Electronic structure of disordered overlayers on metal substrates

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The electronic structure of a random overlayer on a nonrandom substrate, both consisting of transition-metal atoms, is determined theoretically by employing (i) the first-principles tight-binding linear-muffin-tin-orbital method to describe the band structure, (ii) the surface Green's function to treat the layered nature of the problem, and (iii) the coherent-potential approximation to include the influence of disorder in the overlayer. As an application we determine $k_{\parallel}$-resolved as well as $k_{\parallel}$-integrated layer-projected densities of states for the first few layers of an Ag(001) substrate coated with an overlayer of random $Ag_{75}Pd_{25}$.

In this paper we report on the development of a method based on the density-functional formalism for the determination of the electronic structure of a disordered layer on a metal substrate or between two interfacing metals. This technique employs (i) the first-principles tight-binding linear-muffin-tin-orbital (TB-LMTO) method,[1] (ii) the concept of principal layers[2] and the surface Green's function (SGF) approach, and (iii) the coherent-potential approximation (CPA).

The projection of the Green's function (GF) of the ideal semi-infinite solid onto the top principal layer, the SGF, is the central quantity for applications of a GF method to overlayers and interfaces. The great advantage of our approach is the combination of the TB-LMTO and SGF methods with the CPA, which describes reliably the properties of disordered systems. The main purpose of this paper is to extend the theory developed recently for bulk alloys[3] and for ideal surfaces[4] to random surfaces, in particular to the electronic properties of systems consisting of impurities adsorbed on the ordered substrate, which frequently occur in experiment.[5,6] This improves on the simplified treatments based on empirical TB models that currently exist in the literature.

Within the atomic-sphere approximation (ASA),[1] the Hamiltonian is factorized into structure constants characterizing the arrangement of atoms and into potential parameters determining the scattering properties of the individual atoms. The Hamiltonian of a single disordered overlayer (labeled by λ) on a perfect substrate (labeled by σ), both consisting of transition-metal atoms, and in the orthogonal LMTO representation[1,3] γ is given by

$$H_{RL,R'L'} = \sum_{v,v'} \mathcal{H}^{vv'}_{RL,R'L'},$$

$$\mathcal{H}^{vv'}_{RL,R'L'} = C^v_{RL}\delta_{RR'}\delta_{LL'} + (\Delta^v_{RL})^{1/2} S^{\gamma,vv'}_{RL,R'L'}(\Delta^{v'}_{R'L'})^{1/2}, \quad (1)$$

$$S^{\gamma,vv'}_{RL,R'L'} = [S^0(1-\gamma S^0)^{-1}]^{vv'}_{RL,R'L'}.$$

Here, R denotes a lattice point belonging either to the substrate ($v=\sigma$) or to the overlayer ($v=\lambda$), and $L=lm$ is the orbital momentum. The structure of the problem enters only via the structure constants $S^{\gamma,vv'}_{RL,R'L'}$ given in

terms of the nonrandom canonical structure constants $S^0_{RL,R'L'}$ known analytically.[1] The matrices $S^{\gamma,\lambda\sigma} = (S^{\gamma,\sigma\lambda})^{\dagger}$ characterize the geometry of the overlayer-to-substrate coupling. For matters of simplicity, it is assumed that the two-dimensional periodicity of the overlayer as characterized by $S^{\gamma,\lambda\lambda}$ is the same as that of the substrate layers characterized by $S^{\gamma,\sigma\sigma}$ (no reconstruction). We shall also neglect possible layer relaxations of the top layers by using the ideal bulk structure constants. The individual atoms in the overlayer or in the substrate are characterized by site-diagonal potential parameters: matrices $X=C,\Delta,\gamma$ with elements X^v_{RL}. These parameters describe the centers C, widths Δ, and distortions γ of the corresponding bands. For $v=\lambda$, the quantities X^{λ}_{RL} are randomly $X^{\lambda}_{A,L}$ and $X^{\lambda}_{B,L}$ with probability x and $1-x$, respectively, where A and B refer to the two components in the alloyed overlayer. For $v=\sigma$, the quantities X^{σ}_{RL} are those of substrate and therefore nonrandom.

