Effect of impurities on surface stress on an atomic scale

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Atomic-scale calculations of stress induced by a transition metal adsorbate on a metal surface are presented. A newly developed many-body potential is used. We show that Co adatoms strongly reduce local surface stress and lead to an inhomogeneous stress distribution. Barriers of jump and exchange diffusion are determined for Co on Au(001). We predict that the exchange process is energetically favorable. Molecular dynamics calculations are performed to determine the coverage dependence of the adsorbate-induced surface stress.

While the concept of surface stress was introduced by Gibbs at the beginning of the 19th century,[1] the importance of surface stress has become widely appreciated only in the last 10 years.[2] Results of many investigations demonstrated a strong impact of stress on surface diffusion,[3] surface reconstruction[4] and surface morphology.[5] One can consider surface stress as a new parameter in experimental and theoretical investigations on surface growth modes and physical properties of nanostructures.[6] To our knowledge, it is not yet possible to measure stress directly. In all experiments only changes in stress, caused by adsorbates or reconstruction, were determined. Therefore, theoretical studies of surface stress, both *ab initio* and semiempirical, are of a great importance. First-principle calculations of surface stress for several clean metals were performed by Needs *et al.*[7] They found that the kinetic energy of electrons introduce the largest contribution to stress. *Ab initio* studies of Fiorentini *et al.*[8] showed that the reconstruction of the late $5d$ metals is related to the large tensile stress on these surfaces. Semiempirical calculations of surface stress of various metals were performed by means of the embedded atom method and Finnis-Sinclair potentials.[9] Several *ab initio* and semiempirical studies on surface stress in semiconductors were reported.[10]

The interaction between an adsorbate and the surface may change the surface stress and may lead to a structural rearrangement. For example, Feibelman showed that both O and H adsorption relieve tensile stress on Pt(111).[11] The effect of substrate stress on adsorption of oxygen on Ru(100) was found by Gsell *et al.*[12] The first direct experimental proof to our knowledge for anisotropic adsorbate-induced surface stress on W(110) was reported by Sander *et al.*[13] The coupling of the impurity stress to the surface stress can strongly influence the solubility of impurities.[14] The reduction of surface stress could be the driving force for surface-confined intermixing[15] and alloy decomposition.[16] Recent experiments revealed that even moderate changes in surface stress are capable to modify the magnetic properties considerably.[17] Despite the great interest in magnetic properties and the growth modes of magnetic films, there were no theoretical investigations of the effect of transition metal adsorbates on surface stress. Due to a strong impact of surface stress on magnetism,[17] such studies will be of fundamental interest.

In this paper we present atomic-scale calculations of the effect of transition metal adsorbate on surface stress. We concentrate on Co adatoms on Au(001). An alternative many-body potential for Co/Au(001) is used. Relaxations, diffusion barriers, and stresses are studied. Molecular dynamics simulations are performed to reveal the coverage dependence of the Co-induced surface stress.

To construct potentials of interatomic interactions for the Co/Au(001) system we use the scheme developed recently in our group.[18] Our approach is based on fitting of the interaction parameters to accurate first-principle calculations of selected cluster-substrate properties. The potentials are formulated in the form proposed by Rosato, Guillope, and Legrand[19] (RGL) with a modified form of the repulsive part. The cohesive energy E_{coh} is the sum of the band energy E_B and the repulsive part E_R:

$$E_{coh}=\sum_i (E_R^i+E_B^i), \tag{1}$$

$$E_B^i=-\left\{\sum_j \xi_{\alpha\beta}^2 \exp\left[-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)\right]\right\}^{1/2}, \tag{2}$$

$$E_R^i=\sum_j \left[A_{\alpha\beta}^1\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)+A_{\alpha\beta}^0\right]\exp\left[-p_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)\right], \tag{3}$$

where r_{ij} represents the distance between atoms i and j, and $r_0^{\alpha\beta}$ is the first-neighbor distance in $\alpha\beta$ lattice structure, while it is just an adjustable parameter in the case of the cross interaction. ξ is an effective hopping integral that depends on the material, and $q_{\alpha\beta}$ and $p_{\alpha\beta}$ describe the dependence of the interaction strength on the relative interatomic distance.

