QW states. At very low thicknesses, there is only one sp QW state per one thickness. The y-axis of Figure 9 shows the binding energy of a set of QW states that are characteristic of films 2–7 ML thick and the x-axis shows the temperature. When heated, the 3 ML thick film (its QW state is at app. 0.4 eV b.e.) remains stable up to 400 K. Above this temperature, it dissolves into 4 ML and 2 ML thick films whose QW states are at app. 0.05 eV and 1 eV b.e., respectively. Similar stability is displayed by a 6 ML thick film (QW state b.e. is at app. 1 eV). It falls apart at 400 K and two films of 5 and 7 ML thickness are formed instead with QW states at 1.6 eV and 0.8 eV b.e., respectively. The driving force for these processes, in both cases, seems to be the net energy gain when judged on the basis of the QW states energies.²² Note the thermal stability of the 5 ML film. Its QW state has the lowest b.e. and it remains stable up to the desorption temperature of silver from the Fe(100) surface.

CONCLUSIONS

Structural and electronic properties of surfaces and ultrathin metallic films are closely connected. Because of their low dimensionality, it is of the utmost importance to acquire their structural details at atomic level and their electronic structure resolved in energy and momentum at very high resolution. In this paper, we have briefly presented several experimental examples that support these statements.

REFERENCES

1. M. Wilms, M. Schmidt, G. Bermes, and K. Wandelt, *Rev. Sci. Instr.* **69** (1998) 2696–2703.
2. D. P. Woodruff and T. A. Delchar, *Modern Techniques of Surface Science*, Cambridge Solid State Science Series, 1994.
3. N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Brooks Cole; 1th edition, 1976.
4. (a) R. M. Tromp, R. J. Hamers, and J. E. Demuth, *Phys. Rev. B* **34** (1986) 1388–1391; (b) Y. Naitoh, K. Takayanagi, H. Hirayama, and Y. Ohsima, *Surface. Sci.* **433–435** (1999) 627–631.
5. (a) B. Schaefer, M. Nohlen, and K. Wandelt, *J. Phys. Chem. B* **108** (2004) 14663–14670; (b) A. Sinsarp, Y. Yamada, M. Sasaki, and S. Yamamoto, *Appl. Surface Sci.* **237** (2004) 587–592
6. M. Kralj, P. Pervan, M. Milun, J. Schneider, B. Schaefer, A. Rosenhahn, and K. Wandelt, *Fizika A* **8** (1999) 123–130.
7. M. Kralj, P. Pervan, M. Milun, K. Wandelt, D. Mandrino, and M. Jenko, *Surface Sci.* **526** (2003) 166–176.
8. M. Milun, T. Valla, and P. Pervan, *Appl. Surface Sci.* **89** (1995) 375–381.
9. M. A. Van Hove, W. H. Weinberg, and C.-M. Chan, *Low-Energy Electron Diffraction*, Springer, 1986.
10. (a) S. N. Magonov and M.-H. Whangbo, *Surface Analysis with STM and AFM: Experimental and Theoretical Aspects of Image Analysis*, VCH Publishers, 1996; (b) R. Wiesendanger, H. J. Guntherodt (Ed.) *Scanning Tunneling Microscopy III: Theory of Stm and Related Scanning Probe Methods*, Springer Series in Surface Sciences, 1993.
11. M. Kralj, M. Milun, and P. Pervan, *Surface Sci.* **557** (2004) 208–214.
12. For review see articles in *Surface Sci.* **500** (2002) 545–655.
13. S. Hüfner, *Photoelectron spectroscopy*, Springer Series in Solid-State Sciences, Vol. 82, Springer, Berlin, 1995.
14. D. Briggs and M. P. Seah, *Practical Surface Analysis*, John Wiley and Sons Ltd; 2nd edition, 1996.
15. V. Mikšić Trontl, PhD thesis, Faculty of Science, University of Zagreb, November 2005.
16. T. Valla and M. Milun, *Surface Sci.* **315** (1994) 81–92.
17. V. Mikšić Trontl, M. Kralj, M. Milun, and P. Pervan, *Surface Sci.* **551** (2004) 125–131.
18. V. Mikšić Trontl, I. Pletikosić, M. Milun, P. Pervan, P. Lazić, D. Šokčević, and R. Brako, *Phys. Rev. B* **72** (2005) 235418–235429.
19. T.-C. Chiang, *Surf. Sci. Reports*, **39** (2000) 181–235.
20. M. Milun, P. Pervan, and D. P. Woodruff, *Reports on Progress in Physics* **65** (2002) 99–141.
21. F. J. Himpsel, J. E. Ortega, G. J. Mankey, and R. F. Willis, *Advances Phys.* **47** (1998) 511–597.
22. D.-A. Luh, T. Miller, J. J. Paggel, M. Y. Chou, and T.-C. Chiang, *Science* **292** (2001) 1131–1133.

SAŽETAK

Atomska struktura površina i ultra tankih filmova

Vesna Mikšić Trontl, Ivo Pletikosić, Petar Pervan i Milorad Milun

Strukturna i elektronska svojstva površina i ultra tankih metalnih filmova usko su povezana. Zbog niske dimenzionalnosti navedenih sustava od presudnog je značaja provesti istraživanja strukture na atomskom nivou, te istraživanja elektronske strukture u visokoj energijskoj i kutnoj razlučivosti. U članku se daje kratak pregled nekoliko eksperimentalnih primjera koji ilustriraju potrebu za navedenim zahtjevima, te istovremeno naglašavaju neka od važnijih svojstava površina i ultra tankih filmova. Primjeri su ograničeni na one u kojima je za istraživanje strukturnih svojstava korištena skenirajuća tunelirajuća mikroskopija, a za proučavanje elektronske strukture uzoraka fotoelektronska spektroskopija sa pobudnim ultraljubičastim zračenjem.