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SEMIEMPIRICAL ANALYSIS OF SURFACE ALLOY FORMATION

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Abstract

The BFS method for alloys is applied to the study of surface alloy formation. This method was previously used to examine the experimental STM observation of surface alloying of Au on Ni(110) for low Au coverages by means of a numerical simulation. In this work, we extend the study to include other cases of surface alloying for immiscible as well as miscible metals. All binary combinations of Ni, Au, Cu and Al are considered and the simulation results are compared to experiment when data is available. The driving mechanisms of surface alloy formation are then discussed in terms of the BFS method and the available results.

I. Introduction

A recent review article on alloy surfaces and surface alloys [1], indicates that crystallographic studies are very limited - a few tens of binary systems and practically no ternary and higher systems - as are also theoretical predictions of general trends. The shortage is particularly noticeable for surface alloys. The recent finding of a single layer surface alloy of Au deposited on Ni(110) [2] reaffirms the need for a better understanding of surface alloying and its consequences for related fields. Theoretical studies of this problem are also few and limited. Recently, with the advent of semiempirical methods, some interesting results contribute to a deeper insight of the surface structure of such systems. In this work we apply the BFS method for alloys [3] to the study of a group of systems to further verify the validity of the approach and to extract general rules to predict the behavior of more complex systems. The group of elements chosen - Al, Ni, Cu and Au - have been tested with the BFS method in a variety of applications raising confidence in the parameterization used in this work.

II. The BFS Method

The simulations quoted in this work are heavily based on a previous study of Au on Ni(110) [4], where we provided enough theoretical evidence to explain the surface alloying of these immiscible metals at low coverage, in agreement with experiment and an Effective Medium Theory examination of this phenomenon [2]. For the sake of brevity we refer the reader to previous papers on BFS and its application to alloy surface structure [4]. In particular, Ref. 4 provides details on the BFS method, the approach used in the simulation, its advantages and shortcomings.

The choice of elements studied was based on numerous successful applications of BFS, ranging from the defect structure of NiAl [5], segregation profiles of Cu-Ni alloys [6], the surface structure of Cu-Au and Ni-Al alloys [3], growth patterns of Au/Ni(110) [4], and the analyisis of ternary and quaternary alloys of these elements [7].

The BFS method is based on the idea that the energy of formation of an alloy is the superposition of individual contributions ε_i of non-equivalent atoms in the alloy [3]:

$$\varepsilon_i = \varepsilon_i^S + g_i(\varepsilon_i^C - \varepsilon_i^{C_0}). \tag{1}$$

ε_i has two components: a *strain* energy ε^S, computed with equivalent crystal theory (ECT) [3], that accounts for the actual geometrical distribution of the atoms surrounding atom i, computed as if all its neighbors were of the same atomic species, and a *chemical* energy $\varepsilon^C - \varepsilon^{C_0}$ (ε^{C_0} is a reference energy), which takes into account the fact that some of the neighbors of atom i may be of a different chemical species. The ideas of ECT [3] are used to develop a procedure for the evaluation of the energy associated with this 'defect'. The coupling function g_i ensures the correct asymptotic behavior of the chemical energy, is defined as $g_i = e^{-a_i^S}$, where a_i^S is a solution of the BFS strain equation [3]. In the context of BFS, the terms 'strain' and 'chemical' represent quite different effects than the usually assigned meanings. For a better understanding of this work, we direct the reader to Ref. 3. Except for two parameters determined by fitting to experimental or theoretical alloy properties, the method relies on pure element properties. The parameters used in this work are listed in Ref. 7.

III. Results and discussion

Instead of performing a Monte Carlo calculation to determine equilibrium configurations, we opted to study a large set of specific configurations, including some that are energetically unfavorable. By doing so, we expect to develop a better understanding of the ingredients responsible for a specific growth pattern. The simulation of growth of element A on a substrate B was performed on a slab of B atoms several layers deep with a (110) surface, by varying numbers of A atoms located in substitutional sites in the top or inner layers, or as adatoms on hollow sites. No atomic relaxations were allowed and no temperature effects were included. The results are given in terms of the energy of formation of a given configuration. as defined in Eq. (1). Let δH be the energy of formation per impurity atom (in eV/atom) referenced to a pure $B(110)$ surface: $\delta H = (\Delta H - \Delta H_0)/N_A$, where ΔH is the energy of formation of a given configuration, ΔH_0 is the corresponding value for a free $B(110)$ surface and N_A is the number of impurity atoms. We now discuss the results of computer simulations (see Ref. 4 for details) for $A/B(110)$ (A, B = Ni, Cu, Al, Au) in light of existing experimental evidence. Where no experimental results are available, the BFS predictions are compared with other faces. A summary of the results is presented in Table 1.

