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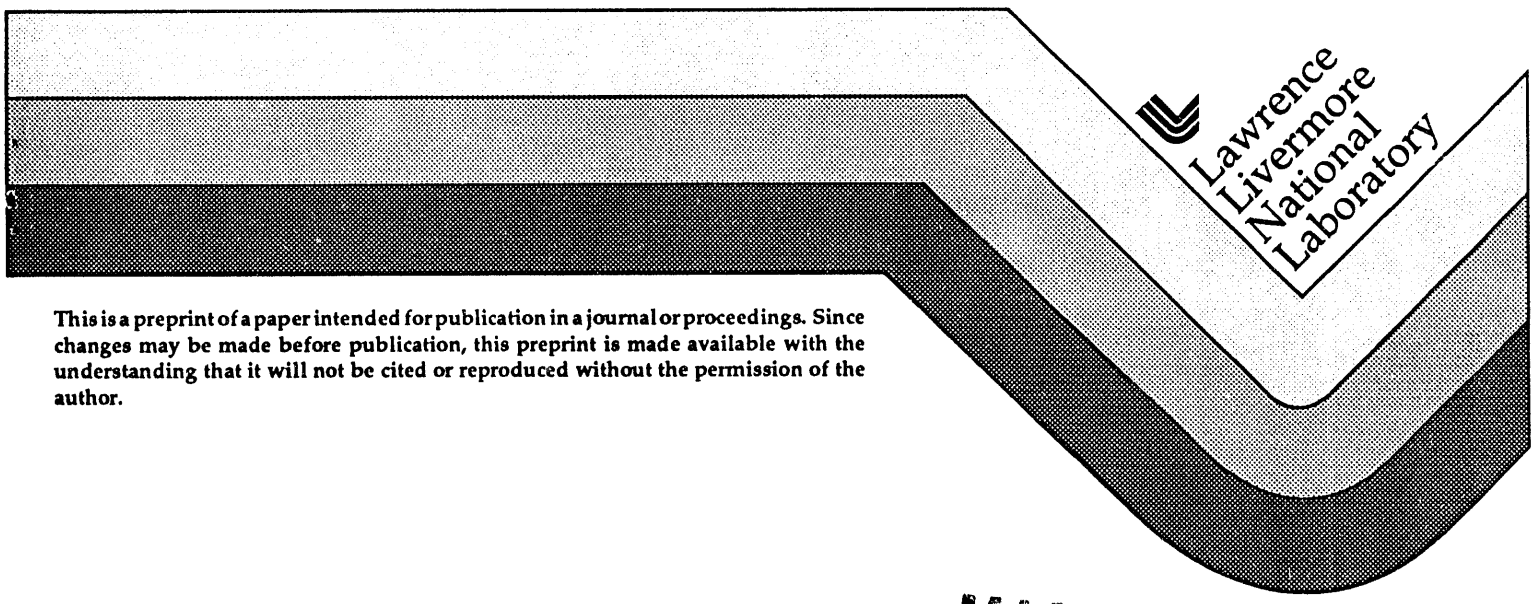

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IMAGING OF SURFACE STRUCTURE WITH ENERGY-DEPENDENT PHOTOELECTRON DIFFRACTION

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Abstract

Energy-dependent photoelectron diffraction (EDPD) has been used to determine the surface structure of a surface alloy. Direct imaging has been achieved by Fourier transformation of experimental energy-dependent photoelectron diffraction data. This holographic method, based upon the intersection of contour arcs associated with each measurement direction, can provide vectorial atomic positions with atomic resolution. Experimental analysis is supported by Fourier transformation of simulations from multiple scattering calculations The surface geometry of c(2x2) Au/Cu(001) has been imaged in an elementally-specific manner, with clear, non-model-dependent discrimination of the surface alloy over the overlayer structure.

