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Energetics of surface alloying: 3d adatoms on the Au(100) surface

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Ab initio studies of energetics of surface alloying on an atomic scale are presented. We demonstrate that site exchanges between 3d transition metal impurities on the Au(100) surface and Au atoms are energetically favorable. These results show that models of epitaxial growth based on an abrupt boundary between components can be inadequate for all 3d transition metal nanostructures on the gold surface. Consideration based on the energetics of impurities in the gold surface leads to the conclusion that a random distribution of isolated impurities is expected in all systems investigated.

In the past few years, much research has been performed on surface alloys. The most remarkable finding is that place exchange processes can result in the formation of surface alloys, even for metals immiscible in bulk form. For example, it was concluded that Co atoms intermix with Cu at the Cu(100) surface by an atomic exchange process.[1] Similar results were found in Fe/Cu(001).[2] The temperature used in these experiments was at or above room temperature. In the case of Fe/Ag(100) Fe adatoms were found to exchange sites with Ag atoms from the top layer at 130 K.[3] Investigation of Fe/Au(100) demonstrated that intermixing occurs at room temperature.[4] Burrowing of Co clusters into Au, Cu, and Ag substrates has been observed.[5] Presumably, burrowing is driven by exchanges between clusters and surface atoms. Recently, the growth of vertical magnetic Co pillars on a gold surface has been reported.[6] A dramatic rise of the blocking temperature in these systems was found. The growth of pillars is also determined by the place exchange mechanism. One of the most exciting phenomena in magnetism—oscillatory exchange coupling—is strongly influenced by the alloying in magnetic layers.[7]

When a material A is deposited on a surface B one needs to know whether intermixing takes place and whether A atoms are isolated or form clusters in a surface layer. Simple arguments to understand the atomic behavior on surfaces are based on such macroscopic properties as surface and interface energies of the components. However, they are rather questionable when applied to an individual adatoms on a metal surface, whose interaction determines the atomic picture in the early stages of thin-film growth. Tersoff has demonstrated that surface-confined mixing arises in systems dominated by atomic size mismatch.[8] Several experimental results on surface alloys can be understood using the main conclusions of his investigation.[8] However, the model proposed by Tersoff takes into account only the strain energy of the system and cannot give detailed information about interactions in the surface. Thus, there is clearly a strong need for *ab initio* studies of these problems.

It is the main goal of this paper to present *ab initio* results on energetics of alloying on an atomic scale. In experiments on Fe,[4] Co,[6,9] and Ni (Ref. 10) nanostructures on a gold substrate the place exchange mechanism was proposed to explain scanning tunneling microscopy (STM) images and the growth process. Therefore, we concentrate on 3d impurities on the Au(100) surface. The unreconstructed surface of Au(100) is used in our calculations. It is well known that the atomic structure of the unreconstructed Au(001) surface can be stabilized with a small amount of metallic impurity.[11] The most recent experiments[12] on Fe/Au(100) with different level of coverage showed that unreconstructed areas spread over the entire surface. We demonstrate that site exchanges between all 3d transition metal impurities and Au atoms are energetically favorable and lead to atomic dispersal in the surface layer.

A Korringa-Kohn-Rostoker Green's function method for surface impurities and clusters is used. The basic idea of this method is a hierarchical scheme for the construction of the Green's function of impurities or clusters by means of successive applications of Dyson's equation. We treat a surface as a two-dimensional (2D) perturbation of the bulk. Taking into account the 2D periodicity of the ideal surface, we find the structural Green's function by solving a Dyson equation self-consistently. After a transformation of the surface Green's function to a site representation, the Dyson equation is used again to calculate self-consistently the Green's function of impurities on a surface. The local density approximation of the density functional theory is used. Spin-polarized calculations are performed for all impurities. Total energies are calculated by applying Lloyd's formula adapted to complex energies. Accurate total energies can be obtained provided that the full charge density, including all nonspherical terms, is used. Relativistic effects are taken into account in the scalar-relativistic approximation (SRA), which gives very good results for the equilibrium properties of 5d metals.[13] Details concerning our method and several of its applications can be found in previous work.[14] Recently, this method was used to explain intermixing at the Cr/Fe(100) interface.[15] Excellent agreement with STM experiments was obtained.

The difference in total energy for the exchange process is shown in Fig. 1. The initial (A) and final (B) atomic configurations are also presented in Fig. 1. Surprisingly, we find that for all 3d impurities it is energetically favorable to exchange with Au surface atoms. The energy gains are large for all impurities. For Fe, Co, and Ni impurities our calculations support the conclusions of the experimental investigations.[4,9,10] In all experiments the temperature was at or above room temperature. Therefore one can assume that

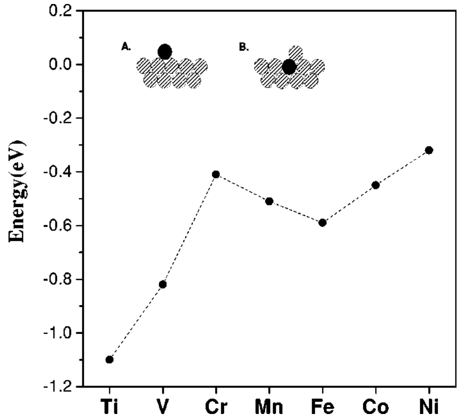

FIG. 1. Energetics of the exchange process. Energy difference between complex *B* and *A* is presented.

the activation barrier is sufficiently small and the exchange process occurs. Indeed, recent computer simulations of Co diffusion on Au(001) demonstrated that the exchange barrier is rather small (0.25 eV).[16] Thus, calculations of energetics of impurities show that surface-confined intermixing can exist for all 3*d* transition metal atoms on the Au(100) surface. The above results suggest that a simple model of epitaxial growth based on an abrupt boundary between components can be inadequate to describe structural and magnetic properties of 3*d* nanostructures on a gold surface.

