Initial Growth of Au on Ni(110): Surface Alloying of Immiscible Metals

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Atomic resolution scanning tunneling microscopy of Au deposited on Ni(110) shows that even though Au is completely insoluble in bulk Ni, it replaces Ni in the first surface layer forming a surface Au-Ni alloy and the squeezed out Ni atoms agglomerate in Ni islands on the surface. This picture is supported by total energy calculations within the effective-medium theory, which also provide a detailed understanding of this surprising phenomenon.

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The growth of metals on metal surfaces is turning out to be considerably more complex and interesting than expected from simple macroscopic considerations [1]. Experimental methods like field ion microscopy (FIM) [2] and scanning tunneling microscopy (STM) [3,4] have made it possible to study the arrangement of the atoms during metal on metal growth. One of the interesting aspects which has been pinpointed is the possibility of intermixing between the growing layer and the substrate. This has been demonstrated for the growth of Au on Cu(100), where a $c(2 \times 2)$ Cu-Au layer is developed [5], and most recently it has been shown that when Au is deposited on Ag(110), the gold atoms are intermixed with the first two Ag layers [4]. Total energy calculations have been an important ingredient in establishing the equilibrium structures for these systems [6,7].

The Cu-Au and Au-Ag systems are characterized by the fact that the two metals involved are miscible. If two metals which do not form stable ordered or disordered alloys are chosen, one would expect the deposited metal to simply grow on top of the surface of the other. In the present Letter, we will show that this is not generally the case. We present detailed STM results showing that when Au is deposited on Ni(110), a very unexpected growth mode results. The incoming Au atoms replace the Ni atoms in the first layer even at the lowest coverages, resulting in the formation of a stable Au-Ni surface alloy, and the Ni atoms that are squeezed out of the first Ni layer agglomerate into anisotropic islands. Calculations of the energetics of the Au-Ni(110) system within the effective-medium theory confirm these observations. On this basis, we develop a set of concepts that can explain in detail why on the one hand Au atoms are more stable *in* the first Ni(110) layer than *on top* of it, while, on the other hand, Au atoms embedded further into the Ni crystal are much less stable than in either sites at the surface.

The experiments, all carried out at room temperature, were performed with a compact, fully automated STM [8], for which atomic resolution images are recorded on metal surfaces on a routine basis with the STM operated in the normal constant-current mode. Normally, a positive tip bias V_t is applied to the sample with the tip at virtual ground. Changing the polarity of V_t did not reveal any spectroscopic effects. The STM is mounted in a UHV chamber with standard facilities for surface characterization. The Au evaporations were all performed at room temperature by resistively heating a conical tungsten wire surrounding a small Au droplet. The Ni(110) sample was cleaned by repeated Ne sputtering-annealing and oxidation-reduction cycles until a perfect, impurity-free (1×1) surface was obtained, as observed by LEED, Auger, and STM.

Prior to the Au evaporations, the Ni(110) surface was scanned by STM, and the surface morphology showed large terraces approximately 1000 Å wide. Evaporation of even very small amounts of Au (0.05 ML) [1 ML (monolayer) = 1.15×10^{15} atoms/cm^2] on the perfect Ni(1×1) surface causes the development of "holes" on the surface, as depicted in Fig. 1(a). The holes are seen to be located at the positions of apparently removed Ni atoms in the topmost layer, and they are quite shallow (~ 0.25 Å). Increasing the Au exposure (0.35 ML) causes, as seen from Fig. 1(b), an increase in the number of holes being formed. Superimposing a (1×1) unit mesh on Fig. 1(b), it is seen that the holes are located exactly on nickel positions, grouped in pairs along the $[1\bar{1}0]$ direction. In the low-coverage Au regime, the majority ($\sim 95\%$) of the holes appear to be double holes, defined as pairs of apparently removed Ni atoms, and only very few monomer and trimer holes are observed.

Correlated with the increase in the density of holes in the Ni(110) surface layer we observe a homogeneous nucleation of two dimensional (2D) islands. The islands are found to grow anisotropically along the $[1\bar{1}0]$ direction as seen from Fig. 1(c). The height of the islands above the Ni(1×1) terrace is 1.24 Å, identical to the height of a monatomic step on Ni(110), and from atom-resolved images, it can be concluded that both the periodicity and registry of the atoms in the islands are identical to a simple continuation of the fcc stacking sequence of the Ni(110) surface.

