Preparation and characterisation of the (0001) surface of single crystal NiIn

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Abstract

NiIn is one of the few intermetallics to adopt the highly unusual CoSn (B35) structure. In this paper we describe the preparation of the clean, ordered (0001) surface of stoichiometric single crystal NiIn in ultra-high vacuum, using Ar ion bombardment and annealing, with characterisation by X-ray photoelectron spectroscopy (XPS), Auger spectroscopy (AES), and low energy electron diffraction (LEED). Preferential sputtering occurs, but a stoichiometric, ordered surface can be obtained by annealing to 700±25 K. This surface appears to be a simple bulk termination, with the same lateral periodicity and composition, indicating the stability of the non-close packed indium layers in the CoSn structure. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Binary intermetallic compounds with the simple 1:1 stoichiometry are generally expected to adopt structures which provide high space-filling and approximately spherical coordination [1]. The CoSn (B35) structure is a rare example of an intermetallic structure to which this does not apply, and Ni–In is one of the few alloy systems in which it occurs. The CoSn structure of NiIn is shown schematically in Fig. 1. It can be considered as two different types of planar layers stacked in the [0001] direction. The layer at \( z = 0 \) is close-packed, and consists of Ni and In atoms in the ratio 3:1. The layer at \( z = 0.5 \) consists of In atoms only, and is a distinctly non-close-packed honeycomb array, resulting in a void centred at \((0, 0, 1/2)\) in the unit cell. Although this structure, first identified in CoSn in 1935 [2] and in NiIn in 1950 [3], has been known for many years, it was not clear that it was a genuine ground state, since the possibility of hydrogen-stabilisation could not be definitively ruled out by X-ray diffraction. However a recent theoretical study [4] investigated the electronic structure of a number of possible geometric structures for CoSn, and concluded that the void structure of Fig. 1 was indeed the most stable, suggesting that the structure of Fig. 1 is indeed a ground state. The competition between metallic and covalent bonding in this intermetallic is believed to be responsible for the unusual structure [4,5], and therefore experimental investigations into the electronic structure are clearly worthwhile.

Electron spectroscopies such as UV photoemission (UPS) and X-ray photoemission (XPS) are ideally suited for studying electronic structure, but are inherently surface
sensitive. The preparation of clean, stoichiometric surfaces is therefore required, which is far from trivial for many alloy systems due to problems with surface segregation and preferential sputtering. In addition, single crystal surfaces are preferred, since they permit the use of angle-resolved electron spectroscopy. The surface properties of NiIn are not without interest in their own right, since a recent study [6] has shown that NiIn may be a suitable ohmic contact to GaN, a highly promising material for optical applications. In addition, we have shown recently [7] that NiIn is a suitable substrate for the growth of In2O3 thin films, a good model for the indium–tin–oxide substrates used in organic based electronic devices.

Previous studies of NiIn alloy surfaces [8–11] have been limited to XPS and X-ray excited Auger (XAES) investigations of polycrystalline samples. There appear to be no surface studies of any of the other CoSn structured intermetallics − FeSn, PtTl, RhPb and CoSn itself − in the literature. Hsu and Williams [8] studied a number of Ni–In alloys, with surface preparation by ion sputtering and annealing. They were unable to prepare a stoichiometric NiIn surface, with their nominal NiIn sample being very Ni rich. Fuggle and co-workers studied NiIn as part of a work describing trends in the valence bands [9], core levels [10] and Auger lineshapes [11] of a large series of Ni and Pd alloys. Their samples were prepared by mechanical scraping, which was found to produce stoichiometric surface compositions for most of their samples, including NiIn. Therefore only these latter works [9–11] can be regarded as characteristic of NiIn.

In this work we describe the preparation of a clean, ordered NiIn(0001) surface, monitored by low energy electron diffraction (LEED) and (electron excited) Auger electron spectroscopy (AES). The resulting surface is then characterised by valence and core level XPS, and XAES.

2. Experimental

The crystal, diameter 4 mm, was obtained from Matek, oriented and polished to 0.5 degrees. Its CoSn bulk structure was confirmed by the oscillation X-ray diffraction method using a HUBER Weissenberg goniometer and Ni-filtered Cu Kα radiation, with the 2Θ positions of the reflections indexed by the DICVOL91 program [12]. The orientation of the single crystal was determined from two oscillation photographs, with oscillation ranges of 170° and 10°. From the directions of the scattering vectors the orientation was determined to be (0001).

The electron excited AES and LEED studies were performed in an ultra-high vacuum system (base pressure ~10⁻¹⁰ mbar) equipped with a Leybold LH10 hemispherical electron energy analyser and VSI ErLEED optics. XPS and XAES measurements were performed using a PHI 5400 XPS spectrometer, while the AES measurements during ion bombardment used a PHI 610 Auger Microprobe.

