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Surface alloying in the Sn/Ni(111) system studied by synchrotron radiation photoelectron valence band spectroscopy and *ab initio* density of states calculations

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Abstract

Photoelectron spectroscopy using synchrotron radiation and *ab-initio* electronic structure calculations were used in order to describe the fine structure of the valence band in the Sn/Ni(111) system. The characteristic contributions of each metal in the valence band photoemission spectra obtained with a photon energy of 80 eV and their changes upon the formation of the ($\sqrt{3}\times\sqrt{3}$)R30° Sn/Ni(111) surface alloy were also born out in the calculated density-of-states curves in fair agreement with the experiments. The Sn-Ni interaction leads to a considerable broadening of the valence band width at the bimetallic surfaces.

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1. Introduction

The controlled growth of metals on metals has drawn attention over the years, partly motivated by the broad range of technological applications of bimetallic systems in materials science, catalysis and microelectronics [1, 2]. Besides the commonly observed ordered overlayers, bimetallic systems may form true surface substitutional alloys, which often lack any direct bulk analogue [3]. Many surface studies have been devoted to Sn-based bimetallic systems and, recently, Sn addition to some transition metals was found to improve their performance in heterogeneous catalysis [4]. The Sn/Ni(111) system has been studied extensively in the past [5-7] as well as recently [8] using a number of surface sensitive techniques, such as Low-Energy Electron Diffraction (LEED), Synchrotron Radiation Photoelectron Spectroscopy (SRPES), ultra-violet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy and temperature-programmed desorption, and the conditions for the formation of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface alloy have been well documented.

Theoretical *ab-initio* studies addressing Sn/Ni surface alloys so far focused on geometrical effects. Due to the fact that the covalent radius of Sn is about 20% larger than that of Ni, the Sn atoms protrude from the first lattice plane. For the (2×2) -Sn(Ni(001) surface alloy, the calculated rippling is found to be 0.36 Å [9], somewhat smaller than the experimental value of 0.44 ± 0.05 Å [7], and for the $(\sqrt{3}\times\sqrt{3})R30^\circ$ Sn/Ni(111) surface alloy, the theoretical result is 0.45 Å [10], compared to 0.44 Å experimentally [6]. As far as the electronic structure is concerned, according to density functional theory calculations the presence of Sn atoms in the (2×2) -Sn/Ni(001) surface alloy structure strongly reduces the density of states at the Fermi energy and almost completely quenches the magnetic moment of the Ni atoms in the topmost surface layer [9].

In this work, a comparison is presented between valence band SRPES data and density-of-states (DOS) curves derived from first principles calculations for corresponding Sn/Ni systems. The comparison is made in the following three cases: clean Ni(111), ~ 1.2 ML of as-deposited Sn overlayer on Ni(111) and the perfect $(\sqrt{3}\times\sqrt{3})R30^\circ$ Sn/Ni(111) surface alloy.

2. Experimental system and calculations

An ultra-high-vacuum chamber (base pressure 5×10^{-8} Pa) was used for the experiments. The chamber, at the Material Science Beam line of the Elettra synchrotron radiation facility, was equipped with a hemispherical electron energy analyser (Specs HA-150) for high resolution SRPES, as described elsewhere [11]. The analyser axis and the direction of the synchrotron light beam were on the same horizontal plane at an angle of 60° , whereas the sample surface was located in the vertical plane and could be rotated around a vertical axis passing through the intersection of the analyser axis and the incident light beam. The latter was plane polarized with the electric field vector lying in the horizontal plane. Photoemission measurements were taken with the normal to the sample surface along the analyser axis. The Ni(111) single crystal substrate, $\varnothing 10$ mm x 1 mm thick (Surface Preparation Laboratory), which could be heated up to 1200 K, was subjected to repeated cycles of 1 keV Ar^+ sputtering at 600 K and annealing at 1000 K in order to remove C, O and Si contamination. Tin was deposited on the clean Ni(111) surface near room temperature from an electron beam evaporation source at deposition rate of 0.04 ML/min estimated by X-ray photoelectron spectroscopy, which was calibrated using the well known Sn coverage of 0.33 ML for the perfect $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface alloy. The latter was obtained upon annealing at 1000 K for 20 min deposited tin in excess of 1 ML, whereby tin in excess of 0.33 ML was dissolved in the Ni bulk. The photon energy in the SRPES valence band

study was chosen at 80 eV, which corresponds to the most surface sensitive conditions for the experiment. The spectra have a 0.15 eV resolution at this photon energy and the photoelectrons, which are detected, come from the first few surface layers.