Al-Ni. The most comprehensive work on this system is that of Lu et al. [8] who found that slow vacuum deposition of Al onto unheated Ni(100) produces partially-ordered one- and two-layer thin epitaxial Al films. Slow deposition onto a hot Ni(100) substrate produce well-crystalized epitaxial films of $Ni_3Al(100)$. The alloy is not confined to just the surface layer, hence it is not a surface alloy. Deposition of Ni on Al(100) does not result in an ordered alloy.

The results of the BFS simulation - for Al/Ni(110) and Ni/Al(110) - largely follow a similar pattern to that found experimentally for the (100) faces. For very low Al coverages on Ni(110), the lowest energy states correspond to the insertion of Al atoms in the surface plane, tending to align patches of Ni_3Al (110) surfaces as coverage increases up to 0.4 ML. Around and above 0.5 ML, the Al atoms form islands in the overlayer with little or no evidence for intermixing, continuing up to 1 ML coverage where a single Al adlayer is energetically favorable. This zero temperature simulation for the Ni(110) surface is similar to the experimental slow deposition onto unheated Ni(100). For Ni/Al(110), the BFS results indicate no surface alloying for any coverage, in agreement with experiment.

Al-Cu. Barnes et al. [9] examined the growth of Cu films on Al(111) and (100), focusing on temperature dependent growth mechanisms. At 120 K growth was epitaxial with defects on Al(111) and disordered on Al(100), presumably due to higher roughness on the (100) surface. At 375 K, there is some, but not definitive evidence of intermixing at low coverages on both surfaces with the possibility of an ordered alloy on the (111) surface. At higher coverages (2 ML) the Cu film is epitaxial on the (111) surface and disordered on the rougher (100) surface. These results suggest that the growth on the rougher (110) surface should be more akin to the (100) results. Unfortunately, we found no experimental results for Al deposition on Cu surfaces.

Our results are in agreement with the low temperature deposition results where no mixing is found. Moreover, for Al/Cu(110) and Cu/Al(110) are in every respect identical to those found for the Al-Ni system: no surface alloy formation for Cu/Al(110) and the likelihood of a single layer Cu-Al alloy corresponding to a Cu_3Al(110) surface. For concentrations of Cu close and above 75 % at. Cu, an ordered phase exists (at low temperatures) with a

fcc structure isotypic with Cu. Compared with typical Ni-Al energies for the same type of configurations, Al-Cu results indicate the possibility that disordering is preferred over the bulk termination pattern observed in Al-Ni.

Au-Cu. Palmberg and Rhodin [10] report the first case where a surface alloy form by diffusion was claimed. Later works by qualitative LEED [11] confirmed these results, finding also probable surface alloys for Au deposited on Cu(110) and Cu(111). Several photoelectron diffraction experiments [12] indicate that beyond a single layer surface alloy, measurable amounts of Au exist in the second and third layers, as well as the possibility of growth of epitactic Cu_3Au through several layers.

Hansen et al, using photoelectron diffraction and photoelectron spectroscopy, report the formation of a surface alloy (for low coverages, up to 0.5 ML) for Au/Cu(100) and its transformation or segregation into a Cu overlayer (1 ML) at room temperature [11]. Wang et al. [13] reported that the two top layers of this system form two layers of $Cu_3Au(100)$. For Au/Cu(110), the only experimental evidence available was provided by Fujinaga et al. [11], which found a similar ordered phase on the surface corresponding to the (110) surface of the bulk Cu_3Au alloy.

The BFS results predict similar behavior for the Au/Cu(100) in the (110) case. At low coverages, Au atoms are immersed in the Cu surface plane, whereas the displaced Cu atoms show a tendency to form islands elsewhere on the substrate. Au atoms tend to substitute perpendicular to the close-packed direction, indicating a tendency for the formation of an ordered surface alloy. In excellent agreement with experiment, for 0.5 ML Au coverage, the lowest energy states correspond to the coexistence of patches of Cu_3Au (110) surfaces and pure Cu islands. While the location of Au atoms in the correct sites is common to all these

low energy states, the difference between them arises only from the relative shape and location of the pure Cu islands formed by the Cu atoms ejected from the surface plane. Hansen raises the issue of the location of the excess Cu, acknowledging that this is still an open question from the experimental point of view. If the Cu islands were eliminated in the calculation, the ground state character of the ordered phase becomes even more apparent, leading us to conclude that the Au/Cu(110) follows a very similar evolution than that observed for Au/Cu(100). The similarity with Hansen's model for Au/Cu(100) extends to the case of 1 ML Au coverage, where BFS predicts that the lower energy state is the pure Au overlayer, indicating that above a certain critical coverage of around 0.5 ML , the dealloying process starts when the additional Au and the one segregated from the ordered surface alloy form a uniform overlayer on the Cu substrate.

