

# Determination of Local Atomic Arrangements in a Bulk-immiscible Surface Alloy

K.R. Witkowski, D.T. Keane, M. Asta, J.P. Quintana

Department of Materials Science & Engineering, Northwestern University, Evanston, IL, U.S.A.

## Introduction

Surface alloying by bulk-immiscible metals has been of interest since the mid-1990s. This surface-restricted alloying is attributed to a competition between driving forces due to chemical bonding and strain energy. Of these bulk-immiscible, surface-alloying systems, Au/Ni(110) has been well studied with scanning tunneling microscopy (STM) and Rutherford backscattering spectroscopy (RBS) by Pleth Nielsen et al. [1-3]. In their STM studies, it was observed that for coverages up to  $\sim 0.4$  monolayer (ML) of Au on Ni(110), the Au randomly substitutes into the first Ni(110) atomic layer either as single Au atoms (monomers) or as two Au atoms together (dimers). From coverages of about 0.4 to 0.8 ML, Au forms [001]-directed dimer-trimer chains that slightly protrude from the first Ni(110) atomic layer. The lengths of the dimer and trimer units within the [001]-directed chains indicate a Au-Au distance that is much shorter than the Au-Au bonding distance in the bulk. Further knowledge about the displacements in the neighboring atoms to Au, in both the random alloy and ordered-chain phases, is necessary to better understand the surface strain that is contributing to this unique alloying condition.

In order to determine the local atomic arrangements in a surface, it is necessary to implement a technique that is both surface-sensitive and capable of yielding accurate bond information. Surface extended x-ray absorption fine structure (SEXAFS) experiments satisfy both of these criteria by obtaining extended x-ray absorption fine structure (EXAFS) spectra from the surface, by using either electron yield detectors or geometry to minimize the contribution of the bulk to the overall EXAFS spectra [4, 5].

## Methods and Materials

During our SEXAFS experiments, a Ni(110) substrate was placed at the center of an ultrahigh-voltage (UHV) chamber ( $P_{\text{base}}$  of  $\sim 3.0 \times 10^{-10}$  torr) located in the 5-ID-C hutch at the DND-CAT beamline at the APS. The Ni substrate was cleaned through  $\text{Ar}^+$  sputtering and subsequent annealing until a clean, sharp Ni(110)  $1 \times 1$  low-energy electron diffraction (LEED) image was observed. Au was then deposited on the surface through evaporation at  $1100^\circ\text{C}$ . After deposition with Au, the sample was

annealed to  $\sim 350^\circ\text{C}$  for 10 minutes. LEED was then conducted on the Au/Ni(110) surface to check for reconstructions due to impurities. After surface alloy formation was ensured, the sample was placed in total external reflection geometry with the polarization direction of the beam approximately parallel to the surface of the sample to yield SEXAFS spectra preferentially influenced by the intra-planar bond information [4]. The incident energy of the beam was then increased through either the Au L2 or Au L3 edge to an energy that was about 500 eV above the respective edge. The fluorescent SEXAFS spectra were measured by using a Ge solid-state detector.

## Results

Over the course of three beam times, SEXAFS spectra were obtained for 2, 4, 7.5, 10, 25 (0.12 ML), 35, and 120 minutes (0.44 ML) of Au deposition on the Ni(110) surface. In analyzing these spectra, the intensity from the solid-state detector was normalized by the reflected beam intensity. WINXAS software was used to extract the background-subtracted SEXAFS oscillations [6]. Typically, EXAFS spectra are analyzed versus an acceptable standard with similar distances and coordination numbers. When such an experimental standard is unavailable, a theoretical standard is often implemented. In our case, the FEFF8 code was used to simulate SEXAFS from the Au/Ni(110) over its varying coverages [7]. First-principles calculations were conducted to determine the approximate atomic positions for a single Au atom embedded in the first Ni(110) layer and for two Au atoms in the first Ni(110) layer [8, 9]. These distances, which can be seen in Table 1, were then used in the models from which the theoretical SEXAFS spectra were simulated. In Fig. 1, background-subtracted SEXAFS spectra from Au on Ni(110) for three different coverages of 0.06, 0.12, and 0.44 ML can be observed with the SEXAFS spectra that were simulated by using the bond distances determined from first-principles calculations. A careful analysis of the fitting shows that the SEXAFS spectra simulated for the monomer cases for both 0.06 and 0.12 ML appear to resemble the experimental data more closely than the dimer-simulated spectra.

TABLE 1. Bond distances for FEFF paths.

FEFF Path	0.06 ML			0.06 ML		
	1st Prin. mono	FIT mono	bond length diff. mono	1st Prin. dimer	FIT dimer	bond length diff. dimer
1	2.580	2.515	-0.065	2.457	2.384	-0.073
2	2.644	2.577	-0.067	2.649	2.570	-0.079
3	2.795	2.723	-0.072	2.653	2.574	-0.079
4	--	--		2.700	2.620	-0.080
5	--	--		2.823	2.739	-0.084
Chi Sq.	4.494			4.309		
Red. Chi Sq.	1.141			2.224		
R-factor	0.012			0.012		

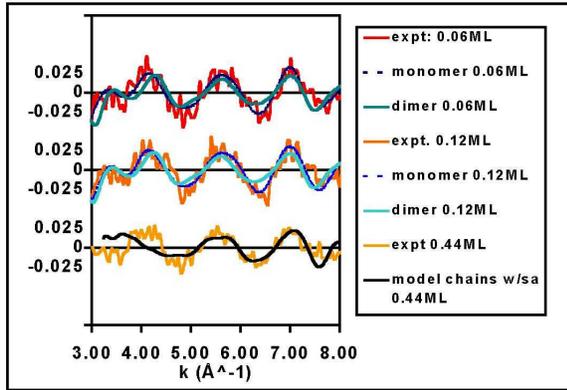


FIG. 1. Background-removed SEXAFS spectra from three different Au-Ni(110) coverages obtained by using WINXAS software [6]. Both 0.06- and 0.12-ML coverages are random Au-Ni(110) surface alloys and are shown with FEFF8 *ab initio* calculated SEXAFS from surfaces incorporating first-principles calculated displacements for both monomer- and dimer-substituted Au atom configurations. Experimental SEXAFS from an ordered dimer-trimer chained structure with a Au coverage of 0.44 ML are shown with FEFF8 *ab initio* calculated SEXAFS from Au positions observed via STM [3].

