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***In situ* structural study of thin-film growth by quick-scanning x-ray-absorption spectroscopy**

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(Received 1 April 1991)

Results of *in situ* quick-scanning extended x-ray-absorption fine-structure measurements during vacuum sputter deposition of thin films are reported. Cu overlayers equivalent to 1–72 monolayers thickness were sputtered onto a substrate. Up to a few monolayers thickness, the Cu seems to form small clusters. At coverages above 38 monolayers, the nearest-neighbor environment remains unchanged, whereas the third- and fourth-nearest-neighbor peaks are still growing: significant structural disorder exists even in the 72-monolayer sample. The changes of the local environment with Cu thickness are also directly visible in the near-edge spectra.

The growth of thin overlayers on smooth substrates is of basic scientific and technological interest. If different materials are deposited on top of each other, it is possible to form periodic synthetic structures with periods of a few monolayers which can be used, e.g., in x-ray optics.¹ However, the first step in the production of such multilayered materials is the deposition of one material onto a smooth surface by molecular-beam epitaxy (MBE), evaporation, or sputtering. The sputtering process is technologically the most important one, because it is extremely versatile and it is possible to deposit almost any solid element, alloy, or compound onto very large substrates. However, the effects of deposition parameters on the structure of the growing film are very difficult to investigate. This is because an analytic method is needed which has a very high surface sensitivity, is applicable in the presence of a sputtering gas, is fast enough to avoid contamination of the open surface, and does not significantly distort the deposition process. In this paper we will show that x-ray-absorption spectroscopy at and above absorption edges is well suited to this task.

The x-ray-absorption spectrum is usually divided into two regions: the x-ray-absorption near-edge structure (XANES) extends up to about 40 eV above the edge, and the extended x-ray-absorption fine-structure (EXAFS) region to about 1500 eV above the edge. The XANES region contains information about the topology of the chemical environment of the absorbing atom and is difficult to

evaluate, whereas the interpretation of EXAFS results is well established and produces accurate atomic distances and coordination numbers by standard procedures. Collection times for EXAFS measurements ranged so far from about 10 to 20 min in the case of concentrated samples, to hours or even days for dilute systems like biological samples or surfaces of monolayer thickness. EXAFS in these latter samples has to be investigated by monitoring secondary processes like fluorescence or electron yield because fractional changes in absorption are too small to be measured directly. However, we demonstrate that with intense synchrotron-radiation sources time-resolved surface EXAFS measurements are possible within a couple of *seconds*, making *in situ* investigations of the growth of thin films possible.

The experiments described here were performed at the 15-period wiggler beamline 10-2 (Ref. 2) at the Stanford Synchrotron Radiation Laboratory (SSRL). The Stanford Positron-Electron Accumulation Ring (SPEAR) was operated at an electron energy of 3.0 GeV and an injection current of approximately 100 mA. The hybrid wiggler was operated at its maximum field of 1.49 T. A double-crystal Si(111) monochromator provided an energy resolution of less than 1 eV at the Cu *K* edge and the intensity of the monochromatized beam after an aperture of 6 mm² was of the order of 10¹¹ photons/s. Choosing the quick-scanning EXAFS (QEXAFS) technique to make measurements, high-quality absorption spectra with

time resolution in the seconds range were feasible.^{3,4} In QEXAFS the monochromator is slewed continuously and the absorption is integrated at each data point for typically 0.01–0.05 s. The absorption was measured in fluorescence using *p-i-n* photodiodes as detectors. A superpolished plate of fused silica ($0.1 \times 1.5 \times 4$ in³) with a surface figure of 0.1 wave and 4-Å rms roughness was coated in a high-vacuum chamber (base pressure better than 10^{-7} Torr) with 500 Å of W and was used as substrate for the sputtering experiments. Deposition of 72-monolayers nominal thickness of Cu was initiated immediately after the termination of the W deposition. The Cu deposition was interrupted after each of the first 20 monolayers to allow QEXAFS spectra to be obtained; at higher coverage spectra were recorded at larger intervals. Chosen was a deposition rate of 14.5 s for one Cu monolayer, and typically two absorption spectra taking 20.9 s each were recorded for the thin samples. All experiments were performed at room temperature. The thickness values stated are “equivalent monolayers” referring to ideal layer-by-layer deposition, whereas in our experiments cluster growth is observed (see later). To obtain a high signal level at low background, the samples were illuminated at grazing incidence below the critical angle of the W substrate. The polarization vector of the x-ray beam was parallel to the surface of the sample. At the selected angle of incidence of 0.35° the x rays are totally reflected by the W substrate and penetrate only a few atomic layers into it. Thus a high surface sensitivity is achieved and a large illuminated surface is contributing to the strength of the fluorescence signal.^{5–7}

