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THE STRUCTURE OF ULTRATHIN Ag FILMS ON Pd(111)

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Dedicated to the memory of Professor Vladimir Šips

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We have performed *ab initio* density functional calculations of thin Ag films on the Pd(111) surface. We have calculated the structural properties and the electronic bands of the Ag/Pd systems. There is a band gap in the electronic density of states around the centre of the two-dimensional Brillouin zone of the Pd(111) surface, which makes possible the formation of localised states in the adsorbed silver films. We find that quantum-well states may form at binding energies around 4 eV.

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1. *Introduction*

Ultrathin metallic films with thickness ranging from a monolayer to a few tens of layers, deposited on low-index surfaces of a different metal, show a wide variety of structural and electronic properties. The scanning tunnelling microscopy (STM) and the angle-resolved photoemission spectroscopy (ARPES) make it possible to closely monitor the growth of the films and the evolution of the electronic states [1,2]. Depending on the difference of the bulk lattice constants of the two metals, the films grow either in registry, where the atoms of the second species take the same positions which would be occupied in further substrate growth, or form layers denser or more open than the substrate often producing Moiré patterns in the STM images. Some form of alloying of the substrate and the deposited metal can also occur. The electronic structure can also show interesting properties, such as the formation of quantum-well (QW) states localised on the adlayers in cases when there is an energy gap of the substrate states, or a symmetry incompatibility between the substrate and adlayer states leads to an effective "symmetry gap" for the adlayer electrons.

Silver and palladium are in many respects quite similar metals. Both have fcc structure, with bulk lattice constants of 0.409 nm and 0.389 nm, respectively.

Experiments show that the silver films on Pd(111) surface start to grow pseudomorphically [3].

In this paper, we report *ab initio* density functional calculations of one to three Ag layers on a Pd(111) surface. We calculate the structural properties, such as the energies of formation of various structures, the equilibrium distances between layers, etc. We also use the Kohn–Sham wavefunctions obtained in the calculation to discuss the electronic structure of the Ag/Pd(111) system, looking in particular into the formation of quantum-well states localised around the centre of the surface Brillouin zone, which can be observed in normal ARPES.

2. Calculation

We have made the *ab initio* density functional calculations using the DACAPO program package [4]. We used periodic boundary conditions in all three spatial directions, modelling the Pd substrate by six hexagonal layers and a vacuum region of sufficient thickness which separates the periodically repeating Pd slabs. The details of the calculations have been described in papers dealing with similar systems [5]. The lattice constant of Pd was taken to be 0.399 nm, which is the equilibrium value for our calculations of bulk Pd, and differs slightly from the experimental value of 0.389 nm. This choice is necessary in order to avoid the appearance of spurious stress in the substrate. The bottom three Pd layers were kept fixed at bulk separation, and the top three layers of the substrate and the silver adlayers were allowed to relax freely in the direction perpendicular to the surface (z coordinate).

3. The structure and growth of Ag films

It has been found experimentally that silver films grow in registry on the Pd(111) substrate, but with a stacking fault between the first and the second layer, resulting in a twinned crystalline structure [3]. Therefore, we have investigated several configurations of Ag layers on a Pd substrate. First, we have taken the fcc palladium (in our calculation that are six hexagonal layers of atoms stacked in the fcc ABCABC order) and added one to three layers of Ag continuing the regular fcc ordering (e.g. ABCABC—AB) and allowing the relaxation. Next, we have calculated the structures in which a silver layer (in particular the second one) goes into the hcp position, resulting in structures like ABCABC—AC, etc. The calculated interlayer distances and adsorption energies are shown in Table 1.

The adsorption energy per atom is around 2.84 eV for Ag atoms in the first layer, decreasing to around 2.50 eV for Ag atoms in the second layer and to 2.52 eV in the third layer. The remarkable fact is that the energy is virtually the same for the second layer adsorbed in "regular" fcc sites (AB) and in the "wrong" hcp sites (AC), i.e. with a stacking fault. The slight preference of 0.4 meV for the regular structure is in fact smaller than the expected accuracy of the DFT calculation. This

TABLE 1. Step heights, interlayer distances (both in nm*) and adsorption energies for* Ag *layers on* Pd*(111).*

	Clean Pd	1 ML Ag	2 ML Ag	2 ML Ag w. stacking fault
Step height		0.237	0.234	0.244
Ag_1–Ag_2			0.242	0.245
Pd_1–Ag_1		0.236	0.234	0.236
Pd_1–Pd_2	0.230	0.230	0.229	0.232
Pd_2–Pd_3	0.230	0.231	0.228	0.230
Pd_3–Pd_4	0.230	0.230	0.228	0.229
Pd_4–Pd_5, Pd_5–Pd_6	0.230	0.230	0.230	0.230
Adsorption Energy (eV)		2.841	2.4997	2.4993

indicates that there is no clear preference for either of the two structures on the basis of the energy of the complete layer alone.