The *ab-initio* electronic structure calculations of Sn/Ni(111) have been done by the Vienna *ab-initio* simulation package [12] using Projector Augmented Wave pseudopotentials [13] and the Perdew-Burke-Ernzerhof (PBE) functional [14]. A cut-off energy for the plane wave expansion of 300 eV and Monk horst-Pack k-point sets of $7 \times 7 \times 1$ are used. All results have been checked for convergence with respect to the number of k-points and the energy cut-off of the plane waves. In all calculations, the Ni substrates are modelled by a slab of 5 layers and all slab structures are separated by at least 9.5 Å of vacuum. The calculations have been performed in a spin-polarized manner. The calculated density of states reported in this paper corresponds to a sum over spin-up and spin-down components for the Ni surfaces in order to facilitate the comparison with the experimental results. The density of states can only be evaluated for valence states, which reach about 10 eV below the Fermi energy. All deeper lying states correspond to core levels in this calculation.

3. Results and discussion

Figure 1 shows SRPE spectra obtained with 80 eV photon energy for the three studied cases. The bottom one is that of a clean Ni(111) single crystal, the middle one is from 1.2 ML Sn/Ni(111) and the upper one was obtained from the perfect $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface alloy. The main contributions from the d-electrons of the Ni crystal are seen in the photoemission spectrum of clean Ni at 0.3 eV, 0.6 eV, 1.3 eV, 2.0 eV and 3.8 eV binding energy, whereas the feature at about 6.2 eV is a plasmon satellite from the metallic nickel. In the photoemission spectrum of 1.2 ML Sn/Ni(111), the expected contribution of tin to the valence band in the region 0.6 to 1.8 eV

[4] overlaps with the fine structure due to the d-electrons of Ni. The presence of deposited Sn strongly reduces the spectral intensity near the Fermi level, however upon alloying the intensity increases again but remains smaller than for the clean Ni(111) surface. New contributions in the photoemission spectrum of the valence band of the perfect $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface alloy are seen at about 0.9 eV and 2.4 eV binding energy and are attributed to a distinct bimetallic interaction upon alloying.

The valence band SRPE spectrum of the clean Ni(111) single crystal with 80 eV photon energy is shown in fig. 2, together with the total density of states (sum of spin up and spin down states) of the first layer of clean Ni as given from the *ab-initio* electronic structure calculations. Both the as-calculated DOS curve and that convoluted with the Fermi function and an energy window of 0.50 eV, to account for instrumental broadening and smoothing factors inherent in the experimental curve, are shown in fig. 2. This convolution is applied in all theoretical DOS curves presented below. In the same figure we also present the corresponding density of states of bulk Ni, in order to compare it with that of the (111) surface. Due to the lower coordination of the surface atoms, the Ni DOS at the surface is slightly narrower than in the bulk and its center is shifted a little bit to higher energies, as expected for late transition metals [15]. As far as the comparison between experiment and theory is concerned, first of all it is important to note that the relative intensities of various features are not expected to coincide in the spectrum and the DOS curve. The experimental intensities for the various electron states are largely determined by the relative photoionization cross-sections, which are both photon energy and state dependent and which were not calculated. Therefore it is not surprising that the large experimental peak near the Fermi level (0.3 eV) is not predominant in the theoretical DOS curve, but more importantly, the relative positions of the various contributions of the d-electrons of Ni predicted

in the theoretical DOS curve are in good agreement with the experiment, although they are uniformly shifted to higher binding energies by 0.1 to 0.2 eV. This small shift lies within the accuracy of the Density Functional Theory calculations, but it might well be caused by an improper description of exchange-correlation effects in the used PBE functional.

The valence band SRPE spectrum of 1.2 ML room-temperature (RT)-deposited Sn/Ni(111) is shown in fig. 3, together with the calculated total density of states for a monolayer of Sn on Ni(111), including also the first monolayer of Ni. In addition, the calculated density of states of bulk Sn is included. Tin, as a sp metal, exhibits a broad sp band, as confirmed in earlier (UPS) studies [4], that extends up to several eV above the Fermi energy. Whereas the states at the Fermi energy are mainly of p character, the states between 8 and 5eV below the Fermi energy are of s character [16]. The contribution of tin below the Fermi energy overlaps with the Ni states, and only the characteristic Ni feature at low binding energy (0.3 eV) is clear, but with decreased intensity compared with clean Ni(111). The increased contribution at about 1.3 eV in the spectrum compared with the DOS curve arises from underlying Ni and is due to the fact that the SRPE spectra probe deeper than the first two layers. The calculated spectrum, on the other hand, consists only of the total density of the first two layers. Furthermore, the calculations do not take into account the difference in the sensitivity with respect to the different layers. Therefore the quantitative comparison between theory and experiment has to be done with caution. Still it is obvious that the DOS at the Sn surface atoms is strongly reduced compared to bulk Sn indicating the strong interaction between Sn and Ni.