Both the density of holes and the surface area covered by islands increase linearly with the amount of Au

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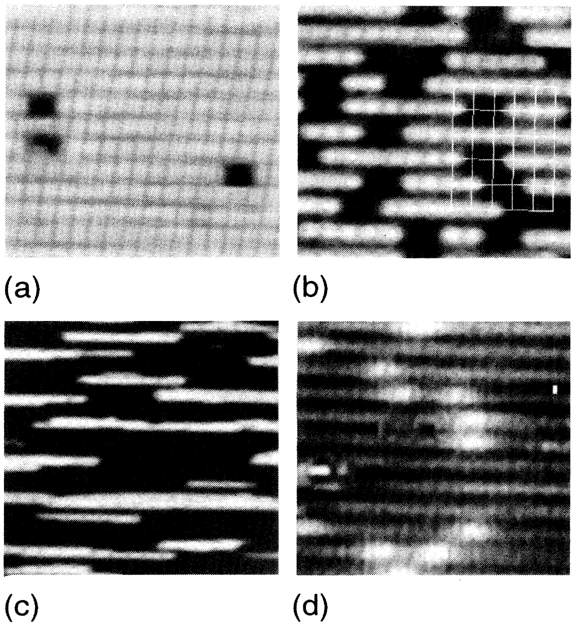

FIG. 1. Atomically resolved STM topographs (36 × 38 Å^2) at Au coverages of (a) 0.05 ML (I_t=7 nA and V_t=2 mV), (b) 0.35 ML (I_t=7 nA and $V_t = -3$ mV), and (d) after a tip change where the holes are transformed into protrusions (~ 0.15 Å) along the [1$\bar{1}$0] direction (0.18 ML, $I_t = -5$ nA and $V_t = -372$ mV). In (b) a Ni(1 × 1) unit mesh is superimposed, and in (a) the corrugations along the [1$\bar{1}$0] and [001] directions are 0.02 Å and 0.10 Å, respectively. (c) STM topograph over a large area (702 × 765 Å^2) at a coverage of 0.17 ML showing the anisotropic growth of 2D Ni islands (I_t=1.7 nA and V_t=20 mV). The grey scale is such that protrusions are white, while depressions are black.

deposited up to a hole and island density of ~ 50%, corresponding to a Au coverage ~ 50%. Furthermore there exists a close to one-to-one correspondence between the density of holes in the topmost layer and the area covered by islands as seen from Fig. 2. At higher Au coverages, a transition from a 2D to a 3D growth mode is observed which will be dealt with elsewhere [9].

Given the fact that Au and Ni do not mix, it would be tempting to interpret the islands which grow during Au exposure as Au islands. The height of the islands, however, strongly suggests that they consist of Ni. We also have to account for the holes in the first Ni layer. They cannot be vacancies because they are quite shallow, and therefore must be due to some atom other than Ni. This is supported by the fact that oxygen exposure locally induces the well known O(2 × 1)/Ni(110) reconstruction of the islands. Further, correlated with a tip change, we sometimes observe that holes are transformed into slight (~ 0.15 Å) protrusions, two protrusions for each hole as shown in Fig. 1(d). We therefore suggest that the holes are actually Au atoms substituted into the first Ni layer.

This interpretation is supported by an extensive set of calculations of the energetics of Au on Ni(110). The theoretical description of the energetics will be based on the the simplest form of the effective-medium theory where the total energy of the system is written as [10]

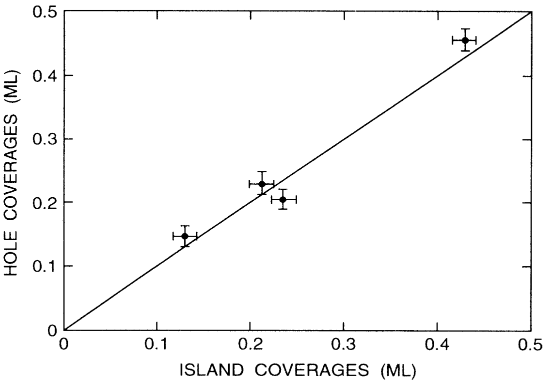

FIG. 2. The density of the Au induced holes in ML, counted from STM topographs with atomic resolution, as a function of the density of 2D Ni islands, measured from height distributions of large area STM topographs as depicted in Fig. 1(c). The solid line corresponds to equal hole and island coverages.

$$E_{\text{tot}} = \sum_i E_{c,i}(\bar{n}_i) + \Delta E_{AS}. \qquad (1)$$

Here the summation is over the atoms in the system. $E_{c,i}(n)$ is the cohesive function describing the variation of the energy of atom i with the electron density around the atom from the surroundings. The cohesive function can be calculated in a reference system where the calculation is simple, for instance, as the embedding energy in a homogeneous electron gas as a function of electron gas density, or from the cohesive energy in a bulk crystal lattice as a function of lattice constant. It generally shows a minimum at some electron density n_0, the optimum density. The correction term ΔE_{AS} describes the energy difference between the real system under investigation and the reference system used.