Let us briefly summarize the basic idea of the TB-LMTO-CPA approach.[3] In random alloys, the Hamiltonian in (1) exhibits both diagonal and off-diagonal disorder, via the random potential parameters, such that the averaging of $G(z)=(z-H)^{-1}$ in the orthogonal LMTO representation γ cannot be performed without additional approximations. However, by transforming to a suitably chosen nonrandom LMTO representation of β, one can define[1,3] an auxiliary resolvent $g^{\beta}(z)=[P^{\beta}(z)-S^{\beta}]^{-1}$. Here $P^{\beta}(z)$ is the so-called potential function, which is a random but site-diagonal quantity, while S^{β} is a nonrandom structure-constant matrix. Now the usual configurational averaging within the CPA can be performed for $g^{\beta}(z)$. The configurationally averaged resolvent $\langle g^{\beta}(z)\rangle = [P^{\beta,c}(z)-S^{\beta}]^{-1}$ is then transformed back to the original LMTO representation γ, using an exact scaling transformation, relating $g^{\beta}(z)$ to $G(z)$. The coherent-potential function $P^{\beta,c}(z)$ is a site-diagonal nonrandom matrix determined from the CPA condition.[3]

The TB-LMTO-CPA can be applied to the present problem keeping in mind that in a semi-infinite system the physical properties vary from layer to layer, since at best a two-dimensional translational symmetry can be assumed.

This of course applies also to the Green's function and consequently to the coherent-potential function. It can be shown,[7,8] however, that in the case of a disordered overlayer on a perfect substrate the CPA condition, i.e., $P^{\beta,c}(z)$, is restricted to the overlayer only. This is an important simplification in comparison to the more general case of a surface of a disordered alloy where, in principle, the coherent-potential functions of all layers are coupled together.[9] Contrary to the bulk, due to lowering of symmetry at the surface, $P^{\beta,c}(z)$ in general is a nondiagonal matrix with respect to L and L' even for cubic lattices. Its form in the present case is given by

$$P^{\beta,c}_{RL,R'L'}(z) = \begin{cases} \mathcal{P}^{\beta,\lambda}_{LL'}\delta_{RR'}; & v=\lambda \text{ (overlayer)}, \\ P^{\beta,\sigma}_{L}\delta_{RR'}\delta_{LL'}; & v=\sigma \text{ (substrate layers)}. \end{cases} \quad (2)$$

The elements of $\mathcal{P}^{\beta,\lambda}(z)$ are found from the following CPA condition[3]

$$\mathcal{P}^{\beta,\lambda}(z) = xP^{\beta,\lambda}_A(z) + (1-x)P^{\beta,\lambda}_B(z)$$
$$+ [P^{\beta,\lambda}_A(z) - \mathcal{P}^{\beta,\lambda}(z)]$$
$$\times \Phi^{\beta,\lambda\lambda}(z)[P^{\beta,\lambda}_B(z) - \mathcal{P}^{\beta,\lambda}(z)], \quad (3)$$

where all involved quantities are site diagonal, $\Phi^{\beta,\lambda\lambda}(z)$ is given by

$$\Phi^{\beta,\lambda\lambda}(z) = N_{\parallel}^{-1}\sum_{k_{\parallel}}\langle g^{\beta,\lambda\lambda}(z,k_{\parallel})\rangle \quad (4)$$

and the vectors $k_{\parallel}$ belong to the surface Brillouin zone (SBZ).

It should be recalled that, in principle, in a semi-infinite system the Green's function has to be determined for all layers. In order to evaluate the layer-projected auxiliary Green's function $\langle g^{\beta}(z)\rangle$ the concept of principal layers[2]