RGL potentials were derived in the second moment tight-binding approximation. It was shown in many calculations that RGL potentials correctly describe surface relaxations, reconstruction, and diffusion on surfaces of fcc transition metals.[20]

In the present work, the parameters of Co-Co and Co-Au interactions are optimized simultaneously to reproduce correctly the first-principle Korringa-Kohn-Rostoker (KKR)

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TABLE I. Data used for the fitting of the potential together with the values calculated with the optimized potential. (Cohesive energy E_c, bulk modulus B, elastic constants C_{ij} from Ref. 19, first-neighbor interaction energy in bulk $E_{1,b}^{\text{Co-}Co}$, solution energy $E_S^{\text{Co in Au}}$, binding energies of Co clusters $E_{1,\text{in Au}(001)}^{\text{Co-}Co}$, $E_{1,\text{on Au}(001)}^{\text{Co-}Co}$, $E_{\text{on Au}(001)}^{trimer}$, $E_{\text{on Au}(001)}^{c4chain}$, $E_{\text{on Au}(001)}^{2\times 2\ island}$ are calculated using the KKR Green's function method.)

	Quantity	Data	Fitted value
Au	a_{Au}	4.079 Å	4.079 Å
(fcc)	E_c	-3.779 eV	-3.779 eV
	B	1.65 Mbar	1.65 Mbar
	C_{11}	1.87 Mbar	1.87 Mbar
	C_{12}	1.54 Mbar	1.54 Mbar
	C_{44}	0.45 Mbar	0.45 Mbar
Co	a_{Co}	2.507 Å	2.516 Å
(hcp)	E_c	-4.386 eV	-4.397 eV
	B	1.948 Mbar	1.973 Mbar
	C_{11}	3.195 Mbar	3.351 Mbar
	C_{12}	1.661 Mbar	1.380 Mbar
	C_{13}	1.021 Mbar	1.152 Mbar
	C_{33}	3.736 Mbar	3.691 Mbar
	C_{55}	0.824 Mbar	0.685 Mbar
Co-Au	$E_S^{\text{Co in Au}}$	0.26 eV	0.26 eV
	$E_{1,b}^{\text{Co-}Co}$	0.001 eV	0.099 eV
	$E_{1,\text{in Au}(001)}^{\text{Co-}Co}$	-0.070 eV	-0.083 eV
	$E_{1,\text{on Au}(001)}^{\text{Co-}Co}$	-0.710 eV	-0.707 eV
	$E_{\text{on Au}(001)}^{trimer}$	-1.330 eV	-1.353 eV
	$E_{\text{on Au}(001)}^{c4chain}$	-1.910 eV	-1.998 eV
	$E_{\text{on Au}(001)}^{2\times 2\ island}$	-2.870 eV	-2.722 eV

Green's function calculations for binding energies of small Co clusters (linear chains and plane island, Table I) on Au(001), the solution energy of the Co impurity in Au bulk, and the energies of interaction of two Co impurities in Au bulk and in the surface layer. Magnetic effects are included implicitly performing the spin-polarized calculations for all clusters. Details of KKR calculations for supported clusters can be found in our previous work.[21] The set of data used in the fitting is given in Table I. The bulk and surface properties are well reproduced. The parameters of interatomic interactions for Co/Au(001) are given in Table II. The application of this method to the Co/Cu(001) system and the computational details have been presented in our recent publication.[18]

We consider firstly the relaxation near a single Co adatom on Au(001) surface. In Fig. 1 the top layer at the minimum-energy configuration is depicted. The Co adatom is only 0.89 Å , above the surface layer, i.e., very close to the center of the top layer. A similar calculation for an Au adatom on Au(001) give the value 1.68 Å , which agrees very well with *ab initio* calculations of Yu and Scheffler for Au/Au(100).[22] The four atoms below the Co adatom are pulled out from Co adatom by 0.26 Å and upward by 0.1 Å . These results suggest that the strong tensile surface stress of Au(001) pulls the Co adatom very close to the surface. To clarify the effect of the Co adatom on the stress we perform calculations of the atomic level stress components:[10]

TABLE II. Parameters of interatomic interactions.

