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Site exchange in ultrathin layers of Ni on Cu(100) studied with element-specific layer-by-layer resolution

T. C. Q. Noakes, P. Bailey, and G. van der Laan*
CLRC Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, United Kingdom

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We use medium-energy ion scattering to determine the composition of each of the topmost three atomic layers of a single crystal of copper coated with an epitaxial submonolayer of nickel as a function of anneal temperature in the range 140–420 K. The technique confers layer and elemental resolution even though the constituents are adjacent in the Periodic Table. At a transition temperature of around 300 K, subsurface copper and surface nickel interchange so that the nickel comes to reside almost exclusively in the subsurface layer, and the top layer of the crystal becomes almost purely copper. Implications of the result for magnetic measurements are briefly sketched.

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Knowledge of the atomic composition of a surface is crucial to understanding its catalytic and magnetic properties. While surface morphology and structure can readily be studied by modern means such as scanning-tunneling microscopy and low-energy electron diffraction, the elemental composition on a layer-by-layer basis is more difficult to determine. Pioneering work[1] using low-energy ion scattering on a Cu/Ni alloy system at 1000 K found surface-segregated Cu and demonstrated the strength of ion scattering techniques in the investigation of bimetallic surfaces. However, that study was unable to analyze the surface composition in the precise layer-by-layer fashion employed in the present work. More recently, interest has focused on the magnetic properties of ultrathin Ni layers on single-crystal Cu (and other materials). The exact composition of the surface and near surface is of prime importance in modeling the magnetism. In this paper we show that application of the medium-energy ion scattering (MEIS) technique to this problem enables an unambiguous separation of the copper and nickel signals at each atomic layer. These results resolve an experimental dispute concerning the layer composition, confirm theoretical thermodynamic predictions, and provide important input for theoretical modeling of magnetism in ultrathin films.

The interest in ultrathin Ni/Cu films, in particular, the Cu(100) system, stems from several sources. Ultrathin ferromagnetic films on nonmagnetic substrates display magnetic properties quite different from those of the bulk and are very sensitive to the atomic structure of both the thin film and the interface.[2] Below a thickness of ~7 monolayers (ML) the magnetization of Ni/Cu(001) is spontaneously oriented in the film plane, switching to perpendicular orientation in thicker films.[3–5] The critical number of layers for this spin-reorientation transition depends strongly on the morphology of the films.[6] Trends in the number of $3d$ electrons and total magnetic moment per atom for ultrathin films of Ni on Cu(100), measured by x-ray-absorption spectroscopy and x-ray magnetic circular dichroism, respectively, disagree with results from *ab initio* band-structure calculations.[7] Other recent electronic band-structure calculations have suggested that Ni on Cu(100) is thermodynamically unstable and, since the surface energy of pure Cu is lower than that of Ni, the Ni prefers to move away from the surface leaving a top layer that is composed predominantly of Cu.[8,9] However, there are conflicting reports in the literature about the precise nature of the layer-by-layer composition. A structural determination using low-energy electron diffraction (LEED) suggested that an enriched Cu surface layer could be seen[10] but more recent work concluded that the similar scattering cross sections of Ni and Cu rendered the technique insensitive and unable to differentiate between them.[11] The present experimental results are able to confirm the theoretical conclusions about the thermodynamics, decide over the conflicting results of previous experiments, might clarify the discrepancies in measured magnetic properties, and provide an improved basis for future band-structure calculations.

We have used MEIS (Ref. 12) to resolve the layer-by-layer composition by directing a beam of 100-keV He^+ into the Cu crystal in three specific low-index crystallographic directions chosen to illuminate just the topmost atomic layer, the top two layers, and the top three layers. The geometries used are shown schematically in Fig. 1. The careful choice of geometries allows individual layer compositions to be determined even though the energy resolving power of the instrument (0.6%) only gives rise to a depth resolution of approximately 4 ML for the conditions chosen. Shadowing minimizes the beam ‘‘seeing’’ further subsurface layers, and the use of double alignment in carefully selected outgoing directions further reduces the undesired subsurface signal. The low thermal vibration at the measurement temperature of 140 K also reduces the subsurface signal. Measurements were carried out in ultrahigh vacuum ($\sim 1\times 10^{-10}$ mbar) on a Cu(100) crystal which had been prepared by many cycles of ion bombardment and annealing to produce a clean well-ordered surface as judged by Auger electron spectroscopy (AES), LEED, and MEIS. For each anneal temperature, Ni was deposited from a resistively heated Ni filament at a rate of about 0.002 MLs to a final coverage of 0.66 ML. Immediately following deposition, MEIS and LEED showed that the surface was still well ordered, MEIS and AES showed that the surface was clean, and MEIS was used to measure the amount of Ni deposited and analyze its depth profile. The films were then annealed for 2 min at the desired temperature and rapidly recooled before we recorded layer-by-layer data. The thermocouple used for measuring the temperature was