In order to investigate the energetics of the initial nucleation of the second silver layer, we have calculated configurations in which on top of a fcc Pd–Ag structure there is an extra silver atom at a 1/4 coverage, either in the fcc or in the hcp threefold hollow site. We used a 2×2 supercell along the surface plane, with three sites in the last layer empty and one occupied. We found that the adsorption energy is around 1.90 eV, which is about 0.6 eV less than the energy per atom in the full silver monolayer. Due to the large energy difference, the silver adatoms will tend to aggregate, favouring island formation and layer-by-layer growth mode.

The energy of the extra adatom is better by around 0.6 meV if it sits in the hcp site instead of the fcc site, but this energy difference is still too small for an unambiguous interpretation. However, even a slight preference for hcp sites in the initial stages of the formation of the second Ag layer may be sufficient to lock the further growth of the layer into the hcp configuration. Once the layer is completed, the resulting stacking fault (AC order of Ag layers) is frozen since there is no simple kinetic path which converts the whole layer into the fcc structure (AB). The third Ag layer then starts growing in fcc sites with respect to the first and second layer, which results in a ACB layer structure. This ordering remains, although according to our calculations a three layer Ag film with ABC structure (which continues the Pd stacking order) would have by 7.5 meV per atom lower energy than ACB structure. Further silver layers grow in the fcc order with respect to the first and second Ag layer, which results in a twinned crystal structure at the Pd–Ag boundary.

Analogous formation of a stacking fault between the first and the second adlayer has been observed during Ag growth on Pt(111) at room temperature, but the second layer reverts to the fcc sites after annealing to 750 K [6]. Further Ag layers continue to grow in a fcc stacking order with respect to the first two Ag layers, i.e. with or without a stacking fault depending on whether the second layer was annealed. The stacking order of thicker Ag films on Pt(111) is not changed by annealing.

We must, however, stress that the energy differences between various configurations obtained in our *ab initio* calculations of Ag on Pd(111) are very small, and cannot be regarded as a definite explanation of the growth mode. It has been suggested that the occurrence of a stacking fault between the first and the second silver layer in the case of Ag growth on Pt(111) is a consequence of the kinetics of the adlayer growth rather than of a more favourable energy [6].

We have also calculated the energies of 1–3 ML Ag films with some other stacking orders, but those appear to have less favourable energies. In particular, the structure where already a monolayer of Ag is in hcp sites has an energy larger than that of the fcc Ag monolayer by around 8 meV, effectively ruling out this mode of growth.

4. Electronic bands and the QW states

In order to understand the electronic structure of ultrathin silver films on Pd(111), we have first made separate calculations of the electronic bands of the palladium bulk and of unsupported silver films.

4.1. Projection of bulk Pd states onto the Pd(111) surface

In Fig. 1 we show the calculated electronic structure of bulk palladium along the ⟨111⟩ direction, and the band structure projected onto the surface Brillouin

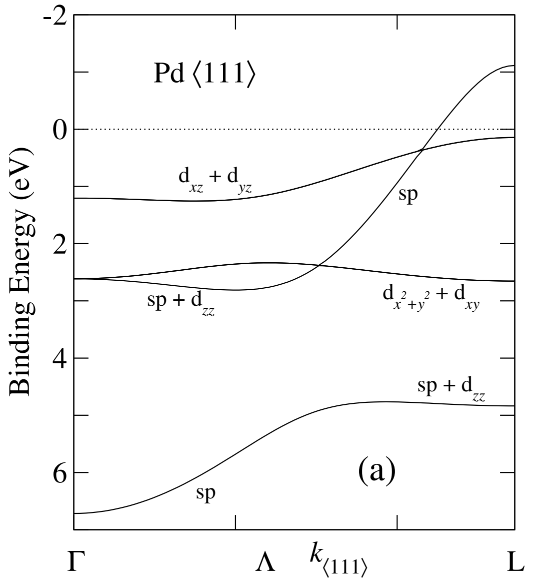

Fig. 1. Calculated electronic structure of bulk palladium. (a) Bulk states of Pd *along k_z direction. (b) Bulk states of* Pd *projected onto (111) surface.*

zone (SBZ) for the (111) surface in the $\overline{\Gamma} - \overline{\mathrm{M}}$ and $\overline{\Gamma} - \overline{\mathrm{K}}$ directions, for around 30 values of k_{111}. At the $\overline{\Gamma}$ point of the SBZ, the d bands occur from just below the Fermi level to 3 eV, and there is an energy gap in the projected states from around 3 to 5 eV binding energy.