These two spectrometers shared a common vacuum system (base pressure 2×10⁻¹⁰ mbar) equipped with a preparation chamber for ion bombardment and annealing. XPS/XAES measurements used monochromated Mg Kα (hν = 1253.6 eV) radiation with an overall resolution of 0.75 eV, or Al Kα (hν = 1486.6 eV) with a resolution of ~1 eV. The sample temperature was monitored using a Chromel–Alumel thermocouple, spot-welded to the sample support wires and in direct contact with the sample.

3. Results and discussion

3.1. Surface preparation

Initial cleaning was performed by cycles of ion bombardment (Ar⁺, beam energy 2 kV, ion density 0.7 A m⁻²) and annealing to 750 K, with surface cleanliness monitored by AES. Fig. 2a shows the AES spectrum obtained after ~10 cleaning cycles. Common contaminants found on transition metal surfaces are C and O from the atmosphere, and Cl and S which segregate from the bulk during annealing. Fig. 2a shows that this initial cleaning procedure was sufficient to produce a surface free of detectable contamination. However, ion bombardment was also found to produce a change in the relative concentrations of Ni and In at the surface, as can be seen in Fig. 3. This shows that ion bombardment results in preferential sputtering of indium, leading to a nickel-rich surface. This phenomenon is well known in multicomponent materials [13], and has previously been noted in Ni–Al alloys [14], where nickel-rich surfaces were also found to occur. Once equilibrium has been reached, and without annealing the sample, the AES spectrum of Fig. 2b results. Note here the relative sizes of the Ni and In peaks compared to Fig. 2a, which is from an annealed surface, and the presence of a

![Fig. 2. Differential AES spectra, primary energy 3 keV, of (a) clean NiIn(0001), (b) after ion bombardment (10 mins, Ar⁺, 2 kV, 0.7 A m⁻²). The dashed lines indicate the expected positions of possible contaminants.](image-url)
small but finite Ar peak at 220 eV, indicating the presence of Ar embedded in the surface. Annealing the sample removes the Ar, and also serves to restore both the surface crystallinity and stoichiometry. Fig. 4 shows the indium concentration as a function of annealing temperature, determined by AES, superimposed on the phase diagram for Ni–In [15]. To produce better surface crystallinity, metal samples are often annealed close to the melting point. However, as can be seen in Fig. 4, this produces two problems in the case of NiIn(0001). Firstly, there is only a narrow annealing temperature range, 50 K centred around 700 K, in which a stoichiometric surface composition results. At higher temperatures Ni segregation occurs, which may well have been the cause of the Ni-rich surfaces obtained by Hsu and Williams. Secondly NiIn has a high temperature β phase, with the CsCl structure [15]. The crystal will become strained as the transition temperature approaches, which will tend to favour the formation of small crystallites rather than long range surface order. The surface crystallinity was monitored using LEED, with the sharpest pattern obtained for an annealing temperature of 700 K, i.e. the temperature at which the stoichiometric surface results. Annealing temperatures below 500 K did not produce a visible LEED pattern, while temperatures above 800 K produced an increasingly diffuse pattern. Annealing for several hours at 700 K did not produce better surface order than a relatively short (10 min) anneal. Further surface segregation of In was not found to occur, in agreement with the XPS results from scraped NiIn [9–11].

### 3.2. Surface characterisation

The LEED pattern from the clean, stoichiometric surface is shown in Fig. 5. The fact that a clear diffraction pattern is obtained indicates that long range order is present. However, the spots are not particularly sharp, implying that the surface order is not particularly good. The pattern has the hexagonal symmetry of the ideal (1×1) surface, and its size is consistent with the bulk lattice parameter. This implies that the surface structure is a simple bulk termination, with no reconstruction occurring, highlighting the stability of the non-close-packed indium honeycomb layers, which might perhaps have been expected to collapse into a more close packed configuration. Note that the surface lattice parameter in this case is 5.2 Å, compared to, for example, 2.5 Å for the close packed Ni(111) surface, hence the relatively small pattern, obtained using 50 eV electrons, in Fig. 5.