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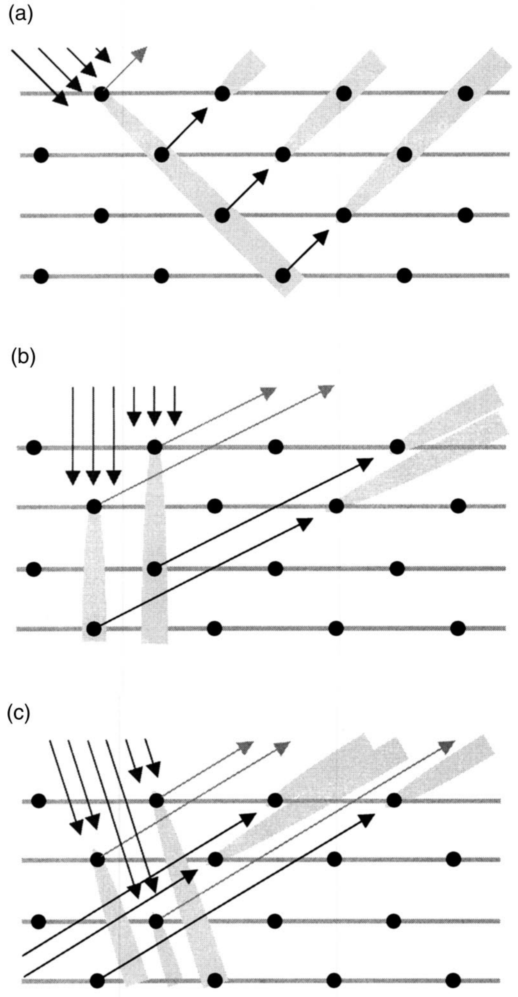

FIG. 1. In our MEIS experiment a beam of 100-keV He$^+$ was directed into the Cu crystal in three specific low-index crystallographic directions chosen to illuminate just the topmost atomic layer, the top two layers, and the top three layers. Shadowing and blocking are shown here schematically in a [001] azimuth for (a) the one-layer illumination geometry ([$\bar{1}\bar{1}0$] in, [110] out: scattering angle (θ) = 90°); (b) two-layer geometry ([$\bar{1}00$] in [120] out: $\theta = 116.6°$); and (c) three-layer geometry ([$\bar{3}\bar{1}0$] in, [350] out: $\theta = 102.5°$).

calibrated subsequent to the experiments to allow the anneal temperatures to be determined with better than 1% accuracy. Energy spectra of the type shown in Fig. 2 are reduced from the raw two-dimensional (scattered ion energy and angle[13]) data, whereupon a peak fitting technique separates the curve into distinct Ni and Cu components. Since the scattering cross sections are well known in this energy range, the peak areas can be related directly to areal densities of atoms. The peak areas are determined by a peak fitting routine that fits asymmetric Gaussians corresponding to the major isotopes of both elements at their calculated energies and known abundancies. Although the atomic numbers of these elements differ only by one and they have several isotopes, it is evident that their respective signals can be separated. The details of the subsequent layer-by-layer analysis, the theoretical modeling, and the data reduction techniques employed to deduce layer compositions are described elsewhere.[14] However, it should be noted that the methodology compensates for effects such as surface relaxation and enhanced thermal vibrations at the surface that, although small, could have a minor effect on the layer-by-layer yields. The application of this layer-by-layer analysis has so far, to our best knowledge, only been applied to systems whose constituents are from different rows of the Periodic Table, such that the use of peak fitting to resolve the constituents represents an extension of the technique to a study of elements with comparable mass.

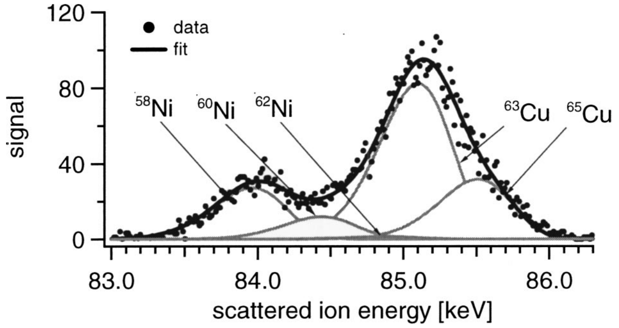

FIG. 2. A typical energy spectrum derived from two-dimensional data showing the clearly resolved signals from the two different elements for the three-layer geometry. The kinematics of the collision process result in different amounts of energy lost by ions scattered from Ni and Cu and gives two peaks in the scattering yield. The components of the fit are labeled.