After RT deposition of 1.2 ML Sn, the sample was annealed at 1000 K for 20 minutes and the perfect $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface alloy was obtained, which was also confirmed by a very sharp LEED image [8]. The corresponding SRPE spectrum of the alloy is seen in figure 4,

together with the DOS of the first monolayer of the surface alloy $(\sqrt{3}\times\sqrt{3})R30^\circ$. The contribution with low binding energy (0.3 eV) due to the Ni substrate is more pronounced now, because the amount of Sn on Ni is reduced down to 0.33 ML. The new contributions to the alloy's valence band SRPE spectrum at 0.9 eV and 2.4 eV binding energy are not very pronounced in the DOS curve of the alloy, however there is a clear broadening of the DOS curve for the alloy, in comparison with both the clean Ni (fig. 2) and the 1.2 ML Sn/Ni (fig.3), which is consistent with the bimetallic interaction exhibited in the SRPE spectrum. It is noteworthy, that the observed shift of 0.2 to 0.3 eV to higher binding energy for the Sn-related features in the valence band upon alloying, as evidenced by comparing figs. 3 and 4, is in the opposite direction of the respective chemical shift of -0.27 eV for the Sn 4d core level observed by SPRES upon alloying and also theoretically predicted at -0.36 eV [8]. This suggests that the valence band changes associated with the bimetallic interaction upon alloying represent a true electronic states re-hybridization.

4. Conclusions

The salient features in the valence band fine structure of Ni(111) and their changes upon near monolayer Sn deposition at RT and subsequent annealing in order to obtain the characteristic $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface alloy could be reproduced by *ab-initio* DOS calculations in fair agreement with the experiment. At the bimetallic surfaces, the spectra cannot be interpreted as a simple superposition of Ni-related and Sn-related features. The results thus indicate a strong coupling between the Sn and the Ni electronic states which leads to a considerable broadening of the surface band width.

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FIGURE CAPTIONS

Fig. 1: Valence Band SRPE spectra of clean Ni(111), of 1.2 ML Sn/Ni(111) and of the perfect $(\sqrt{3}\times\sqrt{3})R30^\circ$ Sn/Ni(111) surface alloy obtained with 80 eV photon energy.

Fig. 2: Comparative figure between the Valence Band SRPE spectrum of clean Ni(111) with 80 eV photon energy and the total density of states (sum of spin up and spin down components) of the first layer and of bulk Ni.

Fig. 3: Comparative figure between the Valence Band SRPE spectrum of 1.2 ML RT-deposited Sn/Ni(111) with 80 eV photon energy and the total density of states (sum of spin up and spin down components) of the first two layers, one Sn and one Ni layer, as well as of bulk Sn.

Fig. 4: Comparative figure between Valence Band SRPE spectra of the surface alloy $(\sqrt{3}\times\sqrt{3})R30^\circ$ Sn/Ni(111) with 80 eV photon energy and the total density of states (sum of spin up and spin down components) of the first alloy layer.