XPS spectra of the Ni 2p levels were measured, and found to be in excellent agreement with those of Hill-ebrecht et al. [10] and are therefore not reproduced here.
particular the 2p satellite, due to unoccupied d-states, was observed with energy and intensity consistent with the data of Hillebrecht et al. [10]. The indium 3d XPS spectrum is shown in Fig. 6. The spectrum was taken using Al Kα radiation, although this gives a lower resolution than Mg Kα, since the In 3d photoemission and MNN Auger features overlap if Mg Kα radiation is used. The curve fits were performed, after the subtraction of the Kα_{3,4} satellite features, assuming an asymmetric Voigt function as the peak lineshape, with an integral form for the inelastic...
background. The 3d$_{5/2}$ binding energy was determined to be 443.4 eV, compared to 443.9 for pure indium [16]. The Ni 2p levels also show a small shift to lower binding energy in going from the pure element to NiIn [10]. The XPS data do not in themselves imply the direction of charge transfer upon alloying, however the small shifts observed suggest that the magnitude of any charge transfer must be sufficiently small that it is masked by relaxation, i.e. final state, effects in the core level photoemission. The 3d peaks are both rather asymmetric. Asymmetry in XPS core level lineshapes is generally due to the excitation of electron–hole pairs around the Fermi level, and is thus expected to be essentially proportional to the density of states at the Fermi level, DOS($E_F$). Given that DOS($E_F$) for NiIn should be rather low [5,9] the magnitude of the asymmetry seen in Fig. 6 is rather surprising. It is possible that there could be an unresolved contamination related peak at around 446.7 eV, since this is the 3d$_{5/2}$ binding energy for In$_2$O$_3$ [17]. However the oxygen contamination level was such that the O 1s line was not seen in XPS, and thus must be less than 1%, i.e. insufficient to produce an effect of the magnitude seen in Fig. 6. There remains the possibility that there are two unresolved intrinsic In features, since there are two distinct In sites in the crystal structure of Fig. 1. However, good fits were obtained using only one spin–orbit split doublet, and it seems unreasonable to add another doublet when one cannot be resolved, even as a shoulder, in the data of Fig. 6. The peak widths were both found to be 1.0 eV, i.e. resolution limited, which suggests that higher resolution studies might be able to resolve two peaks, should there prove to be two peaks. The In 4d levels can be observed using Mg Kα radiation without interference from overlapping Auger features, giving higher resolution than the 3d data of Fig. 6. The indium 4d spectrum, taken using Mg Kα radiation, is shown in Fig. 7. As before it has been fit with asymmetric Voigt functions and an integral background, with a single spin orbit split doublet, constrained, since the components are not fully resolved, to have a 3:2 ratio for the areas of the 5/2 and 3/2 peaks. Again the peaks are rather asymmetric, but a good fit is obtained with the single doublet, with binding energies of 16.5 and 17.4 eV. The individual components were found to have widths of 0.8 eV, again apparently resolution limited.

The X-ray excited indium M$_{4.5}$N$_{4.5}$N$_{4.5}$ Auger spectrum is shown in Fig. 8. According to the theory of Cini [18] and Sawatzky [19] for narrow d-band metals, the Auger spectrum will be quasi-atomic provided that the magnitude of the effective Coulomb interaction between two holes on the same site, $U_{\text{eff}}$, is greater than twice the one-electron bandwidth, $W$. For indium metal, $U_{\text{eff}}$ is 6.8 eV [20], while the width of the spin orbit split contributions to the 4d lineshape in Fig. 7 were found to be ~0.8 eV, clearly satisfying the conditions for a quasi-atomic Auger spectrum should $U_{\text{eff}}$ be of the same magnitude in NiIn. The atomic Auger multiplet for indium has been calculated by Parry-Jones et al. [20], and is shown in bar form in Fig. 8. It is clear from Fig. 8 that the atomic multiplet contains all the significant features of the spectrum, showing that it is well described by the Cini–Sawatzky theory.

The XPS valence band spectrum is shown in Fig. 9. The valence band of NiIn is of particular interest since the mixture of metallic and covalent bonding should give rise to two features in the Ni d-band – a pseudogap at the Fermi level, and a split in the occupied d states [5,9] – which should in principle be observable in photoemission. These were not observed by Fuggle et al. [9], and Fig. 9 shows that they are also absent from our data, which indicates that this was not due to the polycrystalline nature of their scraped surface, but rather to the relatively poor resolution available in XPS. Broadening the calculated density of states [5] to simulate the experimental resolution, as was done by Hsu and Williams [8], gives a valence band lineshape that obscures the presence of both

![Fig. 7. In 4d XPS spectrum, with fitted curves and inelastic background.](image-url)
the pseudogap and the double peak, and in fact closely resembles the data of Fig. 9. The density of states is rather low at the Fermi level, raising the possibility of a fully occupied d-band, but this can be ruled out by the presence of the Ni 2p satellite [10] and the d'satellite, at a binding energy of ~7eV, in the data of Fig. 9, both of which indicate unoccupied Ni 3d states [9,10].

4. Conclusions

Clean, ordered, stoichiometric NiIn(0001) can be prepared in UHV, although careful monitoring of the sample temperature is required. The resulting surface appears to have a (1×1) structure, providing further support to the idea that the void structure of Fig. 1 is a stable ground state. In particular the open honeycomb structure of the indium layers in Fig. 1 is also stable at the surface, without the presence of a covering close packed layer. Note, however, that since hydrogen is essentially invisible to both AES and XPS, hydrogen stabilisation cannot be ruled out, especially given that hydrogen is the largest component of the residual gas in a typical UHV chamber. Surface segregation does not occur at room temperature, which together with the fact that no reconstruction occurs, suggests that the surface preserves the essential characteristics of the bulk electronic structure. However, higher resolution valence band studies are required to determine if the predicted features in the density of states are in fact present.

The XPS data for the indium 3d and 4d levels appear to be resolution limited, and higher resolution measurements are needed to determine whether there are two components due to the two distinct indium sites in the unit cell. The 4d
levels may well be more suitable as they are more easily accessible by high resolution synchrotron radiation excited photoemission.

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