A summary of the layer-by-layer composition as a function of annealing temperature is given in Fig. 3. At the deposition temperature of 140 K it can be seen that the majority of the deposited Ni resides in the topmost plane of atoms, with a small amount in the second layer and no measurable quantity below this. However, at temperatures above 350 K the composition is significantly altered with the surface layer virtually all Cu and the Ni residing mainly in the second layer but present also in the third layer. The transition between these two states can clearly be seen to occur at an annealing temperature of around 300 K. This transition occurs at a temperature well below that expected for diffusion of Ni in Cu (~670 K) or Cu in Cu (~630 K).[15] These tem-

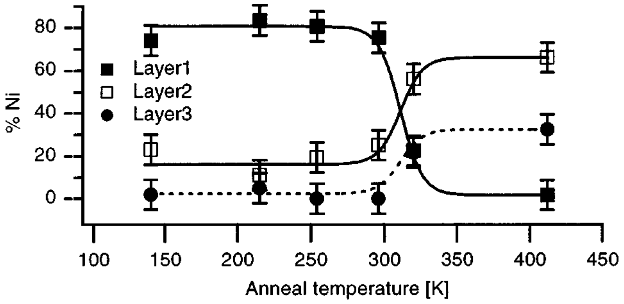

FIG. 3. The layer-by-layer composition as a function of annealing temperature. The amount of Ni at each temperature is quoted as a percentage of the initial deposition. The curves are included to guide the eye and are Fermi functions with their position and width fitted to just the one- and two-layer data.

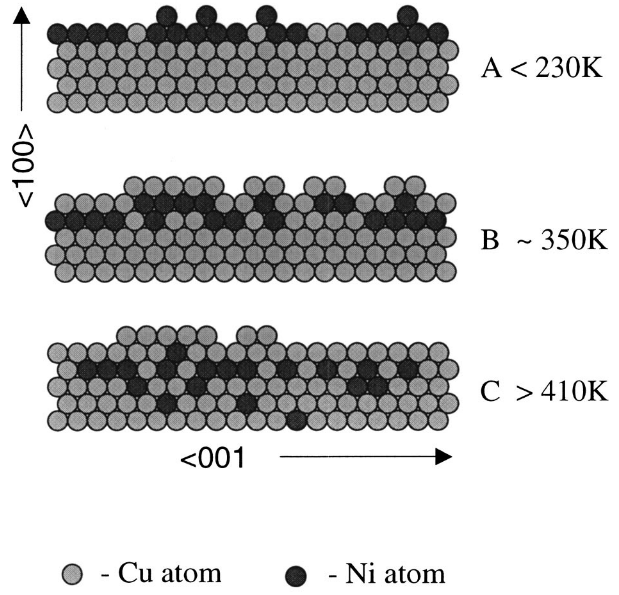

FIG. 4. A graphical representation of the near-surface composition of ~1-ML Ni on Cu(001). Small amounts of Ni are expected in layers beyond the third without full experimental corroboration; a small reduction in overall Ni content is seen for the highest anneal temperature, indicating that some slight degree of further inward movement of Ni atoms may occur.

peratures have been calculated (using bulk activation energies) as those at which a single layer would diffuse to a Gaussian profile of width two atomic planes in the experimental annealing time. In addition, since the top layer becomes Ni deficient as the second layer becomes Ni rich, the composition profiles are inconsistent with a simple diffusion mechanism driven by a concentration gradient. In fact, the nature of the composition change is similar to the so-called surfactant effect,[16] where one elemental species "floats" on top of a growing layer of another species. There are also some similarities to Cu surface segregation observed in a Cu/Ni alloy,[1] although this effect is seen at the much higher temperature of 1000 K at which one expects diffusion to occur. If we treat the loss of Ni from the top layer as a single, thermally activated process, we can use an Arrhenius approach to calculate an activation energy of 0.92 ± 0.02 eV (assuming a thermal vibration frequency of 6×10^{12} Hz). A graphical representation of the near-surface composition of the crystal is presented in Fig. 4. This representation has been created using the layer-by-layer occupations derived experimentally and provides a simple visual picture of the segregation behavior.