(PLs) is used, in which the substrate is viewed as a stack $(i=0,1,2,\ldots)$ of PLs such that S^{β} has nonvanishing elements only between nearest neighboring PLs. A principal layer can include a group of atomic layers and, depending on the substrate face and the number of nearest-neighbor interactions included in S^{β}, defines the dimension D of the problem $[D = N(l^2_{max}+1)$, where N is the number of atomic layers in a PL, and l_{max} is the maximal angular momentum]. In comparison with other treatments, the freedom in the choice of the LMTO representation is the great advantage of our method.[4] In particular we choose the LMTO representation β to be the most localized one[1,3,4,8] (fastest decay of S^{β} with respect to interatomic distances). Using further the nonrandomness of S^{β} and the fact that the bulk-derived structure constants are used, one gets

$$S^{\beta,ii}(k_{\parallel}) = S^{\beta,00}(k_{\parallel}),$$
$$S^{\beta,ij}(k_{\parallel}) = S^{\beta,01}(k_{\parallel})\delta_{j,i+1} + S^{\beta,10}(k_{\parallel})\delta_{j,i-1}. \quad (5)$$

Thus, only $S^{\beta,00}$ and $S^{\beta,01} = (S^{\beta,10})^{\dagger}$ describe the structure-related part of the substrate. The overlayer and its coupling to the top PL ($i=0$) are structurally given by $S^{\beta,\lambda\lambda}(k_{\parallel})$ and $S^{\beta,0\lambda}(k_{\parallel}) = [S^{\beta,\lambda0}(k_{\parallel})]^{\dagger}$, respectively. Note that the overlayer is a single layer by definition, while a PL can include more atomic layers.

The elements $\langle g^{\beta,\lambda\lambda}(k_{\parallel},z)\rangle$ and $\langle g^{\beta,ii}(k_{\parallel},z)\rangle$ of the matrix $\langle g^{\beta}(z)\rangle$ determine the layer-projected densities of states; $\langle g^{\beta,\lambda\lambda}(k_{\parallel},z)\rangle$ in turn is also needed to solve the CPA equations [Eqs. (3) and (4)]. Using the projection-operator formalism[8] or, alternatively, the block-tridiagonal form of $\langle g^{\beta}(z)\rangle$ with respect to indices λ and $i=0$, $1,2,\ldots$ [see Eq. (5)], the above elements are given by

$$\langle g^{\beta,\lambda\lambda}(k_{\parallel},z)\rangle = [\mathcal{P}^{\beta,\lambda}(z) - S^{\beta,\lambda\lambda}(k_{\parallel},z) - S^{\beta,\lambda0}(k_{\parallel})\mathcal{G}^{\beta,00}(k_{\parallel},z)S^{\beta,\lambda0}(k_{\parallel})]^{-1}, \quad (6)$$

$$\langle g^{\beta,ii}(k_{\parallel},z)\rangle = \{[\mathcal{G}^{\beta,00}(k_{\parallel},z)]^{-1} - \Gamma^{\beta,i}(k_{\parallel},z)\}^{-1}, \quad (7)$$

where the $\Gamma^{\beta,i}(k_{\parallel},z)$ are found from a set of recursive equations ($i=0,1,2,\ldots$)

$$\Gamma^{\beta,i+1}(k_{\parallel},z) = S^{\beta,10}(k_{\parallel})[P^{\beta,i}(z) - S^{\beta,ii}(k_{\parallel}) - \Gamma^{\beta,i}(k_{\parallel},z)]^{-1}S^{\beta,01}(k_{\parallel}). \quad (8)$$

In these equations, $\mathcal{G}^{\beta,00}(k_{\parallel},z)$ is the SGF (the top-PL projection of the resolvent of the ideal semi-infinite substrate) as discussed recently.[4] The set of recursive equations is terminated at the surface

$$\Gamma^{\beta,0}(k_{\parallel},z) = S^{\beta,0\lambda}(k_{\parallel})$$
$$\times [\mathcal{P}^{\beta,\lambda}(z) - S^{\beta,\lambda\lambda}(k_{\parallel})]^{-1}S^{\beta,\lambda0}(k_{\parallel}), \quad (9)$$

and corresponds to a hard wall-like boundary condition for the vacuum.[4,10] Note that in Eq. (9) $P^{\beta,i}(z) = P^{\beta,\sigma}(z)$ for all layers of the substrate [see Eq. (2)]. Equations (7) and (8) can be interpreted in physical terms: each subsequent recursion can be viewed as an epitaxial addition of one substrate PL towards the surface, until finally the overlayer is added [Eq. (9)]. In the opposite direction, the whole semi-infinite substrate is added via the SGF, $\mathcal{G}^{\beta,00}(k_{\parallel},z)$.