Parameter	Au-Au	Au-Co	Co-Co
A^1 (eV)	0.0000	-3.8692	0.0000
A^0 (eV)	0.2061	0.0153	0.1117
ξ (eV)	1.7900	1.9024	1.4693
p	10.229	12.4376	12.6960
q	4.0360	7.9290	1.9122
r_0 (Å)	2.8843	2.5335	2.4304

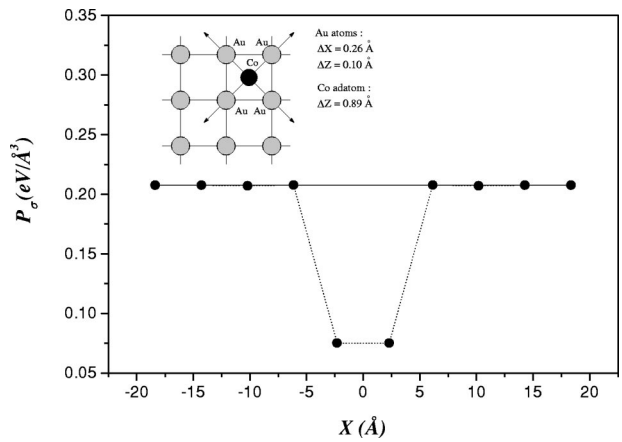

FIG. 1. The X dependence of the hydrostatic stress p_σ (dotted line) for surface gold atoms induced by single Co adatom ($X=0$). The stress for clean Au(001) surface is shown (solid line). Inset: relaxation of the Co adatom and the Au atoms from the topmost surface layer.

$$\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega_0}\left[\frac{p_i^\alpha p_i^\beta}{m_i} + \frac{1}{4}\sum_j (r_{ij}^\beta f_{ij}^\alpha + r_{ij}^\alpha f_{ij}^\beta)\right], \qquad (4)$$

where $(\alpha\beta)\equiv(x,y,z)$, m_i and p_i are the mass and momentum of atom i, $\vec{r}_{ij}$ means the distance between atom i and j, $\vec{f}_{ij}$ is the force acting on atom i due to j, and Ω_0 defines the average atomic volume.

Figure 1 shows the atomically resolved hydrostatic stress $P_\sigma = \text{Tr}(\sigma_{\alpha\beta})$ in the uppermost Au layer. One can see that the stress has abrupt changes over the gold atoms under Co adatom in the nearest-neighbor positions, while the stress for more distant gold atoms is mostly unchanged. Thus, Co adatoms strongly reduce the local tensile stress in Au(001) and lead to an inhomogeneous stress distribution. The above results reveal that the atomistic nature of the surface can be crucial for understanding of the behavior of adatoms at the initial stage of monolayer growth. It is important to note that many experiments revealed that transition metal impurities can stabilize the unreconstructed (001) gold surface.[23] It has been believed, that the surface stress is always reduced by adsorbates, because they increase the number of bonds. Our present results show that for Co adatoms on the Au surface this model works indeed well. However, such view of the effect of adsorbates on the surface stress is oversimplified. Ibach[2] has demonstrated that the sign of the adsorbate-induced surface stress may not follow the rule presented above. He found that several adsorbates can increase the tensile stress of the surface. He also showed that the sign of the

TABLE III. Diffusion barriers for Au/Au(001) and Co/Au(001) systems.