4.2. Unsupported silver films

Next we take a look at unsupported two-dimensional silver films, i.e. one or two layer of Ag atoms with vacuum on both sides. In Fig. 2 we show the electronic structure of a two-dimensional hexagonal lattice of Ag atoms with the interatomic distance of 0.23 nm, corresponding to the interatomic separation of Pd(111), along the high-symmetry directions of the BZ. Narrow d bands are located between 3.5 and 5.5 eV binding energy, while the broad sp band starts from 6.5 eV and crosses the Fermi level near the outer edge of the two-dimensional BZ, hybridising strongly with the d bands while crossing their energy range. The electronic structure of a similar two-layer hexagonal structure, with such interlayer spacing that all distances between the neighbouring silver atoms are around 0.23 nm, is shown by dashed lines in Fig. 2. The bands look similar to the single-layer structure, but their number increases. The similarity is particularly evident around the $\overline{\Gamma}$ point, where the main effect is just the doubling and a small energy offset of the bands.

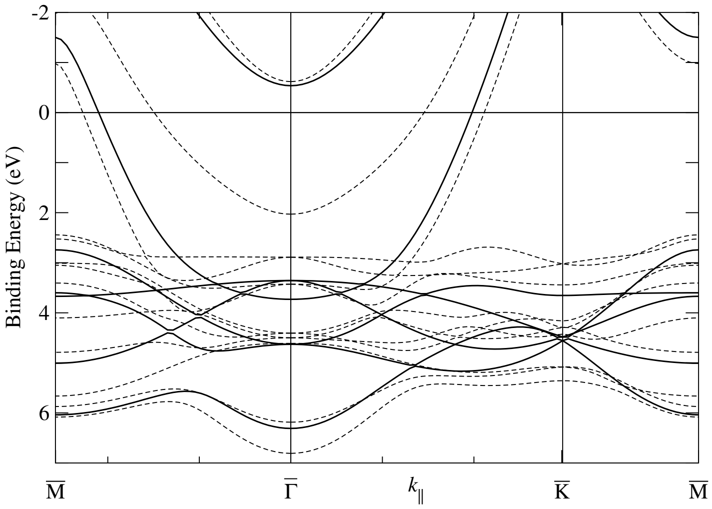

Fig. 2. Electronic eigenstates of unsupported single (full line) and double (dashed line) hexagonal layer of Ag *atoms, along the high symmetry directions in the two-dimensional Brillouin zone.*

4.3. Ag monolayer on Pd(111)

In Fig. 3 we show the band structure of a monolayer of Ag atoms adsorbed on a Pd(111) surface. The bands of a clean six-layer Pd(111) structure are also shown

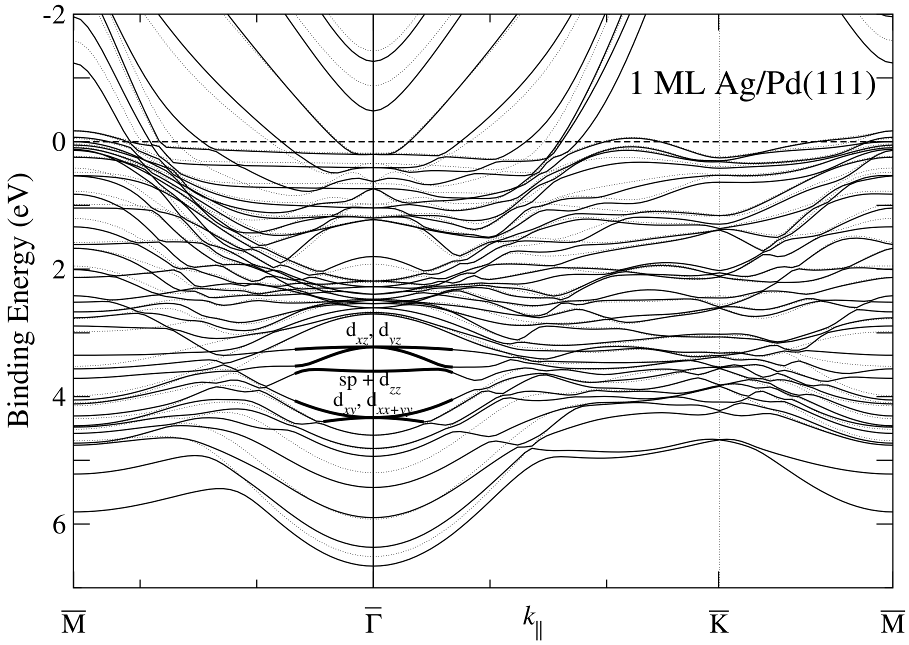

Fig. 3. Electronic eigenstates of a single layer of Ag *atoms adsorbed on a* Pd*(111) surface, along the high symmetry directions in the surface Brillouin zone. The dotted lines show the states of a clean six-layers* Pd *substrate.*