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Introduction

Extraction of structural information from diffraction data is predicated upon conversion of measured variations in angular or energy space into real space dependences. A time-honored and highly precise method is to use trial and error comparison of model dependent calculations of scattering cross sections to fit measured data. A different approach is to Fourier transform (FT) normalized diffraction curves, either energy or angular variation: But for an FT to be meaningful, an accurate theory which condenses down into a simple sinusoidal dependence is required. An interesting idea, originally proposed by Szoke[1] and extended by Barton[2], was to apply a Fourier transformation (FT) to Auger- or photo-electron diffraction intensities over a wide angular range at a fixed kinetic energy. Early experimental work[3] seemed to confirm the validity of this approach. More recent investigations, based on simulated[4,5] and measured[5,6,7] diffraction spectra, have pointed out severe limitations of the single-energy transformation[8,9]. These limitations are due to the presence of artifacts in the reconstructed image in the form of bright spots or streaks at non-atomic positions. While simplified procedures[5,10] requiring more explicit prior knowledge of the structure have been suggested, the most promising method of resolution improvement, twin image suppression and artifact removal in electron holography appears to be the utilization of multiple energies[4,11,12]. It is this necessity of using multiple energies that lead us to consider a variant of photoelectron imaging in which sampling over a wide energy range is utilized.

In this paper we present a combined experimental and computational study that demonstrates direct wave-front reconstruction to obtain surface structure with atomic resolution using spatially resolved imaging of energy-dependent photoelectron diffraction (SRI-EDPD). The theory behind this method and a brief description of the experimental results have been presented earlier[13]. Additionally, while Fourier-transformation (FT) of experimental data provides a direct image of the surface structure, detailed multiple-scattering simulations and transformation of calculated intensities are used to verify the analysis. The system studied was 1/2-monolayer, c(2x2) Au/Cu(001)[14–18]. It will be shown that the c(2x2) surface alloy is clearly observed, and that the surface alloy is easily differentiated from a c(2x2) overlayer. Such a non-model-dependent discrimination of a surface alloy from an overlayer is impossible using more-conventional diffraction techniques.

Although multiple-energy wave-front reconstruction had been carried out using experimental data[19,20], the previous works were done on bulk emission systems in which the structural information was averaged over many layers (i.e., the surface and bulk

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interlayer spacings mixed together). The present study is the first experimental demonstration of data inversion in which single-layer information is obtained. The atomic structure within the surface plane of the c(2x2) Au/Cu(001) system is directly imaged. This system contains strongly scattering Au and Cu potentials. Therefore, multiple wave-number phase-locking is essential to the success of the reconstruction process.

While this is the first demonstration of SRI-EDPD, structural studies with energy-dependent photoelectron diffraction (EDPD) have been done for quite some time[21,22]. Fourier transformation of the data has also been pursued: Early works[23-27], done on a fairly empirical basis, suggested that there was some validity to this method for determining *scalar* distances with normal emission. Subsequent attempts at improvement used energy variations along a few high symmetry directions[26,27]. But again, in these early works the goal was to extract *scalar* distances between the emitter and surrounding scatterers. The present approach involves inverting energy variation curves (over a 200 eV range) at a large number of angular positions, and the idea is to extract *vector* (i.e., direction and distance) information relating and emitter and its neighbors. It is only because of our improved data collection mode that a full data set could be collected in a reasonable amount of time (approximately 12 hours total).

Data Collection and Fourier Transformation Analysis

The experiments were performed at the Stanford Synchrotron Radiation Laboratory using Beamline 8–2. This is a spherical grating monochromator beamline[28,29] which is part of the UC/National Laboratories Participating Research Team (UC/NL-PRT) facilities. EDPD curves were collected at 48 different angular positions in the irreducible $\Pi/4$ solid angle between the (010) plane and $(1\bar{1}0)$ plane of Cu(001), as illustrated in Figure 1. The details of data collection are discussed elsewhere[13,30].

Prior to data inversion, all the EDPD oscillation curves within a set were normalized versus photon flux and then to each other, the latter to eliminate any spurious intensity variations associated with luminosity or electron optics, for example, due to the variation of sample position. Analysis of the experimental EDPD curves followed the procedure set forth in the work of Tong, et. al.[13]. At these kinetic energies, artifacts from multiple scattering can be quite strong. However, using EDPD curves at a variety of angles eliminates the multiple scattering artifacts. This is because Fourier transformation of EDPD curves produces contour arcs, associated with single and multiple scattering path lengths. The single scattering arcs for all EDPD curves intersect at atomic positions[13],