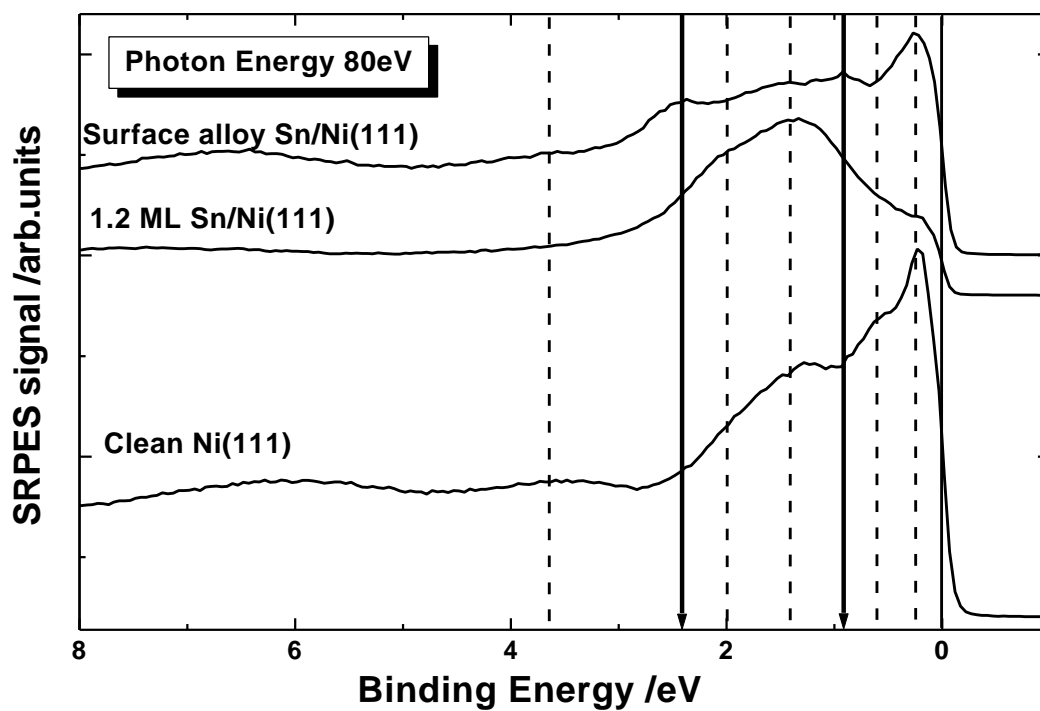


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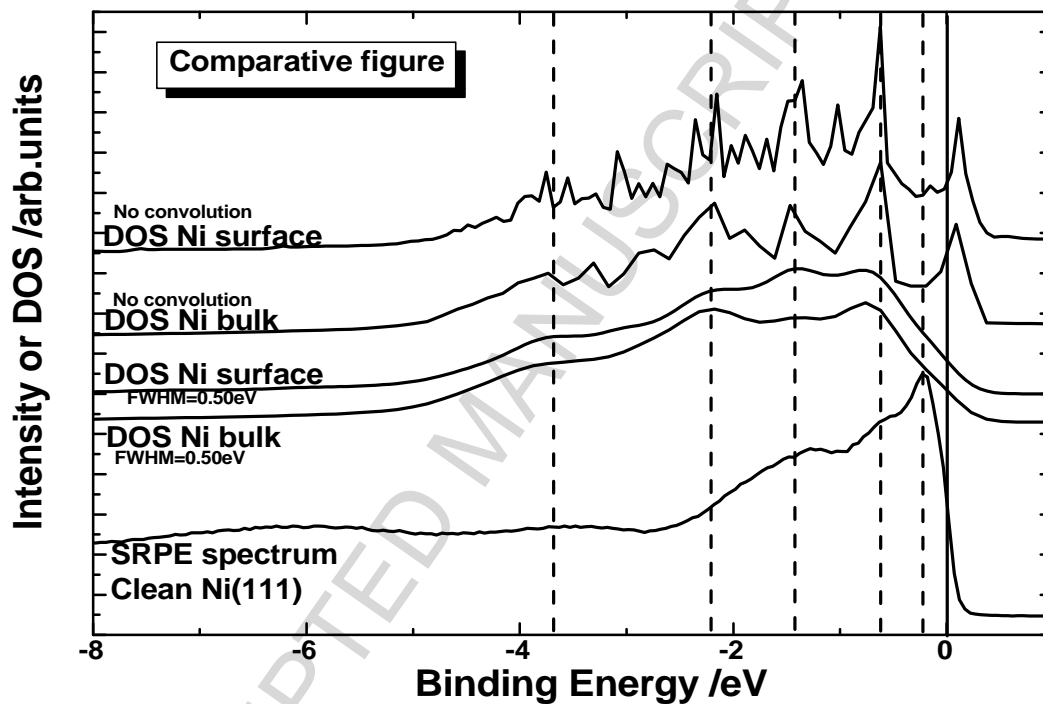


Fig. 2: Comparative figure between the Valence Band SRPE spectrum of clean Ni(111) with 80 eV photon energy and the total density of states (sum of spin up and spin down components) of the first layer and of bulk Ni.