The value of 18% for the second-layer Ni content for the preanneal surface shown in Fig. 3 indicates that the Ni layer is not monatomically flat but has some limited three-dimensional character. In this we include the possibility of Ni islands and Ni adsorption over substrate step edges, such that in each case a Ni atom can be shadowed by another Ni atom in the plane above. MEIS effectively references depths to the outermost plane of atoms. The apparent subsurface Ni cannot be due to the exchange effect at ~300 K since it is seen at temperatures at least 100-K below the transition temperature. Our Ni coverage was chosen to be less than a complete monolayer in order to keep the possibility of Ni island formation to low level and yet maintain sufficient Ni to give a resolvable signal. The actual coverage of 0.66 ML is thus a compromise between the conflicting experimental requirements, and some islanding might be expected. We believe we can discount the deposition process as perturbing the system since the average thermal energy of the Ni atoms leaving the Ni filament (at ~1700 K) is only 0.15 eV, well below that required for movement into the second layer (0.92 eV). It is clear from Fig. 3 that any such morphology is generally no more than two layers in height since the preanneal third-layer Ni content is very low. Referring again to Fig. 3, it can be seen that the third-layer yield increases at much the same temperature as the increase in the two-layer yield and that the level of third-layer occupation after annealing is very similar to the second-layer occupation before annealing. This may provide some limited evidence as to the mechanism by which the surface layer exchange process occurs.

Two potential mechanisms by which the interchange of site occupation occurs can be put forward. First, the effect could simply be due to a direct exchange process between first- and second-layer atoms. In this case the third-layer Ni content should not increase at the same rate since the activation energy for second- to third-layer exchange would be expected to be higher than that for first- to second-layer exchange (if the activation energy for second to third and subsequent exchange processes were the same as for the first to second, then a bulklike diffusion mechanism would ensue). A second potential mechanism involves Cu adatoms from uncovered regions of the surface diffusing over the Ni covered regions. While Cu adatoms are clearly mobile at the transition temperature (having a 0.36-eV activation energy[17]) it is the crossing of the Ni island step that is the important parameter (although this could be a multiple stage process) and to the authors' knowledge no information about the energy barrier for this process is available. For this mechanism the second-layer Ni content seen at low temperature should directly translate into a third-layer signal and hence limited evidence in favor of this mechanism is indicated.

It is also interesting to note that the compositional changes we observe occur without any change in the crystal quality of the surface. Since we measure directly the number of atoms visible to the ion beam, we know that the degree of surface order, as measured by MEIS, does not change as a result of either the Ni deposition or the annealing.

Most importantly, the "surfactant" Cu layer will radically change the magnetic moment of the nickel film. The additional interface with Cu results in a reduction of the magnetic moments through hybridization effects. This leads to a broadening of the Ni bands, an increased overlap between the spin-up and down states, and a diminished exchange splitting. The calculated magnetic moment of Ni on the Cu(001) surface is $\sim 0.30\mu_B$, while as a subsurface layer it is calculated to become nonmagnetic.[8] In CuNi alloys the onset of ferromagnetism is about 42-at. % Ni.[18] While surface alloying is a common observation in systems of this type over the formation of a compact layer, our measurements confirm that in this case theoretical predictions of the formation of a buried Ni layer below a surfactant Cu overlayer is energetically more favorable.[9] Our observation also has important consequences for thicker Ni films. Due to the Cu overlayer the surface-induced enhancement of the Ni moments disappears; at both Ni-Cu interfaces the *d-d* hybridization leads to reduced magnetic moments and to a decrease in the Curie temperature.[19] O'Brien, Droubay, and Tonner[6] found that in the presence of a capping Cu overlayer the critical thickness for the spin-reorientation transition was reduced, reflecting the fact that the Cu-Ni surface anisotropy is weaker than that of Ni. Furthermore, because the observed transition temperature of 300 K for the movement of surface Ni is so close to the temperature at which experiments tend to be carried out, slight differences in the precise temperature or duration of an experiment or series of experiments could produce large variations in the nature of the observed magnetism. It is interesting to note that although band-structure theory predicts that a Ni monolayer is thermodynamically unstable on the (100), (110), and (111) surfaces of Cu,[8,9] the calculation of the transition temperature still remains a challenge.

Summarizing, we have shown that it is possible by using the channeling/blocking configuration in medium-energy ion scattering to resolve the Ni and Cu distributions of each layer near the surface of a Ni/Cu thin-film system. At a transition temperature of approximately 300 K surface Ni and subsurface Cu interchange such that Cu covers the surface and the Ni resides almost exclusively in the subsurface layer. This solves the long-standing problem of the precise composition of these layers and can help to explain their magnetic and catalytic properties.

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*Author to whom correspondence should be addressed. Email address: G. Van Der Laan@dl.ac.uk

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