Figures 1 and 2 show the fluorescence spectra after subtraction of the increasing background typical for fluorescence measurements. The increasing thickness of the Cu layer results in an increasing edge jump, and the evolution to the typical Cu fcc structure is visible in the EXAFS and also in the XANES.⁸ The Fourier transforms of the EXAFS spectra are displayed in Fig. 3 in comparison to the results of a Cu foil. At a thickness of 5 Cu monolayers

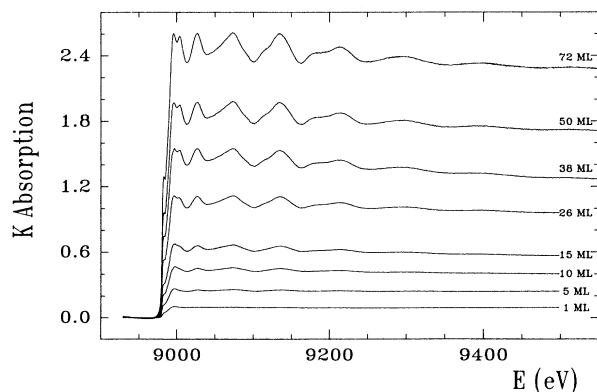


FIG. 1. Cu *K*-edge QEXAFS of 1–72 monolayers of Cu (thickness as indicated) sputtered onto 500-Å W. The spectra up to 26-monolayers coverage were measured in 20.9 s. The spectra of the thicker samples were measured in 40.8 s (38 and 50 monolayers) and 61.4 s (72 monolayers) over an extended energy range and are truncated here.

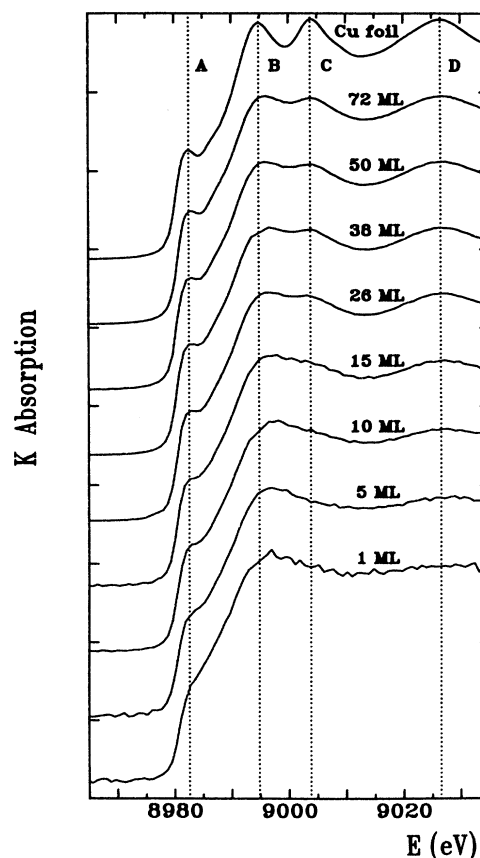


FIG. 2. Normalized XANES of 1–72 monolayers of Cu (thickness as indicated) sputtered onto 500-Å W. The energy range shown here was scanned in 2.7 s (1–50 monolayers) and 5.3 s (72 monolayers), respectively.

