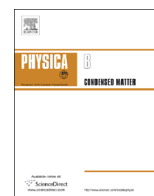




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# Calculated surface, image and quantum well states in Ag/Cu(111) system

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## ABSTRACT

The energy spectrum and the probability densities of the surface, the image and the quantum well (QW) states of the Ag/Cu(111) system have been calculated function of the thickness of the silver film. The layer by layer energy spectrum and probability densities of this system are obtained as a solution of the Schrödinger equation using the discrete variable representation (DVR). In this equation we have used an analytical one-dimensional model potential derived from the potential of Chulkov et al. [1]. Our calculated energy spectrum and probability densities of the surface, image and QW states present coverage dependence in agreement with the experiments and other calculations of the surface states.

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## 1. Introduction

Metal on metal systems find important applications in detector devices and superconductivity. Thin film growth may lead to a different structure with respect to the bulk and to novel electronic and magnetic properties. The formation of quantum well states is one of the intriguing electronic phenomena observed in ultrathin films. The valence electrons can be confined into the thin metallic film by the vacuum-surface and overlayer-substrate barriers. A first condition is that the energies of these electrons lie in the substrate band gap. A second condition is that the film thickness is of comparable size to the electron wavelength. Propagation into the substrate is then forbidden and the electrons are reflected back at the overlayer-substrate barrier toward the front side of the film where the vacuum-surface potential barrier acts as a second mirror. As in the quantum mechanics textbooks discussing the quantum wells, the standing waves and the allowed discrete energies are function of the size of the quantum well or here of the depth of the thin film. Precisely, the condition for the existence of quantum well states (QWS) is given by the phase accumulation model [2]

$$\phi_s + \phi_i + 2k_{\perp}N_{ML}d = 2\pi m \quad (1)$$

where  $\phi_s$  and  $\phi_i$  are the phase shifts upon reflection at the surface and the interface barriers,  $k_{\perp}$  is the quantized wave vector of the

electron perpendicular to the surface,  $N_{ML}$  is the number of atomic layers in the film,  $d$  is the interlayer distance and  $2k_{\perp}N_{ML}d$  is the phase accumulated when traveling in the film. Note that  $m$  is an integer, equal to the number of nodes that a wave function has inside of a box of width  $d$ , when the boundary conditions are contained in  $\phi_s$  and  $\phi_i$ .

QWS were first observed by recording the  $I(V)$  characteristics of metal-insulator thin film sandwiches [3]. More recent works has demonstrated that angle resolved photoemission spectroscopy (ARPES) is an excellent tool for studying the dependence of quantum well states on the substrate and on the film thickness down to monolayer thickness but also the dispersion of the valence band of the overlayer [4]. Usually, in the photoemission process  $k_{\perp}$  is not conserved. Therefore only the projected band structure  $E(k_{\parallel})$  can be determined directly from the photoemission experiment. But for a film,  $k_{\perp}$  is known from the phase condition Eq. (1) and can be assigned to the observed states.

Many studies choose Ag films as overlayer material on matched (like Au) or mismatched (like Cu, Ni, V, Fe etc.) metal substrates. Due to its low surface energy, Ag exhibits layer by layer growth on many metals (but also on semiconductor) substrates and the chemical reactivity at its surfaces and interfaces is rather low. The band structure of a noble metal near the Fermi level is nearly free-electron-like and there is only one band crossing the Fermi level. The spectra are thus much simpler, and the interpretation of experimental data is straightforward.

The Ag/Cu(111) system was intensively studied in the past [5–13]. The Ag/Cu(111) interface is a “model” system presenting QWSs that are easy to see with ARPES. The system exhibits in normal

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emission geometry intense quantum well peaks over a wide range of energies in contrast to Ag/Au(111), Cs/Cu(111) or Na/Cu(111) [5]. While calculating the QWS energy spectrum is easy, modeling the complete photoemission spectra from such QW system is a challenging task. For this reason, there are only few attempts in the past to simulate theoretically the photoemission spectra for QW systems [14–16]. The results based on the interference of two wave functions were good but none of them used: (i) realistic wave functions determined from a realistic potential; (ii) realistic material functions for substrate and overlayer; (iii) the variation of the electromagnetic field at surface was completely neglected. All these (i)–(iii) “ingredients” are necessary for modeling the Ag/Cu photoemission spectra using the recently developed vector potential from the electron density (VPED) [17]. This VPED model was already used for the Al(111) and Al(100) surfaces [17,18].