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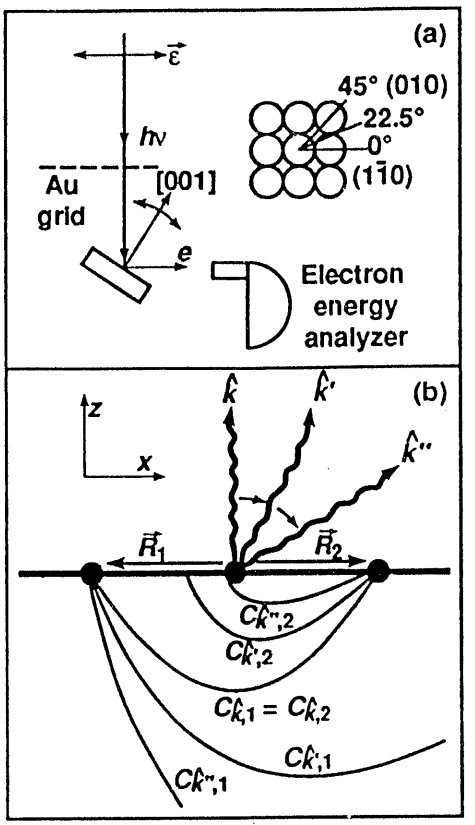

Figure 1. The geometry of the data collection (panel A) and single-scattering contour arcs (panel B). $\vec{\varepsilon}$ is the photon electric vector, and e is an ejected electron. In panel B, the intersections of the contour arcs correspond to atoms placed at ±2Å along the x-axis, relative to the emitting atom at the origin. The contours are due to emission directions $\hat{k}(0°)$, $\hat{k}'(30°)$ and $\hat{k}''(60°)$. The z-axis has been expanded by a factor of two relative to the x-axis.

producing an amplitude peak scaling as N, the number of EDPD curves (Figure 1). The multiple scattering contour arcs, on the other hand, intersect only two at a time, and these intersections spread diffusely over real space. Because intensity is equal to the amplitude squared, the intensities of the single scattering arc intersections (at atomic positions) tend to increase over multiple scattering intersections (at artifacts) by a ratio of $(N/2)^2$. Hence, with 48 EDPD curves, ideally the single scattering to multiple scattering ratio should be $(24)^2$ or 576. Because of the finite energy range of the EDPD curves, which broadens the contour arcs in real space, and the tendency for multiple scattering contour intersections to occur near to each other, the actual ratio is not as large as the ideal case. Nevertheless,

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sufficient reduction of multiple scattering effects occurs to essentially eliminate any artifacts inside the first two nearest neighbor shells. On a scale of 1 to 105, along the [110] direction, the image of the nearest neighbor atom (Cu) has an intensity of 103, and the third neighbor atom (Au) has an intensity of 73. Along the [100] direction, the second neighbor atom (Au) has an intensity of 60 and the fifth neighbor atom has an intensity of 6. All artifacts have intensities below 5. Although some peak distortion and shifting relative to the true positions can be observed in Figure 2, all of this is easily within 1Å. Along with direct FT of experimental data, multiple scattering simulations and FT of these simulations have also be performed. These observations and results will be discussed below.

Discussion

The crucial results are shown in Figure 2. The first in-plane nearest neighbors (Cu) and second and third in-plane nearest neighbors (Au) are imaged with atomic resolution, *without the intrusion of artifact peaks*. The system studied, 1/2-monolayer, c(2x2) Au/Cu(001),[14-18] is a particularly severe test of this imaging technique, because of the complexity of this system which exhibits competing growth modes involving surface-alloying, bulk-alloying, and overlayer formation.

Also shown in Figure 2 are two Fourier transformations of calculated EDPD curves, generated by applying multiple scattering theory to the c(2x2) Au/Cu(001) surface alloy and overlayer models. (Note the strong agreement between the experimental results and those of the alloy model.) Even in images obtained from the theoretical curves, some peak position shifting occurs. The shifts are due to anisotropic factors (both in phase and magnitude) of the Au and Cu scattering factors[31]. A salient result in Figure 2 is that the FT of both the surface alloy and overlayer simulations recover the essence of each real space model, without the addition of artifact peaks. However, it appears that peak position shifting becomes progressively worse moving away from the central emitter. Thus only first and second nearest neighbor positions can be determined accurately with this database. (The data ranges used in the theoretical and experimental inversions are identical.) In the case of the overlayer, a less areally dense structure, the second nearest neighbors are 5.1Å away, but in the surface alloy these atoms are now third nearest neighbors and exhibiting greater shifting as well as peak splitting. Splitting of outer shell atomic images, due to shadowing by an inner shell atom and multiple scattering, has been observed previously in simulations[13]. The lateral distortion of the nearest neighbor Cu peaks in the experimental FT is absent in the surface alloy simulation: This appears to be related to surface vibrations in the real sample as well as systematic uncertainties in the data acquisition, such as sample alignment, and the limited size of the data set.