The above formalism is applied to the evaluation of the electronic structure of a single random $Ag_{75}Pd_{25}$ [1×1]

overlayer in the fourfold hollow position on top of the (001) face of fcc Ag. For the fcc lattice the use of screened structure constants S^{β} allow a restriction to first-nearest-neighbor interactions. A principal layer therefore consists of a single atomic layer.[4] The $k_{\parallel}$- and layer-resolved spectral densities as well as the $k_{\parallel}$-integrated layer-resolved densities of states (DOS) are then determined from the projections $\langle G(z)\rangle^{\lambda\lambda}$ and $\langle G(z)\rangle^{ii}$ of the physical resolvent $\langle G(z)\rangle$, related directly to $\langle g^{\beta,\lambda\lambda}(z)\rangle$ and $\langle g^{\beta,ii}(z)\rangle$, respectively.

The choice of potential parameters $X^v_{\alpha L}$, $X=C,\Delta,\gamma$ ($\alpha=Ag,Pd$) is of central importance for any alloy problem. In order to avoid charge self-consistency, the best ad hoc choice is the use of potential parameters derived from charge-self-consistent film calculations,[11] which not only supply layer-resolved potential parameters but also describe the boundary conditions at the substrate surface properly. In addition, the use of results from charge self-consistent supercell calculations seems to be a reasonably

good choice. In this report, however, we use the self-consistent bulk potential parameters of constituent atoms.

Even if one neglects relaxation of the top substrate layers, the problem of atomic relaxations in the overlayer due to different sizes of the Ag and Pd atoms remains. In order to discuss size mismatch in the overlayer, two limiting models are considered: (i) all overlayer interatomic distances are those of the substrate (perfect epitaxial growth, no relaxations), and (ii) respective overlayer interatomic distances correspond to the values in the pure metals (relaxed case). In the latter case we relate the relaxed structure constants to ideal ones by a simple scaling law.[3,12] As a result, one can still use the ideal structure constants but with correspondingly modified potential parameters γ_l and Δ_l. In other words, by considering modified hoppings in the Hamiltonian (1), lattice relaxations can be introduced within the tight-binding framework.

A study of ultrathin Pd overlayers on Ag indicates perfect epitaxial growth at least for the first monolayer.[5] If this is also the case for (Ag,Pd) disordered overlayers then the model without relaxation is justified. Since there are no experimental data available for the (Ag,Pd) overlayer system, the results for both cases described above are presented.

The layer-resolved DOS's in the overlayer and in the top three substrate layers are presented in Fig. 1 for an unrelaxed and a relaxed overlayer of random $Ag_{75}Pd_{25}$ on Ag(001) together with the componentlike DOS for Ag and Pd in the overlayer. Because of the reduced number of Pd neighbors at the surface the Pd-impurity peak at about -0.30 Ry is much sharper than the corresponding peak for the bulk $Ag_{75}Pd_{25}$ alloy[3] and survives as a shoulder above the d-Ag band only in the top substrate layer. As one can see from Fig. 1 the DOS for the second and especially the third substrate layer is already close to the DOS for bulk Ag. Since the average distance for Pd atoms is larger in the unrelaxed case, the Pd-like component DOS is broader in the relaxed case than in the unrelaxed case. The Ag-like component DOS in the overlayer remains essentially the same in both cases.

