RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 8 15 SEPTEMBER 1988-I

Origin and structural sensitivity of surface Auger extended fine structure

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(Received 18 March 1988; revised manuscript received 20 June 1988)

Extended fine Auger structure (EXFAS) spectra of Ag(111) and of thin (4–60-Å) Cu films deposited on Ag(111) have been recorded with a retarding grid electron spectrometer. The temperature dependence of the Ag $N_{23}\epsilon V$ EXFAS of the Ag(111) surface provides strong evidence of a local rather than a long-range origin of the phenomenon. The utility of EXFAS for surface structural studies is demonstrated by its sensitivity to structural changes as a function of the thickness of Cu overlayers evaporated on the Ag(111) substrate. For Cu coverages of less than 2 monolayers (ML) an expansion of the Cu-Cu nearest-neighbor distance is observed, consistent with epitaxial growth in registry with the larger lattice size of the Ag substrate. At coverages above 5 ML the Cu-Cu distance is essentially identical to that of bulk Cu. These EXFAS results are consistent with low-energy electron-diffraction and surface-extended energy-loss fine-structure results on the same system.

I. INTRODUCTION

Extended fine Auger structure[1–3] (EXFAS) is a series of weak features which can be observed above the discrete Auger lines in many published secondary-electron spectra. Early interpretations[4,5] invoked diffraction of secondary electrons, analogous to Kikuchi lines in transmission electron diffraction. More recently a locally sensitive, backscattering modulation mechanism similar to extended x-ray absorption fine structure (EXAFS) has been proposed.[1–3] This mechanism[2,3,6] involves a modified Auger decay in which the continuum core-ionized electron recombines with the core hole. The origin of extended energy-loss fine structure (EELFS), normal Auger and that proposed for the EXFAS signal are compared in Fig. 1. According to this model, the EXFAS signal is closely related to the EELFS signal, with both arising from interference between the core excited and backscattered components of the final state wave function.

If the proposed EXAFS-like origin of EXFAS is correct, it provides a very attractive, simple alternative to surface EXAFS[7,8] and surface electron energy-loss fine structure (EELFS)[9] for studies of surface and near-surface structure at an atomic level. Very recently, Woodruff[10] has reviewed the existing experimental evidence concerning extended Auger fine-structure phenomena and has argued in favor of a longer range, diffraction origin of these features. In this work we present new experimental results which strongly support the shorter-range, EXAFS-like origin of the Auger extended fine structure. In a companion paper,[6] we present in detail the temperature and edge dependence of the EXFAS signal of clean Ag(111) and clean polycrystalline Cu surfaces and provide a full discussion of the evidence for a local structure, EXAFS-like origin of EXFAS. Here we demonstrate the strong, R-dependent temperature dependence of the Ag $N_{23}\epsilon V$ (Ref. 11) EXFAS of Ag(111) and illustrate an application of EXFAS to the determination of the structure of epitaxially grown Cu-Ag interfaces. The

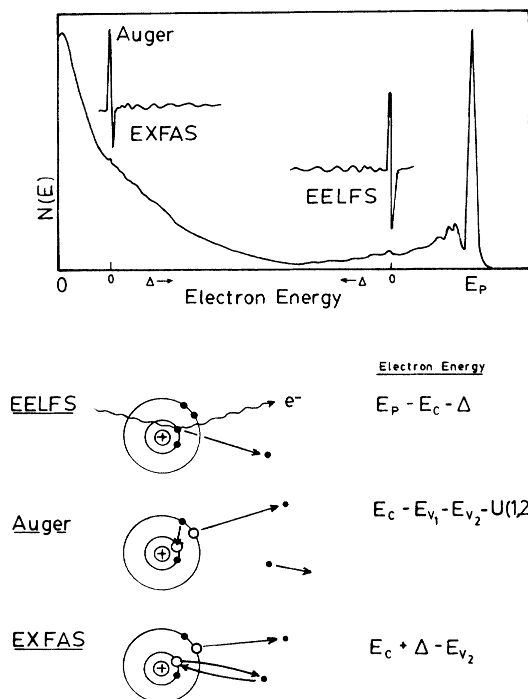

FIG. 1. Schematic of the energy distribution of electrons reflected from a surface. The initial creation of the core hole is detected as the extended energy loss fine structure (EELFS). In the conventional Auger process the core hole is filled by an electron from an occupied level of the core-excited atom and another valence electron is ejected. In the proposed extended fine Auger structure (EXFAS) mechanism, the core-ionized electron takes part in the core hole decay, either as the ejected electron (autoionization resonance) or as the electron that fills the core hole. The equations give the relationship between the energy of the detected electron and the energy levels of the target for each spectroscopy. $U(1,2)$ is the Coulomb-Coulomb interaction of the two holes in the Auger final state while Δ is the amount by which the energy of the ionized electron exceeds the ionization threshold.