Au-Ni. An STM study has been performed on systems formed depositing Au on Ni(110) [2] demonstrating the formation of a surface alloy. A complete BFS study of this system was reported in Ref. 4.

Cu-Ni. Epitaxial layers of Cu on Ni(100) and the sandwich Ni-Cu-Ni(100) system have been studied by photoelectron diffraction [14], finding that the 'buried' Cu layer tends to diffuse rapidly onto the top layer at temperatures significantly lower than those needed for the mobility of bulk vacancies. The opposite approach, depositing Ni on Cu(100), was investigated by Alkemade et al. [15] suggesting partial incorporation of Ni atoms in the Cu layer during deposition. Their work leads to a model for the formation of stable CuNi surface alloys on a Cu(100) substrate at high temperatures, in which both Cu (by segregation or by surface diffusion from regions which are not yet covered) and Ni (from the gas phase) are continuously incorporated in the outermost one or two atomic layers. Our BFS simulation

results are not directly comparable to the experimental situation reported by Alkemade et al. [15] in that no growth beyond one single overlayer is allowed, added to the fact that no temperature effects are included in the calculation. However, the BFS results for Ni/Cu(110) do indicate a tendency towards the formation of a two layer Cu-Ni alloy in the outermost two layers as configurations where Cu and Ni atoms mix are energetically favored against those where Ni atoms form a thin film on the Cu(110) substrate with no intermixing. A similar effect is observed in the Cu/Ni(110) case, for which no experimental data is available for comparison. We would expect that entropic effects can only lower the free energy increasing the likelihood for the formation of a thin CuNi film on Cu(110), as is also observed on the (100) case. Moreover, deposition of Cu on Ni(110) shows a reversal in behavior to other systems (Au/Ni, Au/Cu, etc.) where the larger atom shows a tendency to substitute smaller substrate atoms in the surface plane. For low coverages, the lowest energy state always corresponds to Cu atoms distributed in the overlayer, a trend that continues up to 1 ML coverage. However, configurations that display intermixing of Cu and Ni atoms are very close in energy, enough to expect that entropic effects might alter that delicate balance.

Au-Al. No experimental data is available for this system. The Au-Al system is the only one of the 12 reported in this work where heats of formation are negative for both Au/Al(110) and Al/Au(110) except for very low coverages. Al/Au(110) is characterized by the fact that for all coverages, adatoms tend to group in the overlayer with no intermixing, whereas for Au/Al(110) a very distinct pattern, only found for this system, is seen: the formation of an Al-Au-Al sandwich consistent with the formation of an ordered alloy of equal concentration of Au and Al. Such a phase is found in the phase diagram, although no specific structure has been recognized for such alloy.

IV. Conclusions

There is an interest in being able to find a property which will predict the formation of surface alloys [16]. Recently, we and others [2,4] have proposed that the effective coordination may be such a property (i.e. an atom A immersed in a substrate B has the same energy that it would have in an environment with an effective number of A nearest neighbors (m_A) at equilibrium nearest-neighbor distances). Conversely, an atom A would need to have n_{eff} B atoms at such distance in order to simulate the A-bulk environment. These concepts, based on the idea that a given element is in its lowest energy state at the coordination and lattice parameter of its ground state crystalline structure, only account for BFS strain energy effects but can be clearly taken as an indication of the driving mechanisms for surface alloy formation. The solution of the perturbation equations inherent in BFS [3] provide a direct evaluation of this quantity [4]. For a (110) face, the effective coordination m_A is given by $m_A = n_s(a_B/a_A)^{p_A}e^{-\alpha_A(a_B-a_A)/\sqrt{2}}$ and $n_{eff} = n_s N/m_A$, where n_s is the number of nearest-neighbors of an atom in a surface site ($n_s = 7$ for fcc (110) surfaces), N is the bulk coordination ($N = 12$ for fcc elements), a_A and a_B are the equilibrium values of the lattice parameter of pure A and B crystals and α and p are BFS parameters. This concept can be extended to layers below the surface. In Table 2 we show the values for these properties for insertion of an A adatom on a $B(110)$ substrate, concluding that incorporation of the A into the surface is favored when the effective coordination for that atom approaches the bulk elemental coordination (12 for fcc elements). Of all the systems that form surface alloys, those with effective coordination for the second layer smaller than bulk coordination appear to form two-layers alloys: Ni/Cu (which is found to form a thin CuNi film on a Cu substrate)