As an example of $k_{\parallel}$- and layer-resolved spectral densities, the $k_{\parallel}=0$ case is shown in Fig. 2. The most striking effect of disorder is the appearance of the Pd-related peak at about -0.30 Ry, which survives as a shoulder only in the top substrate layer. In the following layers the spectral density quickly approaches its bulk counterpart. The unrelaxed and relaxed cases are distinctly different only in the region of the Pd-impurity peak (the corresponding Pd-induced peak is again narrower in the unrelaxed case). It should be noted that the convergence of the $k_{\parallel}$-resolved DOS to the bulk value is weaker than for the $k_{\parallel}$-
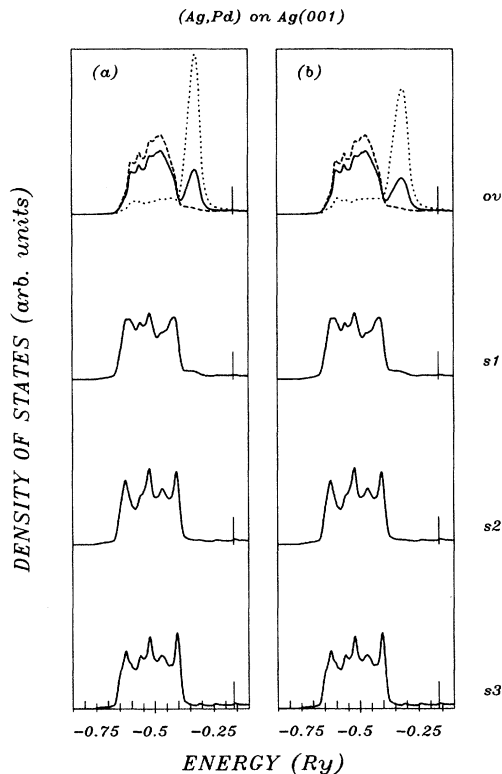

FIG. 1. Layer-resolved DOS's (solid lines) for an overlayer (ov) of random $Ag_{75}Pd_{25}$ on Ag(001). The first three layers of the substrate are denoted by $s1$, $s2$, and $s3$, respectively. For the overlayer the componentlike densities of states for Ag (dashed line) and Pd (dotted line) are shown. The vertical lines denote the position of the substrate Fermi level. (a) refers to the unrelaxed case and (b) to the relaxed case.
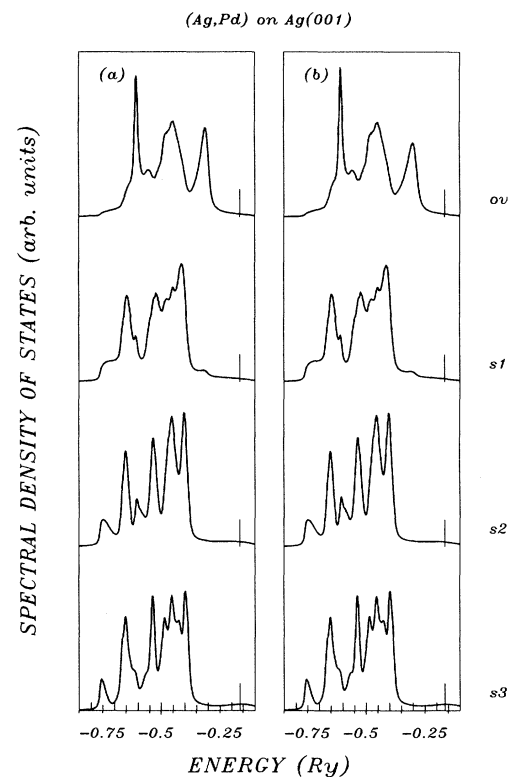

FIG. 2. $k_{\parallel}$- and layer-resolved spectral densities for an overlayer (ov) of random $Ag_{75}Pd_{25}$ on Ag(001) and $k_{\parallel}=0$. The first three layers of the substrate are denoted by $s1$, $s2$, and $s3$, respectively. The vertical lines denote the position of the substrate Fermi level. (a) refers to the unrelaxed case and (b) to the relaxed case.

integrated DOS.

We have presented a method with which to study the electronic structure of substitutionally disordered monolayers on ordered substrates. The importance of our approach is its ability to describe properly both the varying monolayer composition and the semi-infinite nature of the underlying substrate within the framework of density-functional formalism. The method is simple, easily implemented numerically, and yet sufficiently accurate. It allows the consideration of a number of interesting applications, such as the study of high-Miller-index (covered) surfaces, the investigation of properties of disordered interfaces or graded heterojunctions between two metals, a generalization to randomly covered semiconductor surfaces, etc. The theory can be improved in some technical aspects, namely, by including the effect of the top-layer relaxation or by considering more realistic boundary conditions for the sample-vacuum interface or by using layer-dependent potential parameters as obtained from the slab or supercell calculations. Quite clearly this theory is currently limited by the use of muffin-tin or spherically averaged atomic potentials. Consequently it is not suitable, for example, to calculate work functions.

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