In this paper we restricted to the first step of the VPED model i.e. the systematic calculation of the wave functions and energy spectrum of the Ag/Cu(111) system. We proposed a realistic continuous potential derived from the self-consistent density functional theory (DFT) calculations within the local density approximation (LDA) potentials of Chulkov et al. [1] for the pristine Ag(111) and Cu(111) surfaces. In the literature, such a potential for metal on metal system has been proposed for one monolayer of Na on Cu(111) [19], but its particular structure prevents the extension to many Na layers. A specific potential was constructed for Pb on Cu(111) by adding a long range image potential to the effective potential obtained also in the DFT/LDA approximation [20]. With this specific potential calculations were performed in the Pb/Cu(111) system for Pb coverages varying from 1 to 28 monolayers. Our analytical potential constructed for the Ag/Cu(111) system is based on a linear variation in the first Ag plane between the copper and silver bulk potentials. It has the advantage that it can be extended to any desired number of Ag layers and can be adapted to other metal on metal systems. Such a potential has been only suggested by Bendounan et al. [9] in the past.

Using our model potential, the energy spectrum and the wave functions are obtained by solving the Schrödinger equation in the discrete variable representation (DVR). The advantage of this algorithm is that the entire spectrum is obtained in a single calculation. From the energy spectrum we obtained information about the band structures of the two metals and the relative positions of the gaps, the energies of the surface, image potential and quantum well states (QWSs) and their coverage dependence.

The variation of the surface state energy with the number of Ag layers has been studied using the normal photoemission technique (NPES) [9,10]. In the literature, the energy and probability density of the surface states of this system were calculated by Bendounan et al. [9]. These authors have solved the Schrödinger equation for a given surface state using a Numerov propagation algorithm. The results, comparable with ours, will be discussed in Section 3.

The evolution of the image states with the Ag coverage is unfolded by the two photon photoemission spectroscopy (2PPE). Up to 0.9 monolayer (ML) of silver the first image state of Cu(111) is observed together with the image states of the silver adlayer. Above this coverage only the first and second image states of silver can be observed [8]. There are many theoretical calculations for the image states performed for simple metals but few for composed system (see Refs. [19,20,25]).

The quantum well states were observed in normal emission spectroscopy above 10 ML silver coverage [5,6,10,11]. A number of theoretical approaches have been used in the past in order to describe the QWSs energies and functions. Quasi-one-dimensional models such as the one-dimensional well potential based on the phase accumulation model has been used successfully to calculate the energy of the QWSs [21,22]. In these approaches the wave

functions were taken analytically as Whitaker functions [21] or calculated numerically [22]. Tight binding [2] and layer Korringa–Kohn–Rostoker [23] approaches were also used. For few systems (Na/Cu(111) [24,25], Ag/V(100) [26] and Ag/Au(111) [27]) the QWSs have been calculated by self-consistent density-functional calculations. There are no theoretical calculations of the QWSs, image states or their interaction for the Ag/Cu(111) system.

This paper is organized as follows. A description of the potential is presented in Section 2. In Section 3 the energy spectrum and probability densities of the Ag/Cu(111) system are analyzed and compared to the experiments. The last section is a conclusion.