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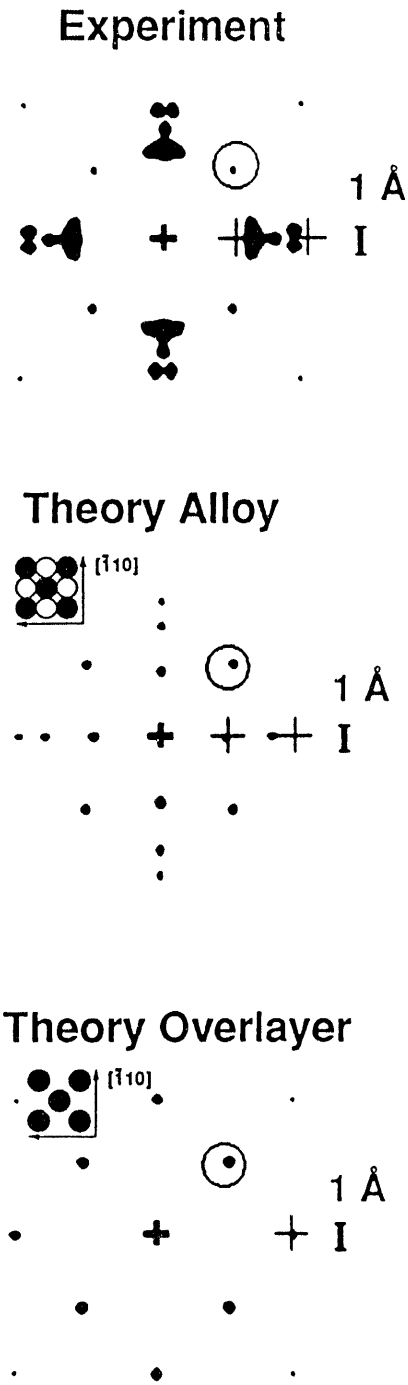

Figure 2. Images reconstructed from experimental spectra (top), calculated spectra for the surface alloy model (middle) and overlayer model (bottom). In each picture, the thick cross marks the Au emitter's position, thin crosses and the circle mark the expected atom positions of neighbors in a Π/4 sector.. The plane-of-view passes through the nuclei of surface layer atoms, see insets for surface models. [Au=solid circle, and Cu=hollow circle.] The experiment clearly agrees with the surface alloy model.

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Summary

The surface alloy system Au/Cu(001) has been imaged using a variant of energy-dependent photoelectron diffraction (EDPD) or holography. This variant directly addresses the issue of artifact generation from multiple scattering, unlike the originally proposed conception of electron holography that borrowed wholesale the assumptions built into laser holography (e.g., measure angular variations at a single energy and assume the single-scattering holds). In fact, electrons are strong, multiple-scatterers at all but the highest energies. Our approach has the multiple-scattering effects built in a priori. It is the intersection of the contour arcs that amplify the magnitude of the single scattering peaks (atomic positions) relative to the multiple scattering peaks. Thus, multiple scattering is an intrinsic part of this theory but its impact is reduced by the intersection overlap method.

Thus, the reconstruction formula for inverting EDPD spectra has been applied to experimental data. First results for the c(2x2) Au/Cu(001) system are encouraging, demonstrating two-dimensional vectorial imaging. By achieving atomic resolution of less than 1Å, the reconstruction image shows directly and conclusively that the Au/Cu(001) system involves alloying in the surface layer. This is consistent with the results from photoelectron spectroscopy (core shifts and surface state shifts)[16], photoelectron diffraction (PD)[16,17], low energy electron diffraction (LEED)[15], and scanning tunneling microscopy (STM)[18]. Although the imaging experiment cannot match the resolution of multiple scattering analysis of PD[16] or LEED[15], it does allow a direct surface structure determination, independently of any model-based assumptions. The combination of both experiments, using elementally-specific FT imaging and multiple scattering is the most efficacious: The imaging could provide rough structural parameters and the multiple scattering calculations could be used to zero-in upon the correct values within the reduced parameter space provided by the imaging. Ultimately, it would be highly useful to include spin-dependence in these measurements, via spin-detection or circular polarization[32].

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