This method has proven accurate for calculating structural and thermal properties of metals, including metal surfaces, and structural energies in metal alloys [10,11]. In particular the method gives a good description of the Au heat of solution in Ni (+0.21 eV/atom which should be compared with the experimental value of +0.28 eV/atom [12]). Important for the present purposes is that the effective-medium theory permits energies of relaxed configurations of systems consisting of several hundred atoms to be conveniently calculated.

First we establish that the effective-medium total energies corroborate the interpretation presented above of the experimental observations. Table I summarizes the energies of Au for various configurations. In cases where the Au atom substitutes a Ni atom, the adsorption energy depends on the configuration of the Ni atom after the substitution has taken place. Two possibilities are shown,

TABLE I. Energy of adsorption for different structures. All energies are in eV per Au atom and measured relative to the energy per atom in bulk Au (−3.80 eV).

	Chemisorp.	Subst. 1st layer + Ni added row	Subst. 1st layer + Ni island	Subst. 2nd layer + Ni island
Monomer	−0.22	−0.42	−0.48	−0.03
Dimer	−0.37	−0.42	−0.48	⋯
1 ML	−0.39	−0.33	−0.39	⋯

the Ni atoms forming an added row or forming a large island. The added rows along the close-packed direction are almost, but not quite, as stable as a large island. An atom in an added row has as many nearest neighbors as in the island, but the number of next-nearest neighbors is smaller. The Ni islands formed during the experiments are strongly anisotropic [see Fig. 1(c)] reflecting that the nearest-neighbor bonds along the close-packed rows are much stronger than the next-nearest-neighbor bonds perpendicular to them. The results in Table I show a strong tendency for Au to be embedded in the first Ni layer. Furthermore, there is a strong attraction between Au adatoms, whereas there is a repulsion that increases with coverage between Au atoms substituted into the first layer. The substitution therefore must stop at some coverage, in agreement with the STM observations discussed above. Table I also includes a result for a Au atom in the second layer. This is clearly not as stable as in the first.

According to the calculations, the substituted dimer is as stable as the monomer but not more. The experimental observation of about 95% dimers therefore cannot be explained in the present framework as being due to a larger stability of the substituted dimer. The adatom dimer is, however, much more stable than the adatom monomer. It is likely that the deposited Au atoms first diffuse along the close-packed rows on the surface, form dimers, and then exchange (probably by the concerted exchange process observed by FIM [2]) into the first Ni layer, and we suggest that the predominance of dimers is due to a predominance of the adatom dimer precursor.

The incorporation of Au atoms into the first Ni(110) layer results in relaxation of the nearest-neighbor Ni atoms in the close-packed rows at the surface by 0.05 Å away from the Au atom. The Au atoms themselves are situated 0.2 Å above the Ni(110) plane.

The STM observations of a strong tendency to incorporate adsorbed Au into the first Ni(110) layer are therefore borne out by the effective-medium modeling. We can therefore ask the question why this surface alloying takes place, and, in particular, why it is energetically favorable for Au to be incorporated into the first Ni layer, while incorporation into the bulk Ni is clearly unfavorable. To do so, we compare three situations: (1) a Au adatom on the Ni surface, (2) a Au atom substituted into the first Ni layer (with the substituted Ni atom in a large Ni island), and (3) the same substitution process into the bulk.

Table II shows the energies of these three cases, both for *unrelaxed* and *relaxed* structures. Clearly relaxations tend to stabilize the structures, but even the unrelaxed configurations show the correct trend. For the unrelaxed case, the contributions from the cohesive function for both Au and Ni and from the atomic sphere correction are shown. It can be seen that the variation in the sum of the two E_c terms completely determines the overall trend.

Let us first consider the variation in the Ni energy for the three cases. The cohesive function is plotted in Fig. 3 for Ni as a function of the number of Ni neighbors N at the equilibrium Ni-Ni distance rather than as a function of the electron density. The coordination number is considered a continuous density variable. This is equivalent to a renormalization of the density so that the equilibrium density n_0 corresponds to the equilibrium Ni coordination number of 12. When a Au atom is substituted into bulk Ni, the 12 Ni atoms surrounding the Au atom will feel a different electron density because the Au electron density is more extended than the Ni density. The 12 Ni atoms will therefore experience an electron density slightly larger than optimum or, equivalently, an effective coordination number larger than 12, and the energy will increase, as observed in Table II.

The situation is quite different for the Ni atoms at the (110) surface. These atoms have a lower (7) than optimum coordination number (12), and the extra density provided by the Au atoms increases the density and thereby the effective coordination number, thus lowering the energy. The energy gain for the Ni atoms is largest for chemisorbed Au because here there are four Ni surface atoms that each get an increase in the effective coordination number of more than one, whereas for a Au atom in the first Ni layer, there are only two first layer Ni atoms

TABLE II. The energy of Au chemisorbed on the Ni surface, substituted into the first Ni layer (assuming the squeezed-out Ni to form large islands), and substituted into bulk Ni. For the *unrelaxed* configurations, the energies are shown distributed on the contributions from the E_c terms and the ΔE_{AS} term. All energies are in eV per Au atom and measured relative to the energy per atom in the bulk.