All adatoms considered in the present work are magnetic on the Au(100) surface. To understand the impact of magnetism on energetics, we perform energy calculations for paramagnetic Co adatoms on Au(100). We find that in this case the gain of energy due to intermixing is 1 eV, which is much larger than in the magnetic case (cf. Fig. 1). Thus, magnetism tends to stabilize Co adatoms on the surface and prevents site exchange.

Now we discuss the interaction energies of 3*d* impurities at nearest-neighbor sites on the surface (adatom positions) and in the first surface layer (terrace position) of Au(100). Figure 2 shows the calculated energies.[17] Negative energy means attraction and positive energy repulsion between atoms. Only Fe and Co impurities show attraction, but the attraction is weak and not significantly different from zero. It was shown by Hoshino *et al.*[18] that the fundamental characteristic features of the phase diagrams can be qualitatively explained by the nearest-neighbor interaction of impurity pairs. The attractive interaction leads to segregation, the repulsive one to a solid solution. Thus, we expect that the distribution of 3*d* impurities on the gold surface and in the surface layer can be very different: cluster formation on the surface and a strong tendency to disordering in the surface layer. Recent experimental studies[4] on Fe/Au(100) at the initial stage of monolayer growth showed that Fe atoms in the Au substrate remain isolated and do not form clusters. Similar results were reported for Cr impurities in Fe(100).[19] These results are in contrast to those for other surface alloys, where clustering was observed.[8,20]

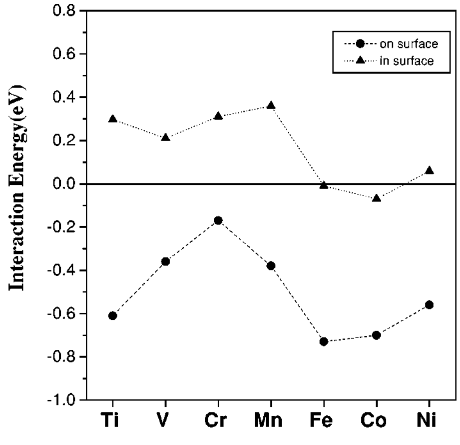

FIG. 2. Interaction energies of 3*d* impurities on the nearest neighbor sites on the Au(100) surface and in the surface layer.

Our calculations neglect the lattice relaxations at the surface and around impurities. This should be well justified. Tersoff[8] demonstrated that relaxations tend to stabilize impurities in a surface layer. Similar findings were reported by Nielson *et al.*[20] and Levanov *et al.*[21] It is also useful to recall our recent atomic scale simulations of Co impurities on Au(001) performed by means of quasi *ab initio* molecular dynamics.[16] We found that in the fully relaxed geometry surface alloying is also energetically favorable. Therefore, we expect the gain of energy due to intermixing in a relaxed geometry to be even larger than in the ideal geometry for all 3*d* impurities. Moreover, relaxation effects will increase the tendency to a random distribution of isolated impurities in the surface layer,[22] i.e., impurities will repel each other more strongly than we found in the present calculations. Thus we can say that none of our conclusions will be changed by the inclusion of relaxations.

It is interesting to compare the interaction between impurities in Au(100) and Ag(100) surfaces. The Ag(100) surface is isoelectronic and chemically rather similar to Au(100). Interatomic distances are very close on both substrates. Such a comparison reveals a drastic effect. We find, for example, that the attractive interaction between Fe impurities in Ag(100) is about 20 times stronger than in Au(100) (the Fe-Fe interaction in Ag is -0.2 eV). Co impurities in Ag(100) also attract each other much more strongly than in Au(100) (the Co-Co interaction in Ag is -0.19 eV). Similar results are obtained for all 3*d* impurities in Ag(100). This suggests that the relativistic effects, which are very important for Au,[23] lead to a strong repulsive interaction in Au surfaces. It is known[24] that relativistic effects in 5*d* metals lead to a longer *sp* tail and to a *d* band that is wider and closer to the Fermi level than in 4*d* metals. Thus, relativistic effects increase the hybridization between electronic states of 3*d* impurities and electronic states of the Au surface and decrease the attractive interaction between impurities. The spin-orbit coupling (SOC) interaction energy in 3*d* metals is fairly small as compared to the 3*d* bandwidth.[25] Also, the hybridization between *d* states of 3*d* adatoms and the Au *d* band is rather weak. Therefore, we believe that the calculated interaction energies cannot be seriously affected by SOC. Several recent applications of the SRA for calculations of energetics of adatoms and clusters on surfaces of 5*d* metals showed very good agreement with experiments.[26]

To give a direct demonstration of relativistic effects, we performed a nonrelativistic calculation for Co pairs in Au(100). We find that the interaction energy is indeed decreased by a factor of 2, i.e., Co impurities strongly attract each other, with the energy of the interaction being very close to the result obtained for the Ag substrate. It is interesting to note that because of relativistic effects the Au surface has a tensile stress twice as large as that of the Ag surface.[24]

In summary, using first-principle calculations, we have investigated the energetics of the place exchange mechanism on an atomic scale. We have found that exchanges between isolated $3d$ transition metal impurities and Au surface atoms are energetically favorable. This suggests that a diffuse rather than chemically abrupt interface can exist in these systems. The above results confirm the recent STM experiments on the place exchange process for Fe, Co, and Ni on a gold substrate. A strong suppression of the nearest-neighbor attractive interaction between impurities in the gold surface has been predicted by our calculations. This finding leads to the conclusion that a random distribution of isolated $3d$ impurities in the gold surface is energetically favorable. For Fe on Au(100) our results are in agreement with recent experiments.

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