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Alloy formation in the Au{1 1 1}/Ni system – An investigation with scanning tunnelling microscopy and medium energy ion scattering

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ABSTRACT

Using the techniques of scanning tunnelling microscopy (STM) and medium energy ion scattering (MEIS), we examine the growth and annealing behaviour of ultrathin Ni films on Au{1 1 1} at 300 K. As has been shown previously, submonolayer growth of Ni on Au{1 1 1} is strongly influenced by the presence of the herringbone reconstruction with two-dimensional clusters nucleating at herringbone elbows. Second layer growth commences prior to the completion of the monolayer. After multiple layers have been deposited, the surface morphology retains a similar cluster-like appearance. Annealing produces surfaces exhibiting long range Moiré structures and, at higher temperature, triangular misfit dislocations. We use MEIS to examine the composition and structure of these surface alloy phases and conclude that in each case, they consist of an essentially pure Au surface layer on a bimetallic second layer.

1. Introduction

The creation of bimetallic surfaces by hetero-epitaxial metal growth offers the potential to grow artificially structured materials with novel physical and chemical properties [1]. In heterogeneous catalysis, bimetallic surfaces often display higher stability, activity and/or selectivity than their monometallic analogues [2–4]. Au/Ni and Au/Pd catalysts are examples of bimetallic systems where the enhancement of catalytic behaviour was predicted on the basis of ultrahigh vacuum (UHV) model studies. In the former case, a high surface area Au/Ni catalyst for steam reforming [5] was designed in the light of detailed surface science measurements on single crystal surfaces [6–8]. In the latter case, Au/Pd colloidal catalysts [9] were shown to display enhanced selectivity for acetylene coupling reactions as predicted by UHV based studies on single crystal surfaces [10].

The bulk Au/Ni phase diagram exhibits a large miscibility gap suggesting that no alloy should be formed at low temperature [6,11]. However, in both the Ni{1 1 1}/Au and Ni{110}/Au systems, STM [6,8], LEED, low energy ion scattering [11] and theoretical calculations [5–7] have confirmed that a surface alloy restricted to the outermost layer is energetically favourable. Both Au and Ni have fcc bulk crystal structures but due to a 15.7% lattice mismatch, (Au: 4.079 Å; Ni: 3.524 Å) it is energetically unfavourable for Au to form a pseudomorphic monolayer on Ni{1 1 1} and there is likely to be considerable strain produced at the interface. Umezawa et al. [11] reported that the growth of a (9×9) Au overlayer on Ni{1 1 1} occurs in two discrete modes. This finding was supported by Jones et al. [12] who concluded that the density of Au is substantially higher in the ultrathin film than that of bulk Au. Katona et al. [13] examined the deposition of Ni (~13 ML) on Au{1 1 1} and reported that upon thermal treatment at between 643 and 733 K, Au atoms preferentially segregated on top of the Ni film, followed by the dissolution of Ni atoms into the Au single crystal with further thermal treatment.

In this paper, we examine the growth of thin Ni films on Au{1 1 1} using scanning tunnelling microscopy (STM) and medium energy ion scattering (MEIS). We analyse in detail the annealing temperature range between 300 and 660 K. Using STM, we identify the formation of long range Moiré and dislocation structures which are explored in terms of their depth dependent composition and structure using MEIS.

2. Experimental

Two ultrahigh vacuum (UHV) systems were used in this study. The first system consists of an Omicron variable temperature-STM chamber (base pressure 1×10^{-10} mbar) which has facilities for sample cleaning and characterisation via STM and LEED/Auger.

The MEIS studies were performed at the UK National MEIS facility at STFC Daresbury Laboratory [14]. This facility comprises an ion source and accelerator producing a 100 keV beam of He^+ ions. A beamline transports the ions with a well-defined energy (<0.1%)

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and low angular divergence (<0.1°) to a multi-chamber UHV end station. The end station consists of a scattering chamber, a sample preparation and characterisation chamber (including facilities for metal vapour deposition, LEED, Auger and argon ion bombardment), a sample transfer system and a fast entry load lock.

The scattering chamber contains a precision six-axis goniometer to allow accurate alignment with the beam and a toroidal electrostatic energy analyser with position sensitive detector to measure the scattered ion intensities as functions of scattering angle and ion energy. The detector system produces two-dimensional intensity maps of the ion intensity over a 1.6% range of pass energy and a scattering angle range of 27° with a resolution of 0.3% and 0.3°, respectively. Full two-dimensional data sets are accumulated by taking a series of 'tiles' which cover the required angle/energy range and joining them together electronically to produce a single scattered ion intensity map. Whilst two-dimensional data sets provide a complete picture of the scattering behaviour it is normal to process the data by integrating over a range of angles or energies to produce one-dimensional plots. Plots of ion intensity versus scattering angle give structural information that can be used to calculate parameters such as surface layer relaxation and to verify the alignment of the sample with respect to the beam. Energy spectra can be used to obtain quantitative compositional information. A detailed discussion of the MEIS technique can be found elsewhere [15].

In all experiments, the Au{1 1 1} sample was cleaned by cycles of sputtering (Ar^+, 0.9 kV, ~6 μA) and annealing to 873 K until the LEED pattern characteristic of the Au{1 1 1}-($\sqrt{3} \times 22$) herringbone reconstruction was obtained and no impurities were observed by AES. Ni deposition was achieved by resistively heating a W filament around which was wrapped Ni wire. The growth of the Ni (848 eV) Auger signal and the attenuation of the Au Auger feature at 69 eV were used to estimate the film thickness. The Au{1 1 1}/Ni surfaces were annealed to a pre-determined temperature (for 5 min), cooled to room temperature and then transferred into the scattering chamber and data collected in the [−1−12] azimuth of the Au{1 1 1} sample.

