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Epitaxial growth of fcc Cr on Au(100)

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Synchrotron x-ray diffraction and anomalous dispersion measurements of 25Å Cr layers epitaxially grown on (100) Au surfaces indicate the presence of fcc Cr domains, while extended x-ray absorption fine-structure spectra are consistent with the usual bcc phase of Cr. Together these data suggest that the fcc phase is a major fraction of the larger epitaxial Cr domains, but that most Cr atoms are in a bcc environment with much smaller domain sizes. This unusual, epitaxially stabilized fcc Cr structure may be related to previously reported low-temperature resistance anomalies.

I. INTRODUCTION

The crystal structure of a heteroepitaxial layer may differ from the intrinsic structure of the material due to the registry imposed at the epitaxial interface. Epitaxially grown multilayers of Au-Pd-Au,[1] for example, have large in-plane stresses in the normally cubic Pd which produce a tetragonal distorted phase of Pd, which in turn have altered electronic and magnetic properties. This paper reports observations of an apparent metastable phase of Cr epitaxially grown on Au (100) substrates. Because the lattice constant of fcc Au [$a_0=4.078$ Å (Ref. 2)] is larger than the lattice constant of bcc Cr [$a_0=2.88$ Å (Ref. 2)] by almost exactly a factor of $\sqrt{2}$, the (100) planes of each element are square arrays of equal unit cell size (Fig. 1).[3] An ideal (100) Cr/Au interface should produce no in-plane stresses, with the transition from fcc to bcc only causing a $\sqrt{2}$ decrease in the interplanar spacing. The present x-ray diffraction investigation of the Cr structure yields strong evidence that in some cases the Cr overlayers maintain the Au fcc structure for a distance of 25 Å, corresponding to a Cr density which is a factor of $1/\sqrt{2}$ less than that found in the stable bcc Cr phase.

The possibility of epitaxial fcc Cr is of special interest because of low temperature resistance anomalies which have been observed on Cr/Au samples prepared in exactly the same manner as the x-ray specimens.[4,5] Abrupt changes in resistance have been interpreted as being the result of a superconducting transition. Since neither Au nor Cr are superconductors in their usual crystalline forms, a new structure such as the fcc Cr described here would appear to be required. An fcc structure would produce major changes in the electronic properties of Cr; a band structure calculation[6] for fcc Cr with a somewhat smaller lattice constant than that assumed here found a very high density of states at the Fermi level, which would enhance the possibility of superconductivity.

II. EXPERIMENTAL DETAILS AND RESULTS

Specimens were prepared by vapor depositing 2000 Å of Au onto cleaved (100) NaCl substrates, followed by 25 Å of Cr and a final 10 Å of Au to inhibit subsequent oxidation of the Cr layer. Fabrication details have been reported elsewhere.[7,8] Because a 25 Å thick Cr crystal is a very weak scatterer of x-rays, all measurements were performed at the Cornell High Energy Synchrotron Source (CHESS), where diffraction, EXAFS, and anomalous dispersion measurements were made at one high-intensity station.

Diffraction scans revealed weak bcc Cr reflections, corresponding to crystalline bcc domains oriented with the (100) planes parallel to the (100) Au surface as shown in Fig. 1(b). When scans were made of the principal [200] Au reflection normal to the surface, however, pronounced satellites were observed in the tails of the [200] Au Bragg peak. These satellites are equally spaced and appear to be coherent with the [200] reflection, i.e., the satellite wave vectors differ from the [200] wave vector by integer multiples of the satellite interval. In one specimen these satellites were observed out to at least fourth order, as shown in Fig. 2. The regular satellite separation of 0.25 Å^{-1} and the coherence with the Au [200]

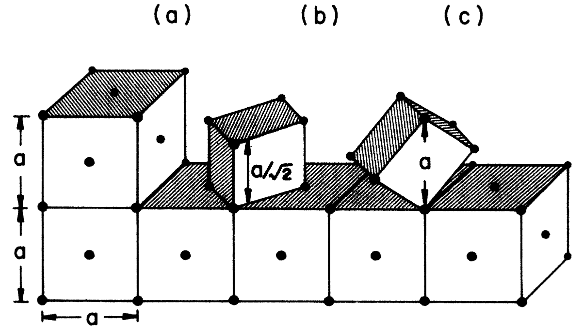

FIG. 1. Schematic representations of possible epitaxial arrangements of Cr on Au(100): (a) (100) fcc Cr on (100) fcc Au; (b) (100) bcc Cr on (100) fcc Au; (c) (110) bcc Cr on (100) fcc Au.

reflection indicate that crystalline domains exist in these specimens which have a uniform thickness of $d = 2\pi/0.25 \simeq 25$ Å, and which have the same interplanar spacing as the Au (100) planes.