Process	Present	*Ab initio*
Au jump	0.53 eV	0.58 eV
Co jump	1.10 eV	-
Au exchange	0.43 eV	0.40 eV
Co exchange	0.25 eV	-

induced surface stress may change either with coverage or temperature. Application of particle bombardment for stress relaxation revealed drastic nonmonotonic changes in surface stress.[24] The principle reason why the bond-counting picture might be inappropriate is that adsorbate and substrate relaxations can have a strong impact on surface stress. It is important to note that recent investigations of Bogicevic[25] have clearly shown that rebonding view of adsorbate bonding is invalid in many metal systems. Therefore, we believe that the effect of the adsorbate on the surface stress can be clarified only if relaxations effects are taken into account.

Now we turn to the results on barriers for Au and Co surface diffusion. It was shown by Yu and Sheffler[22] that the surface diffusion of Au adatoms on Au(100) is proceeded by atomic exchange. They found from *ab initio* calculations that the exchange diffusion is activated by a large stress of Au(100). Our results for the jump and exchange diffusion of Au and Co adatoms are presented in Table III. One can see that for Au adatoms the agreement with *ab initio* results is rather good. For Co adatoms we predict that the exchange process is clearly favorable. To our knowledge neither *ab initio* nor semiempirical calculations for Co diffusion on the Au surface have been performed so far. Our total energy calculations show that the replacement of an Au atom by a Co atom is preferred by 0.4 eV. The actual meaning of the exchange mechanism for Co/Au system is the following. Both Au and Co adatoms easly incorporate into the Au surface. The incorporated Co adatoms are replaced by isolated Au adatoms, i.e., the process involves Au self-diffusion. On the experimental side, it appears, that the intermixing at Co/Au interfaces exist.[26]

Finally, we present molecular-dynamics calculations of the coverage dependence of the adsorbate-induced surface stress. Periodic boundary conditions are applied to the simulation cell in the x and y direction. The size of the cell includes the 7th layer slab with 1058 atoms per each layer.

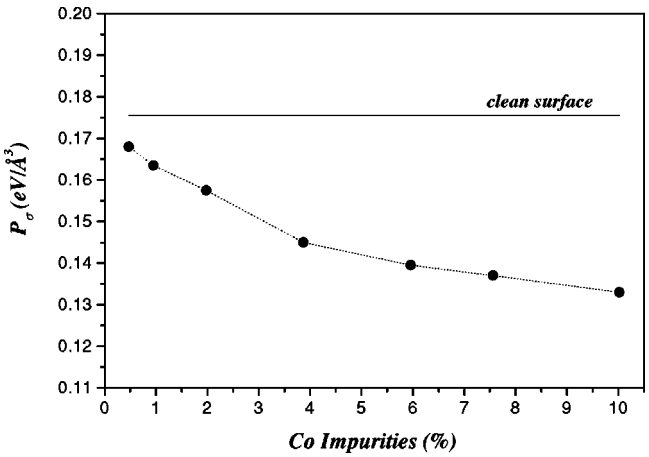

FIG. 2. Coverage dependence of the adsorbate-induced surface stress: the hydrostatic stress p_σ in the topmost surface layer (dotted line); the stress of clean gold (001) surface is shown(solid line).

Calculations are performed at room temperature. Figure 2 shows the hydrostatic stress in the topmost Au layer for different concentrations of Co impurities. Some of the deposited Co atoms exchange sites with Au atoms in the substrate. Substitutional Co atoms exhibit random distribution in the substrate. A significant decrease of stress is seen in Fig. 2.

In conclusion, we have presented atomic-scale simulations of the relaxations, barriers of diffusion, and stresses for transition metal adsorbates on the metal surface. Interatomic potentials for Co/Au have been constructed using *ab initio* data of bulk and surface properties. A strong reduction of the surface stress induced by Co adatoms is found. Inhomogeneous stress distribution in the surface is expected at the initial stage of Co growth on Au(001). We predict that the exchange mechanism for diffusion of Co adatoms on Au(001) is favorable. The coverage dependence of the adsorbate-induced surface stress shows the reduction of surface tensile stress. We hope that the present results will motivate experimental efforts to study stresses induced by transition metal adatoms and nanostructures on metal surfaces. We believe that many-body potentials for Co/Au will be useful in many atomic-scale simulations.

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