Fitting of the contribution from the first shell of atoms around an absorbing Au atom was conducted by utilizing ARTEMIS and IFEFFIT software [10]. While fits of both the monomer and dimer models appear similar to the experimental data as seen in Fig. 2 and Fig. 3, the errors in the fitting variables and bond lengths are clearly seen in Table 1 to be different.

## Discussion

IFEFFIT was used to fit the experimentally obtained SEXAFS spectra with theoretical standards. The

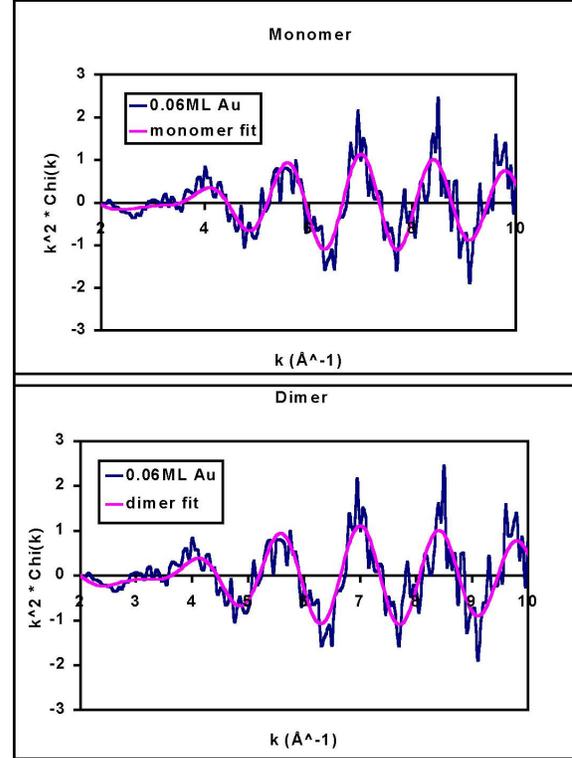


FIG. 2. Plots of  $k^2 \chi(k)$  versus  $k$  for the 0.06-ML Au-Ni(110) data as well as the fit determined for the contribution of the seven nearest neighbors to a Au atom in the monomer and dimer configurations from using FEFF8 and IFEFFIT with the following parameters:  $k$ -range = 2–10  $\text{\AA}^{-1}$ ,  $k$ -weight = 2,  $R$ -range = 1–3  $\text{\AA}$  [7, 10].

result was a good fit coming from bond distances that are within the commonly expected error of first-principles-determined bond lengths. The variables that were used in fitting both the monomer and dimer models to the data exhibited smaller errors in the fit from the monomer model, resulting in smaller differences between the predicted and resulting bond lengths for that model. Further analysis is continuing regarding fitting additional shells and incorporated multiple-scattering paths to further refine the fit in order to attain more certainty about the bond length distances and a greater understanding of the impact of the Au atoms further away from their substituted location.

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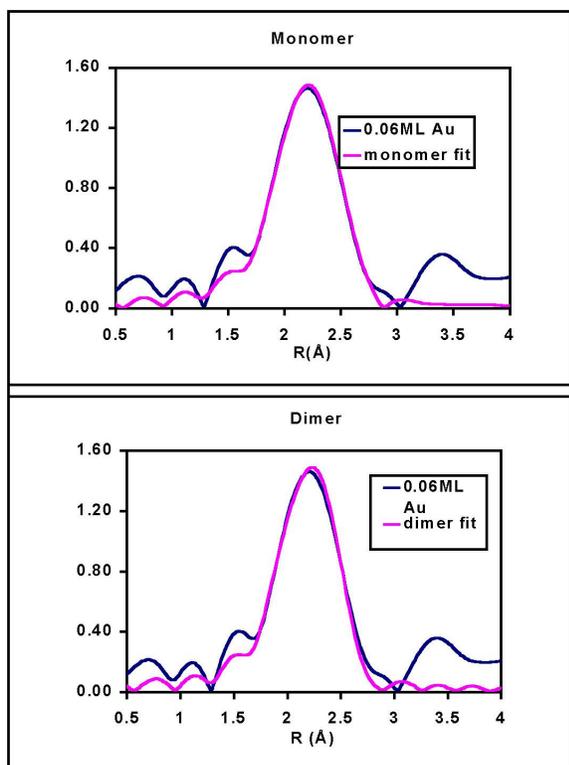


FIG. 3. Plots of the Fourier transformation of  $k^2 \cdot \chi(k)$  of the 0.06 ML Au-Ni(110) experimental data as well as the fit determined for the contribution of the seven nearest neighbors to a Au atom in the monomer and dimer configurations from using FEFF8 and IFEFFIT with the following parameters:  $k$ -range = 2–10  $\text{\AA}^{-1}$ ,  $k$ -weight = 2,  $R$ -range = 1–3  $\text{\AA}$  [7, 10].

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