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latter results complement those determined from Cu M_{23} SEELFS of the same Cu/Ag(111) samples.[12] Further experimental evidence for an EXAFS-like origin of the extended Auger fine-structure signal has been reported in a recent study of Cr (Ref. 13) performed with an angle-resolved hemispherical analyzer.

II. EXPERIMENT

The EXFAS spectra were acquired with a retarding grid low-energy electron-diffraction (LEED) and Auger angle-integrating electron energy analyzer. The electron beam used (2000-eV impact energy, ca. 1–2 μA) impinged at normal incidence. The Cu/Ag(111) samples were studied at ambient temperature while the clean Ag(111) surface was studied as a function of temperature between 150 and 600 K. The 600-K data were recorded as the Ag crystal cooled from 650–550 K since the electron-beam heater generated background signal. The EXFAS spectra were acquired using 6 or 8 V peak-to-peak modulation of the second grid, along with lock-in detection of the second harmonic (first derivative mode spectra). The Cu overlayers were deposited by evaporation on an Ag(111) substrate which had previously been cleaned by Ar ion bombardment and annealed to produce a surface with only Ag Auger signal and a good (111) LEED pattern. A quartz microbalance was used to monitor the average thickness of the Cu overlayers. More complete details of the spectrometer, sample preparation, data acquisition, and analysis are presented elsewhere.[6,12]

III. RESULTS AND DISCUSSION

A. Temperature dependence of Ag $N_{23}\epsilon V$ EXAFS of Ag(111)

The EXFAS and Fourier magnitudes of the extended fine Auger signal isolated from first derivative $[N'(E)]$ Auger spectra of clean Ag in the region of electron kinetic energies above that of the Ag $N_{23}VV$ Auger line are presented in Fig. 2. Both the EXFAS signal and transform radial distribution curves change greatly with temperature, as has been noted previously.[4,5] Indeed, it is exactly this strong temperature dependence which indicates a structural dependence, and which distinguishes EXFAS from the conventional Auger signal which has a solely electronic origin. At elevated temperature the higher R signal from longer scattering path lengths is strongly suppressed relative to the nearest-neighbor signal. The selective damping of higher R signal with increasing temperature is the behavior expected for an EXAFS-like origin since the increased thermal motion has a much larger damping effect on longer distances involving more weakly correlated motions.[14–16] By contrast, secondary-electron diffraction[4,5,7] would have a T dependence similar to that for LEED.[17,18] Relative to EXAFS, the damping of diffraction signals with increasing T is both less rapid and more uniform over the distance scales. The full implications of the temperature dependence on the EXFAS mechanism and the relative levels of agreement with EXFAS versus a diffraction origin of the signal are discussed elsewhere.[6]