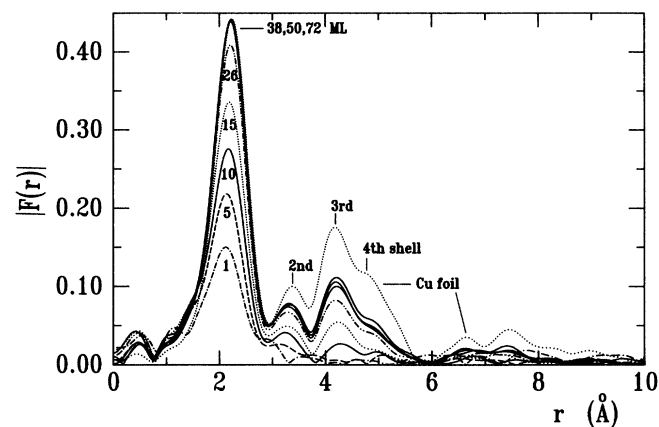


FIG. 3. Fourier transforms of the EXAFS data shown in Fig. 1. Indicated is the number of Cu monolayers. In the case of Cu foil the height of the main peak, which represents the next-nearest-neighbor shell, was normalized to the 72-monolayer (ML) sample. Additionally, the locations of the second to fourth nearest neighbors are indicated. (Transformation parameters: $k = 1.84\text{--}11.66 \text{ \AA}^{-1}$, Kaiser-Bessel window function, k^1 weighting.)

the EXAFS spectrum is dominated by one frequency yielding the nearest-Cu-neighbor peak in the Fourier transform. This spectrum also clearly demonstrates that there is no significant contamination by light atoms, as in an *ex-situ* prepared sample which showed C or O neighbors in a peak at 1.57 Å in the Fourier transform.⁴ Up to 5-monolayers Cu coverage there is no significant contribution beyond the second-nearest-neighbor shells visible. For 10 monolayers the third- and fourth-nearest-neighbor shells show up and are obvious in the 15-monolayer sample. The spectra for even thicker overlayers closely resemble Cu bulk material. Whereas the nearest-neighbor peaks of the three thickest samples are of the same height, the peaks due to the second, third, and fourth coordination shells and of neighbors up to at least 8 Å are still growing. However, even at 72-monolayer thickness, the EXAFS modulations are smaller compared to the bulk material and do not exhibit the high-frequency oscillations which are related to structures in the Fourier transform at large distances. This is due to disorder in the thin film which is also indicated by the larger ratio of the heights of the first- and third-nearest-neighbor peaks in comparison to the bulk material.

The XANES data of a pure Cu foil shown in Fig. 2 exhibit four peaks labeled *A-D*. For the 1-monolayer material, peaks at positions *A* and *C* are missing: only a maximum at higher photon energies than feature *B* is visible, and a second broad structure in the region of peak *D*. Those structures become more prominent up to 10 monolayers and at 15 monolayer the maximum close to feature *B* broadens and splits up into a double-peaked structure at more than 26-monolayers coverage. Greaves *et al.*⁸ have calculated the XANES for different cluster sizes of fcc Cu. For the smallest cluster, having just the first-nearest-neighbor shell, they find two peaks above the edge: one at higher energies than *B* and another broad feature close to location *D*. While feature *D* remains basically at the same energy and becomes sharper as cluster size increases, the maximum close to feature *B* shifts to higher energies upon adding the second-nearest-neighbor shell and then splits up when the third neighbor is added in the model. No additional peaks show up when the fourth shell is added. These features are in good agreement with our experimental data. In their calculation Greaves *et al.*⁸ have to remove the electron lifetime broadening to reproduce structure *A* in the edge. We observe a continuous sharpening of feature *A* with growth of the Cu overlayer, thus adding more significant peaks to the Fourier transforms. For samples with more than 38-monolayers coverage there is also a significant contribution from radial distances larger than 6 Å. Thus those peaks, which are in some cases artificially enlarged by multiple scattering effects, may also be responsible for the sharpness of feature *A*. Compared to XANES from a pure Cu foil, the reduced XANES amplitude even at 72-monolayers coverage shows that significant disorder exists in the sputtered overlayers.

A quantitative evaluation of the Cu EXAFS during the deposition process is presented in Fig. 4. The edge jump versus thickness of the Cu overlayer can be approximated by a linear relationship as expected. The position of the