	Chemisorption	Substitution	Bulk subst.
E_c (Ni)	−0.53	−0.36	+0.12
E_c (Au)	+0.26	+0.01	+0.18
E_c total	−0.27	−0.35	+0.30
ΔE_{AS}	+0.07	+0.02	+0.12
E_{tot} unrelaxed	−0.20	−0.33	+0.42
E_{tot} relaxed	−0.22	−0.48	+0.21

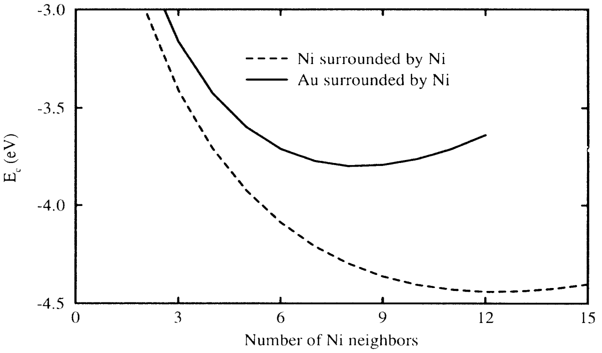

FIG. 3. The E_c function plotted as a function of coordination number N for a Ni atom and for a Au atom, in *both* cases surrounded by *Ni neighbors* at the equilibrium Ni bulk nearest-neighbor distance.

that get an increase in coordination number of less than one. In the latter case there are also four second layer Ni atoms that gain energy, but since they have a coordination number of 11 before the substitution, the energy gain is rather small. One can say that the Au atoms help lowering the Ni surface energy, and this is most effective for Au on top of the Ni layer.

Now consider the Au atom surrounded by Ni. Because the Ni lattice constant is much smaller than the Au lattice constant, a Au atom will feel an electron density contribution from a Ni atom at the equilibrium Ni-Ni distance that is considerably *larger* than that from a Au atom at the equilibrium Au-Au distance. (This is so even though the Ni atoms are smaller.) A plot of the Au cohesive function versus the Au coordination number in Au would look very much like the corresponding function for Ni in Fig. 3. If on the other hand the Au cohesive function is plotted as a function of the Ni coordination number on a Ni lattice, we get the Au cohesive function shown in Fig. 3. This has a minimum not at coordination number $N = 12$ but around $N = 8$ simply because eight Ni neighbors at the Ni-Ni equilibrium distance contribute as much electron density around the Au atoms as twelve Au neighbors at the much larger Au-Au equilibrium distance. This means that in bulk Ni, where $N = 12$, Au has a high energy, whereas substituted into the Ni (110) surface, where $N = 7$, the Au atom is close to the minimum energy. For chemisorbed Au on the surface, where $N = 5$, the electron density is too small, and the energy is again high. It is this trend that makes Au most stable in the surface layer, and since this is a direct consequence of the nonlinearity of the cohesive function, we can conclude that it is a true many-atom interaction effect that could not be described in a simple pair-wise interaction model [11].

In conclusion, we have provided experimental evidence that Au deposited on a Ni(110) surface alloys in the first Ni layer despite the fact that Au and Ni show absolutely no tendency for alloying in the bulk. We have provided theoretical evidence to support this observation and have provided a detailed physical picture of the alloying process showing why this unexpected phenomenon is observed.

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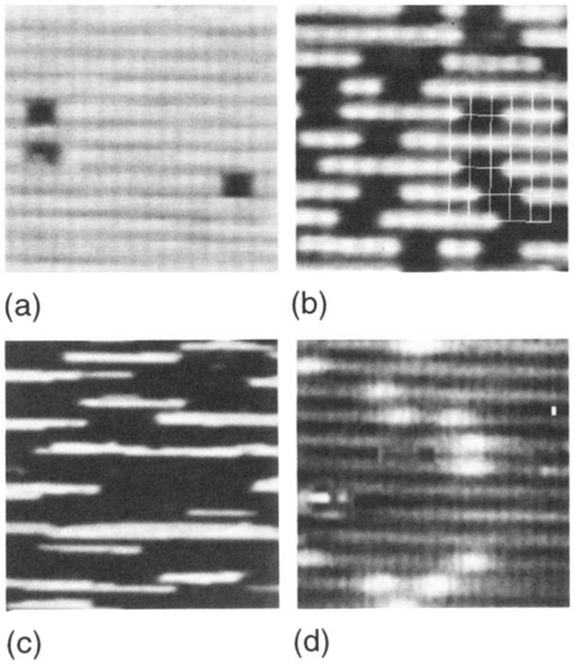

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