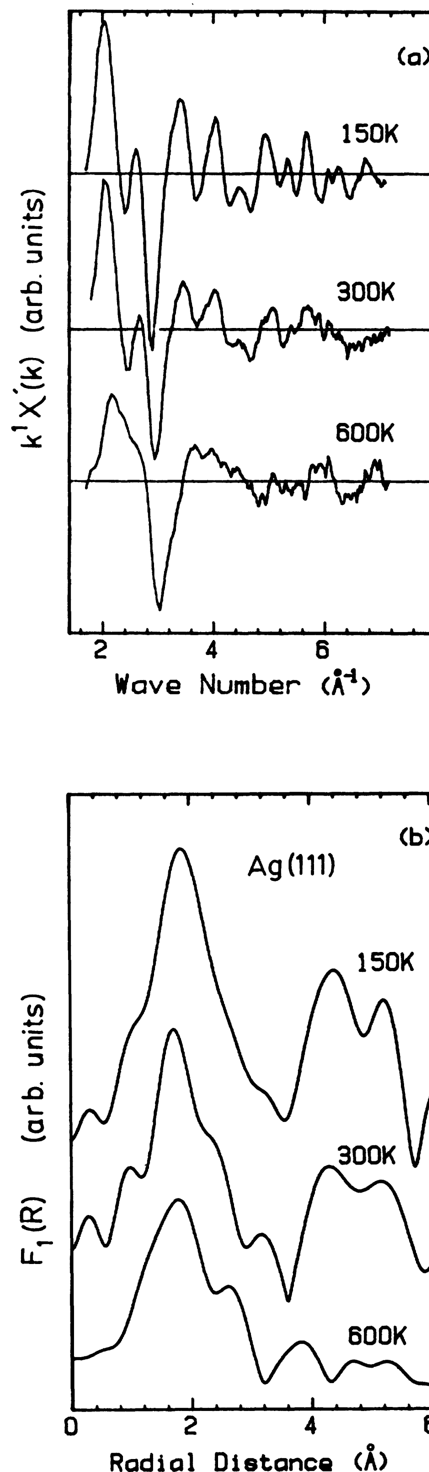

FIG. 2. (a) EXFAS isolated by two-section cubic spline background subtractions from the first derivative spectra of Ag(111) above the Ag $N_{23}VV$ Auger line (35 eV), recorded at the indicated temperatures. The origin of the k scale was taken as 45 eV, the minimum of the main Ag $N_{23}\epsilon V$ Auger line and thus somewhat higher in energy than the Auger energy but below the XPS binding energy for the Ag N_{23} edge. The temperature-independent structure at 3.2 Å^{-1} is the Ag N_1VV Auger line. (b) Fourier transforms of the Ag $N_{23}\epsilon V$ EXFAS as a function of temperature.

The nearest-neighbor signal dominates the Ag $N_{23}\epsilon V$ EXFAS at higher temperatures but there are strong contributions from higher shells to the low-temperature EXFAS. At all temperatures Fourier filtering isolates a first-shell signal that is in good agreement with that from the first-shell dominated, 600-K EXFAS. The second-shell EXFAS signal around 4.4 Å arises from several higher-shell Ag-Ag distances in this region. The apparently larger contribution of higher path-length signals to EXFAS (Refs. 1 and 3) than to EELFS or EXAFS may be related to the interplay of the core-hole lifetime and the transit time for backscattering. This point is considered in detail in Ref. 6, as is the phase shift required for quantitative distance determination by EXFAS.

B. Cu/Ag(111) interface

The k^1-weighted EXFAS derived from the first derivative Auger spectra of a series of Cu overlayers [4, 10, 60 Å and bulk (poly-c) Cu] are presented in Fig. 3. The signal derived from the spectrum of clean Ag(111) in the same energy region is also shown for comparison. The Fourier-transform magnitudes of these signals are presented in Fig. 4. The transform for the 4-Å Cu film is somewhat distorted by the underlying Ag $N_{23}\epsilon V$ signal, which in turn, is very different from that of the Ag $N_{23}\epsilon V$ EXFAS (Fig. 2) because the k-scale origin is appropriate for Cu $M_{23}\epsilon V$ but incorrect for Ag $N_{23}\epsilon V$ EXFAS. For coverages above 10 Å the general shape of the Cu $M_{23}\epsilon V$ EXFAS agrees very well with that recorded from polycrystalline Cu, as well as with that for the Cu(111) surface measured with a partially angle-resolved cylindrical mirror analyzer (CMA).[2] In all of the spectra the dominant signals in the Fourier transform occur around 2 and 4 Å. These signals shift to higher R as the Cu overlayer gets thinner, in agreement with the results of a complementary SEELFS study of the Cu/Ag(111) interface.[12] The results of both spectroscopies are consistent with commensurate layer-by-layer, epitaxial growth of the first 2–3 layers with a gradual evolution of the bulk Cu structure in the next few layers. Within the sensitivity limits of the extended fine-structure techniques, the Cu overlayer appears to be indistinguishable from bulk beyond the fifth layer. These structural conclusions are also supported by our qualitative LEED results[12] and by literature RHEED and transmission electron diffraction studies of the Cu/Ag interface.[19,20]

The normal incidence excitation of these EXFAS spectra leads to a lower surface sensitivity than in the case of glancing incidence SEELFS.[12] Even so a reasonable surface sensitivity is achieved since the secondary electrons in the Cu $M_{23}\epsilon V$ EXFAS have kinetic energies between 80 and 400 eV, corresponding to mean free paths between 2 and 5 Å in bulk Cu (Ref. 21). The changes in the Cu $M_{23}\epsilon V$ EXFAS observed as a function of the Cu film thickness indicate that the technique may have useful applications to surface structure determination.

The good agreement between the Cu $M_{23}\epsilon V$ EXFAS of the 60 Å Cu(111) film and that of polycrystalline Cu (Figs. 3 and 4) provides further evidence in favor of the local, EXAFS-like interpretation. The features would be expected to be significantly stronger in the Cu(111) epitaxial film than in polycrystalline Cu if the origin was diffraction dominated and thus sensitive to a relatively long-range order.