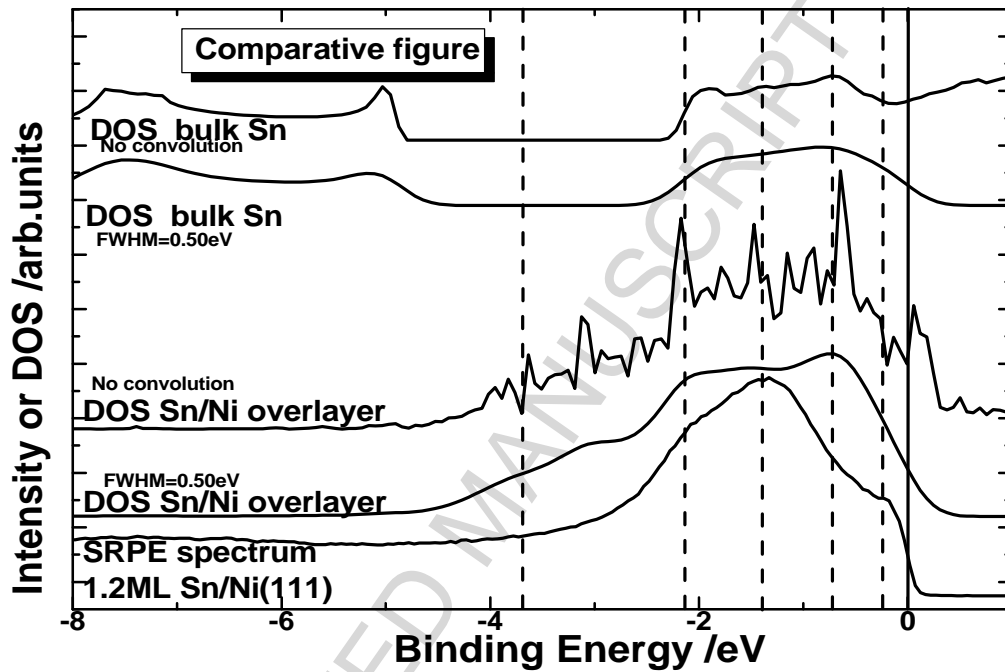


Fig. 3: Comparative figure between the Valence Band SRPE spectrum of 1.2 ML RT-deposited Sn/Ni(111) with 80 eV photon energy and the total density of states (sum of spin up and spin down components) of the first two layers, one Sn and one Ni layer, as well as of bulk Sn.

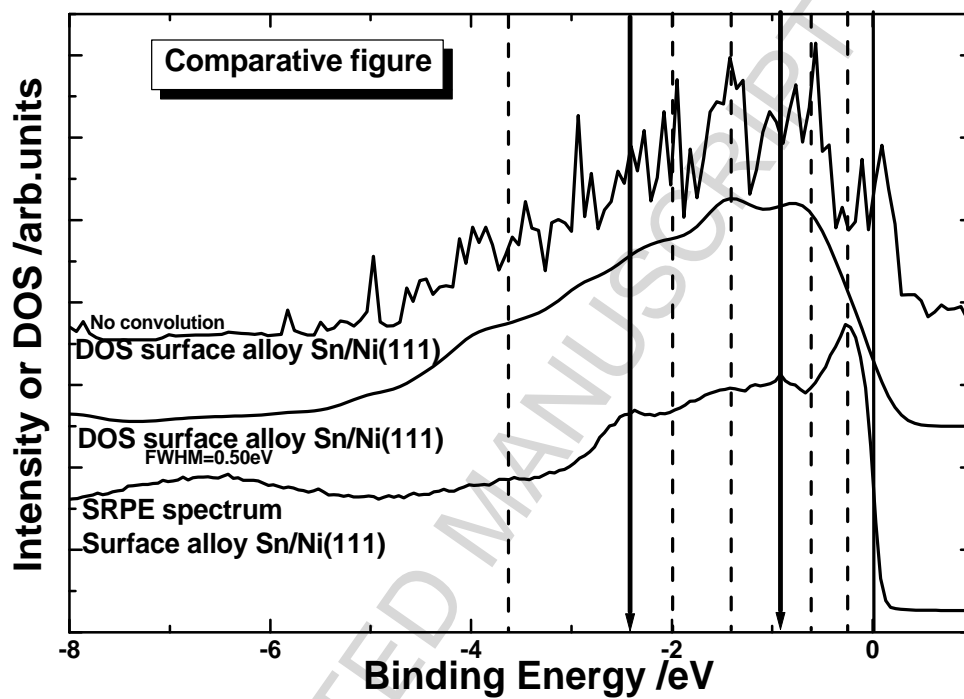


Fig. 4: Comparative figure between Valence Band SRPE spectra of the surface alloy $(\sqrt{3}\times\sqrt{3})R30^\circ$ Sn/Ni(111) with 80 eV photon energy and the total density of states (sum of spin up and spin down components) of the first alloy layer.