## 2. Model

The simplest quantum well theoretical model will treat differently the electrons movements parallel and perpendicular to the surface: (i) the electrons parallel to the surface (coordinate  $\vec{r}_{\parallel}$ ) move freely, the potential being independent of  $\vec{r}_{\parallel}$ ; (ii) the electrons perpendicular to the surface (coordinate  $z$ ) move in the potential  $V(z)$  and the solution is numerical. Separating the motion in  $\vec{r}_{\parallel}$  and  $z$ , the one electron Schrödinger equation in the perpendicular coordinate  $z$  reads

$$-\frac{\hbar^2}{2m} \frac{d^2 \varphi_n(z)}{dz^2} + V(z)\varphi_n(z) = E_n \varphi_n(z) \quad (2)$$

where  $\varphi_n$  is the one-dimension wave function, and  $E_n$  is the corresponding eigenvalue.

In the quantum well systems like Ag/Cu(111) the interaction potential of the electron can be divided in three regions: (i) bulk metallic Cu, (ii) Cu–Ag interface modeled as a linear variation in the first Ag plane between the Cu and Ag bulk potentials, (iii) Ag(111) bulk and surface. More precisely this piecewise quantum well potential reads

$$V(z) = V_1^{\text{Cu}}(z) + V_1^{\text{Cu-Ag}}(z) + V_2^{\text{Cu-Ag}}(z) + V_1^{\text{Ag}}(z) + V_2^{\text{Ag}}(z) + V_3^{\text{Ag}}(z) + V_4^{\text{Ag}}(z) \quad (3)$$

where

$$V_1^{\text{Cu}}(z) = A_{10}^{\text{Cu}} + A_2^{\text{Cu}} \cos\left(\frac{2\pi z}{a_s^{\text{Cu}}}\right), \quad z < 0 \quad (4)$$

$$V_1^{\text{Cu-Ag}}(z) = A_{20}^{\text{Cu}} + A_2^{\text{Cu}} \cos\left(\frac{2\pi z}{a_s^{\text{Ag}}}\right), \quad 0 < z < z_m^{\text{Ag}} \quad (5)$$

$$V_2^{\text{Cu-Ag}}(z) = A_{20}^{\text{Cu}} + \left[ A_2^{\text{Cu}} + \frac{(A_{10}^{\text{Ag}} - A_{20}^{\text{Cu}} + A_1^{\text{Ag}} - A_2^{\text{Cu}})(z - z_m^{\text{Ag}})}{(a_s^{\text{Ag}} - z_m^{\text{Ag}})} \right] \times \cos\left(\frac{2\pi z}{a_s^{\text{Ag}}}\right), \quad z_m^{\text{Ag}} < z < a_s^{\text{Ag}} \quad (6)$$

$$V_1^{\text{Ag}}(z) = A_{10}^{\text{Ag}} + A_1^{\text{Ag}} \cos\left(\frac{2\pi z}{a_s^{\text{Ag}}}\right), \quad a_s^{\text{Ag}} < z < a_{\text{ML}} \quad (7)$$

$$V_2^{\text{Ag}}(z) = A_{20}^{\text{Ag}} + A_2^{\text{Ag}} \cos(\beta(z - a_{\text{ML}})), \quad a_{\text{ML}} < z < a_{\text{ML}} + z_1^{\text{Ag}} \quad (8)$$

$$V_3^{\text{Ag}}(z) = A_3^{\text{Ag}} \exp[-\alpha(z - z_1^{\text{Ag}} - a_{\text{ML}})], \quad a_{\text{ML}} + z_1^{\text{Ag}} < z < a_{\text{ML}} + z_{\text{im}}^{\text{Ag}} \quad (9)$$

$$V_4^{\text{Ag}} = \frac{\exp(-\lambda(z - z_{\text{im}}^{\text{Ag}} - a_{\text{ML}}))}{4(z - z_{\text{im}}^{\text{Ag}} - a_{\text{ML}})}, \quad z > a_{\text{ML}} + z_{\text{im}}^{\text{Ag}} \quad (10)$$

$V_1^{\text{Cu}}$  represents the periodic lattice of copper while  $V_1^{\text{Ag}}$  to  $V_4^{\text{Ag}}$  represents the Chulkov et al. [1] potential for Ag. At the interface, in order to construct a continuous potential, we used for  $V_1^{\text{Cu-Ag}}$  the copper parameters but the Ag interlayer spacing  $a_s^{\text{Ag}}$  (because we

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