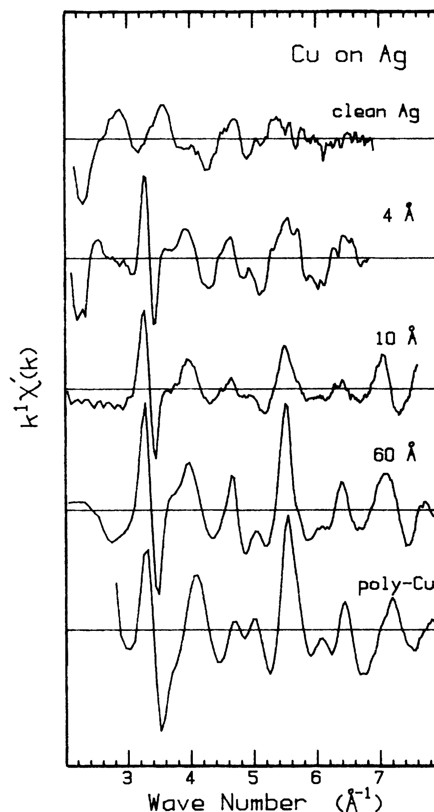

FIG. 3. The k^1-weighted EXFAS structure derived by two-section cubic spline background subtractions from the spectra of clean Ag(111), polycrystalline Cu and a series of Cu overlayers deposited epitaxially on Ag(111). The Cu coverage as measured by a quartz thickness monitor is indicated. The origin of the k scale was taken as 60 eV, the minimum of the Cu M_{23} Auger line. The sharp signal at 3.4 $Å^{-1}$ contains strong contributions from the Cu M_1VV Auger line.

One can consider in the most general case that photoelectron diffraction (PhD), secondary-electron diffraction and EXAFS-like modulations could all contribute to extended Auger fine-structure signal. The rapidly developing field of PhD (in both swept-energy and angle-scan modes)[22] is clear evidence that the ionized electron is diffracted during its escape from the solid. The possible contribution of this type of signal to reflection electron scattering has been considered theoretically by Mila and Noguera.[23] Similarly the diffraction of electrons in the range of secondary-electron distribution is well known in the form of LEED. Its persistance, even with highly-angle-integrated detection has been a major limitation to extended appearance potential fine structure spectroscopy.[24] Both of these types of electron diffraction will be much more important in angle-resolved than angle-integrated studies. Thus the use of a retarding grid spec-

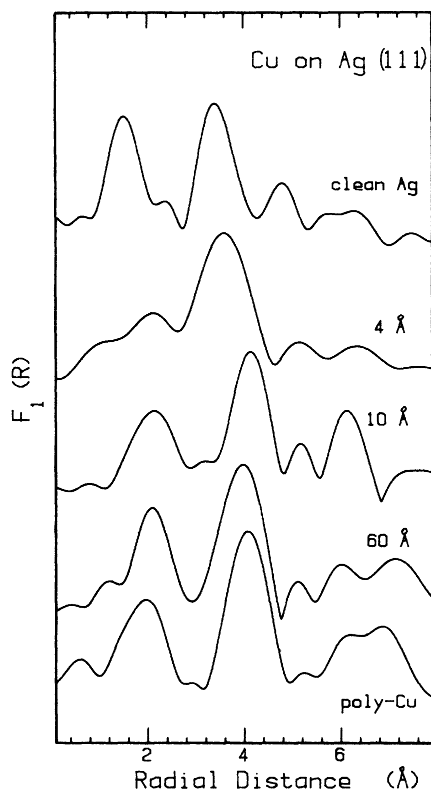

FIG. 4. Magnitudes of the Fourier transforms of the Cu M_{23} EXFAS of polycrystalline Cu and of Cu films evaporated on a Ag(111) substrate (Fig. 3). The curve for 4 Å Cu/Ag is distorted by the underlying Ag N_{23} EXFAS signal.

trometer in this work may be an important factor in achieving local-structure sensitivity via an EXAFS-like origin of the signal. In several cases angle-resolved and angle-integrated spectra of the same surface have been found to be very similar.[2,13,25] However, we have recently observed substantial differences between the Auger fine-structure signal recorded with the angle-integrating, retarding grid system used in this work and a highly-angle-resolved (2° acceptance angle) hemispherical analyzer. This suggests that phenomena other than the proposed, EXAFS-like backscattering mechanism may be operative. These results will be presented in a subsequent paper.[6] A detailed study of the dependence of extended Auger fine structure on scattering angle and extent of angle integration is needed to determine with greater precision the relative contributions of diffraction and EXAFS-like signals.

In summary, the temperature dependence of the extended fine structure above the $N_{23}VV$ Auger lines of a Ag(111) surface supports an EXAFS-like rather than a diffraction origin for the observed features. The surface sensitivity of the technique has been demonstrated by measurement of the structural changes in the first few layers of Cu epitaxially grown on Ag(111).

ACKNOWLEDGMENTS

We thank Dr. J. Stöhr for providing the Ag(111) crystal used in this experiment and Natural Sciences and Engineering Research Council NSERC (Canada) for financial support, in particular for an International Scientific exchange grant for Dr. De Crescenzi.

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