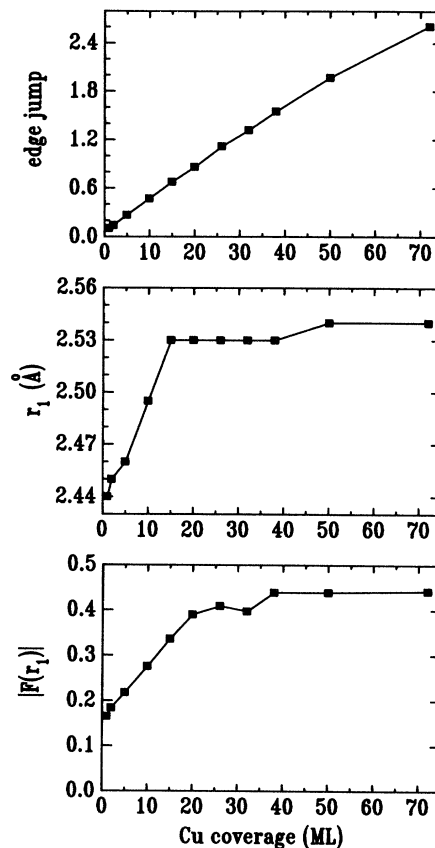


FIG. 4. Evaluation of the EXAFS measurements during vacuum sputter deposition of Cu overlayers onto 500-Å W as a function of the Cu coverage. Top panel: height of the Cu *K* edge. Center panel: position of the first maximum in the Fourier transform, phase corrected. Bottom panel: height of the first maximum in the Fourier transform.

first maximum in the phase-corrected Fourier transform (using the peak shift of the Cu foil) increases from 2.44 Å in the case of the 1-monolayer sample to 2.53 Å in the case of 15 monolayers. At higher coverages only a slight increase to 2.54 Å can be observed. This apparent increase in the nearest-neighbor distance is correlated to an increase of the height of the first peak in the Fourier transform which shows a steep increase between 1- and 20-monolayers coverage and only a small increase upon further deposition of Cu. Our results can be interpreted by assuming that the Cu deposition starts with small Cu clusters. In this case due to an asymmetry in the radial distribution functions, the interatomic distances seem to be smaller than in the bulk material and also the coordination number is lower than expected.^{9,10} This is most obvious in EXAFS studies of amorphous solids,^{11,12} where a large static disorder exists. However, as calculated by Hansen *et al.*¹³ for the case of Cu clusters, this asymmetry stems from the anharmonicity of the motions of the atoms and is most important if such small clusters are investigated at room temperature, as in our experiment. They conclude that only small changes in the average bond length

occur when the size of the particles is varied, thus resolving contradictions of measurements of Cu clusters in Cu/C multilayers¹⁴ and matrix isolated clusters in Ar (Ref. 15) which were performed at different temperatures. In the case of the thicker samples investigated here, however, it is obvious that a *static* disorder is also present. Here, too, the position of the first maximum of the Fourier transform indicates an interatomic distance which is smaller by 0.02 Å than that of the bulk material, and the height of the first peak of the Fourier transform (which is related to the coordination number) is only 0.44 which is significantly lower than the value of 0.64 obtained for Cu foil. Our results clearly demonstrate that with the specific parameters selected for the sputtering of the Cu overlayers, significant deviations from an ideal homogeneous deposition exist. To obtain more perfect Cu layers, it may be necessary to cool the substrate or to anneal the sample to remove defects in the crystal structure.

Those measurements, therefore, demonstrate that it is possible to perform real time structural evaluations on metal overlayers in the presence of *in situ* conditions which occur in a realistic multilayer manufacturing process. It is especially important that, due to the short

measuring times feasible with the combination of the QEXAFS technique and the grazing incidence geometry, it is possible to follow the evolution of sputter-grown films under clean uncontaminated conditions with only minor distortions. These results, therefore, also demonstrate a more general capability for studying surface structures as a function of thickness, time, or chemical conditions.

We want to thank E. R. Fought and B. L. Olsen for their help during the measurements at SSRL and for the design and construction of the *in situ* chamber which they did together with P. A. Waide. W. Drube, B. Lengeler, W. Niemann, and J. Wong made helpful comments on the manuscript. One of us (R.F.) is grateful to the Lawrence Livermore National Laboratory, especially to J. Wong, for hospitality and support during an extended stay. This work is supported in part at LLNL under U.S. Department of Energy Contract No. W-7405-ENG-48. The experimental work was carried out at SSRL, which is operated by the U.S. Department of Energy, Division of Chemical/Material Sciences. The help of the staff of SSRL during setup of the QEXAFS experiment is gratefully acknowledged.

¹For an overview, see articles in MRS Bull. **15**, issue No. 2 (1990).

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