The MEIS data (dose 2×10^{15} ions/cm^2) were taken from a sample with ~8 ML of Ni grown on Au{1 1 1} as a function of annealing temperature. In this case 1 ML refers to 1.39×10^{15} atoms/cm^2 (i.e. the atomic density of the unreconstructed Au{1 1 1} surface). At the ion energy employed in MEIS, a randomly aligned ion beam is able to penetrate many layers into the bulk of the material. However, aligning the ion beam along the crystallographic directions of the Au{1 1 1} sample as shown in Fig. 1, a three layer incident geometry is achieved and, by utilising the phenomenon of blocking, 1-, 2- and 3-layer specific outgoing directions can be achieved. In reality, it is not possible to achieve perfect layer specificity even with a single crystal surface of a pure metal since surface layer relaxation and thermal vibrations of surface and sub-surface atoms act to enhance the visibility of sub-surface layers [16].

3. Results

3.1. Scanning tunnelling microscopy (STM)

It is well-established that the deposition of metals on the Au{1 1 1}-($\sqrt{3}$x22) surface [17] leads to nucleation of 2D clusters at the elbows of the herringbone reconstruction for a wide variety of metals including Ni [18], Fe [19], Co [20], Pd [21], and Rh [22].

Fig. 2a–c displays STM topographic images of the Au{1 1 1}-($\sqrt{3} \times 22$) surface as a function of Ni coverage at 300 K. Initial growth occurs, as previously reported [18], via nucleation of 2D clusters at the elbows of the herringbone reconstruction. With increasing Ni coverage (Fig. 2b), the Ni islands coalesce to form 2D Ni ribbons. Fig. 2c shows that increasing the coverage of Ni above 1 ML results in growth of Ni in the second layer prior to completion of the first layer. Areas of exposed Au surface are clearly visible. After 4 ML Ni deposition, the surface morphology retains a clustered appearance as previously reported by Katona et al. for a much thicker (13 ML) Ni film on Au{1 1 1} [13], indicating that the surface morphology is influenced by the initial submonolayer growth.

Annealing the Au{1 1 1}-4 ML Ni surface produces a range of differing surface morphologies and structures depending on the annealing treatment. Annealing of the bimetallic Au/Ni surface from 300 K to 500 K results in progressive flattening of the 3D Ni clusters (Fig. 3a–c). Annealing to 550 K reveals a well-resolved Moiré structure as presented in Fig. 3d. The Moiré structure has a hexagonal appearance and exhibits a relatively long range periodicity (~7.5 nm) along the close packed directions of the Au{1 1 1} surface. Moiré structures have previously been observed for Ni growth on Au{1 1 1} via electrochemical deposition [23] and for Au growth on Ni{1 1 1} [6], though these have much shorter (~2 nm) periodicities. Further annealing of the bimetallic surface to 600 K reveals (approximately equilateral) triangular misfit dislocations as presented in Fig. 3e. The sides of these triangular features are typically ~9 nm in length and are aligned along ⟨1 1 2⟩ type surface directions. Similar morphological features have been observed following thermal treatment of Au films on Ni{1 1 1} [6] albeit again with a much shorter periodicity (~2 nm). Further annealing to 650 K (Fig. 3f) results in the reappearance of the Au{1 1 1} herringbone reconstruction.

3.2. Medium energy ion scattering (MEIS)

Fig. 4a–c displays plots of ion intensity versus energy as functions of annealing temperature measured at scattering angles corresponding to outgoing 1-, 2- and 3-layer geometries of Au{1 1 1}. For ease of comparison, the background due to bulk Au has been removed from each spectrum. Elastic collisions between the impinging helium ions and surface Ni and Au atoms should result in two peaks whose energetic position will depend on the scattering angle employed. However, following the deposition of ~8 ML Ni onto Au{1 1 1} and for relatively low annealing temperatures, we routinely observe three peaks. The lowest energy peak is consistent with ions scattered from Ni atoms in the near-surface region. The peak intensity is relatively weak in comparison to the Au peak since the scattering cross-section is proportional to the square of the atomic number. The peak observed at the highest energy is consistent with ions having been in collision with surface Au atoms. Particularly at lower annealing temperatures, a third peak is observed at an intermediate energy.

From 300 to 410 K, the surface Au peak decreases in intensity. Between 460 K and 510 K this peak grows dramatically in intensity and continues to grow until following annealing to 630 K, it resembles that of clean Au in both intensity and position. The Ni peak similarly decreases in intensity with increasing annealing temperature and disappears following annealing to 630 K.

With progressive annealing of the sample, three shifts of the third peak occur. At 460 K, the peak shifts to lower energy – i.e. away from the Au peak. At 510 K the peak shifts back to a higher energy by ~1 keV. From 510 to 570 K, the peak shifts to a lower energy and broadens. From 570 to 630 K, the peak decreases in intensity and broadens until eventually disappearing at 630 K.

Fig. 5a–c shows the ion intensity versus scattering angle data for the Ni surface, Au "near-surface" (i.e. top few atomic layers) and Au sub-surface regions as a function of annealing temperature. Provided there is sufficient mass separation, MEIS is uniquely capable of resolving blocking features from different elements in the near-surface region, enabling element specific structural informa-