and Au/Al (which forms a Al-Au-Al sandwich). Another interesting fact is that the ratio between n_{eff} and m_A shows a surprising degree of correlation with the type of intermixing that takes place: low values of this quantity (below 0.5) correspond to no alloy formation, values close to 0.5 (Cu-Ni, Al-Au) show a weak tendency for mixing and high values correlate with the formation of predominantly ordered alloys. To provide a more accurate description, the effective coordination concept should be extended to include chemical effects which would help explain the patterns formed at higher coverages. Necessarily, these concepts are valid to the extent that the BFS results properly reproduce what is seen experimentally. This analysis will be the subject of a forthcoming publication. In this paper we have shown that semiempirical methods can be, once tested against experimental data, a very useful tool for the atomistic description of surface alloys formation. In excellent agreement with experiment, these BFS calculations provide a useful initial step for the study of the energetics of these systems at the same time that they allow for a straightforward interpretation of the driving mechanisms.

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System	Experiment	System	BFS results
Al/Ni(100)	Epitaxial Al films at low T [Lu] Epitaxial films of Ni_3Al at high temperature [8]	Al/Ni(110)	Two layer $Ni_3Al(110)$ patches at low coverage. Epitaxial Al film for coverages greater than 0.5 ML.
Ni/Al(100)	No alloy formation	Ni/Al(110)	No surface alloy formation
Cu/Al(100)	Layer-by-layer growth at low T. Some intermixing at high T [9]	Cu/Al(110)	No alloy formation
Al/Cu	No experiment available	Al/Cu(110)	Single-layer Cu-Al alloy corresponding to a $Cu_3Al(110)$ surface.
Au/Cu(111)	Epitactic Cu_3Au growth through several layers [10,11].Reversible phase transformation: alloying for low coverages, dealloying for coverages greater than 0.5 ML. [11]	Au/Cu(110)	Phase transormation: formation of $Cu_3Au(110)$ surface for coverage less than 0.5 ML. Formation of Au monolayer above 50 % coverage
Au/Cu(110)	$Cu_3Au(110)$ surface alloy [11]		
Au/Ni(110)	Surface alloy (STM [2]) for low coverages, dealloying for coverages greater than 0.4 ML	Au/Ni(110)	Complete agreement with exp. (see Ref. 4)
Cu/Ni(100)	Epitaxial Cu film [14]	Cu/Ni(110)	Epitaxial Cu film
Ni/Cu(100)	Partial surface mixing of Cu and Ni atoms. Formation of a CuNi film on Cu substrate [15].	Ni/Cu(110)	Formation of a two-layer CuNi disordered alloy film.
Al/Au	No experimental data available	Al/Au(110) Au/Al(110)	No intermixing with substrate Formation of an ordered Al-Au-Al sandwich.

Table 1: Summary of experimental and theoretical results

A	B	a_A	a_B	p_A	α_A	m_A	n_{eff}	Surf. alloy?
Cu	Ni	3.615	3.524	6	2.935	7.26	11.57	No
Ni	Cu	3.524	3.615	6	3.105	6.72	12.50	Yes
Cu	Au	3.615	4.078	6	2.935	5.52	15.22	No
Au	Cu	4.078	3.615	10	4.339	8.68	9.67	Yes
Cu	Al	3.615	4.050	6	2.935	5.61	14.97	No
Al	Cu	4.050	3.615	4	2.105	8.49	9.89	Yes
Ni	Al	3.524	4.050	6	3.015	5.25	15.98	No
Al	Ni	4.050	3.524	4	2.105	8.78	9.56	Yes
Ni	Au	3.524	4.078	6	3.015	5.16	16.28	No
Au	Ni	4.078	3.524	10	4.339	8.90	9.44	Yes
Al	Au	4.050	4.078	4	2.105	6.90	12.17	No
Au	Al	4.078	4.050	10	4.339	7.12	11.80	Yes

Table 2: Surface (m_A) and bulk (n_{eff}) effective coordination for an element A in a $B(110)$ surface lattice site (see text).The last column indicates if there is experimental evidence for intermixing.

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