as dotted lines, making it possible to identify the additional features introduced by the silver layer. The silver-induced bands, which lie in the energy gap of Pd around the centre of the surface Brillouin zone, are drawn by thick lines, and their symmetry at $\overline{\Gamma}$ point in terms of atomic orbitals is indicated. The absence of propagating (bulk) states in Pd in this $E-k$ region makes the palladium substrate almost as confining to the silver electrons as the vacuum on the other side, so that they acquire the character of quantum-well (QW) states, well localised within the silver adlayer. These QW states are the prime candidates to be seen as narrow peaks in photoemission experiments in the direction along the normal to the surface.

However, in calculating the electronic bands of ultrathin silver films on the V(100) surface, we have found that the silver d states appear about 1 eV too close to the Fermi level when compared to the peaks observed in the photoemission experiments. This deficiency of the Kohn–Sham eigenstates of d orbitals obtained in density functional calculations of silver and other noble metals has been known for some time [7], and we presume that the same will be the case in this calculation. If we shift the calculated d bands of silver downwards for around 1 eV, only the bands of d_{xz}, d_{yz} symmetry will stay within the energy gap of Pd. Furthermore, our calculations do not include the spin-orbit coupling, which leads to a splitting of degenerate d bands of silver, clearly observable in photoemission experiments on Ag films on V(100) surface [8].

We can thus expect that the most prominent feature in normal photoemission from 1 ML Ag/Pd(111) films will come from the QW states of d character in the region around 4 eV binding energy. Preliminary experimental results show that this is indeed the case [9]. The normal PE spectra from silver monolayer on Pd(111), in addition to broad maxima centred around 1 eV and 2 eV due to the palladium substrate, show two narrow peaks just below 4 eV, interpreted as d QW states separated by a spin-orbit splitting of around 0.3 eV.

5. *Conclusions*

We have made *ab initio* density functional calculations of the structure and electronic properties of ultrathin Ag films on Pd(111) surface. We have shown that energetically most favourable configuration of the first Ag layer is the one in which the atoms occupy the fcc three-fold hollow sites, continuing the substrate structure (with somewhat different interlayer spacing, of course). The second Ag layer, however, has almost the same energy whether the atoms sit in fcc or in hcp three-fold hollow sites. We have found that the first extra atoms to adsorb on a completed first layer in fact prefer the hcp site, which makes it likely that this mode of growth continues up to the completion of the second layer. This is a possible explanation of the experimentally observed stacking fault between the first and the second Ag layer. We have also calculated the electronic band structure of Ag/Pd(111) systems. We have found that around the centre of the two-dimensional surface Brillouin zone of Pd(111) there is an energy gap in the density of states in the 3–5 eV energy range. Upon adsorption of a monolayer of Ag, quantum-well states of predominantly d character form at binding energies around 4 eV.

Acknowledgements

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References

[1] M. Milun, P. Pervan and D. P. Woodruff, Rep. Prog. Phys. **65** (2002) 99.

[2] T.-C. Chiang, Surf. Sci. Rep. **39** (2000) 181.

[3] B. Eisenhut, J. Stober, G. Rangelov and Th. Fauster, Phys. Rev. B **47** (1993) 12980.

[4] http://www.fysik.dtu.dk/campos/Dacapo

[5] M. Kralj, P. Pervan, M. Milun, P. Lazić, Ž. Crljen, R. Brako, J. Schneider, A. Rosenhahn and K. Wandelt, Phys. Rev. B **68** (2003) 195402.

[6] G. Rangelov, Th. Fauster, U. Strüber and J. Küppers, Surface Sci. **331-333** (1995) 948.

[7] G. Fuster, J. M. Tyler, N. E. Brener, J. Callaway and D. Bagayoko, Phys. Rev. B **42** (1990) 7322.

[8] M. Kralj, P. Pervan, M. Milun, T. Valla, P. D. Johnson and D. P. Woodruff, Phys. Rev. B **68** (2003) 245413.

[9] P. Pervan and M. Milun, private communication.

STRUKTURA TANKIH SLOJEVA SREBRA NA (111) POVRŠINI PALADIJA

Upotrebom teorije funkcionala gustoće napravili smo ab initio račun za tanke slojeve srebra na (111) površini paladija. Odredili smo strukturna svojstva te elektronske vrpce za Ag/Pd sistem. Postojanje energetskog procijepa u elektronskoj gustoći stanja oko centra dvodimenzijske Brillouinove zone (111) površine paladija omogućava stvaranje lokaliziranih stanja u adsorbiranim slojevima srebra. Našli smo da stanja kvantnih jama mogu nastati na energijama vezanja od oko 4 eV.