These satellites are consistent with domains of Cr maintained in the fcc Au structure [Fig. 1(a)] for the entire 25 Å layer thickness.[9] This can be supported by examining the structure factor of this configuration, using the simple kinematic x-ray theory. Considering only the z-components normal to the (100) surface, the structure factor of a crystal made up of N planes of Au and M planes of Cr with the same interplanar spacing $\mathbf{a}_0 = a_0\hat{\mathbf{z}}$ is

$$S(k) = \sum_{n=0}^{N-1} f_{\mathrm{Au}}(k)e^{-inka_0} + \sum_{n=N}^{N+M-1} f_{\mathrm{Cr}}(k)e^{-inka_0}, \qquad (1)$$

where k is the scattering wave vector in the z direction. The scattered intensity is proportional to the square of the structure factor,

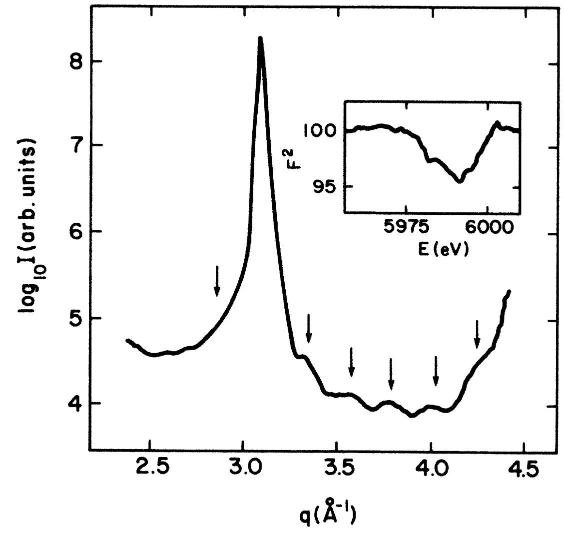

FIG. 2. Diffracted intensity vs scattering wave vector showing satellites about the Au [200] reflection, indicated by arrows. Inset: Diffracted intensity vs incident x-ray energy for the second high-order satellite, normalized to 100% away from the Cr K absorption edge at 5988 eV.

$$S^2(k) = f_{\mathrm{Au}}^2\left[\frac{\sin(\frac{1}{2}Nka_0)}{\sin(\frac{1}{2}ka_0)}\right]^2 + 2f_{\mathrm{Au}}f_{\mathrm{Cr}}\cos[\tfrac{1}{2}(N+M)ka_0]\left[\frac{\sin(\frac{1}{2}Mka_0)\sin(\frac{1}{2}Nka_0)}{\sin^2(\frac{1}{2}ka_0)}\right] + f_{\mathrm{Cr}}^2\left[\frac{\sin(\frac{1}{2}Mka_0)}{\sin(\frac{1}{2}ka_0)}\right]^2 . \qquad (2)$$

For $N \gg M$, the scattering is dominated by the f_{Au}^2 term. The Bragg peaks occurring at $ka_0 = 2n\pi$ are separated by N satellites, which cannot be experimentally resolved for large values of N. The f_{Cr}^2 term also produced Bragg peaks at $ka_0 = 2n\pi$, but with intensities reduced by $(Mf_{\mathrm{Cr}}/Nf_{\mathrm{Au}})^2$. More importantly, the M satellites separating the Bragg peaks are easily resolvable for small M. Substituting the 25 Å Cr layer thickness for Ma_0 determines a satellite spacing of $\Delta k = 2\pi/Ma_0 \simeq 0.25$ Å^{-1}, which is in good agreement with the data (Fig. 2).

Other possibilities must be considered before concluding that a greatly expanded fcc phase of Cr is responsible for the data. If the 10 Å outer layer of Au were instead close to 25 Å due to malfunction of the quartz crystal thickness monitor, for example, a similar satellite profile could be obtained. The unique, continuous energy spectrum of synchrotron radiation allowed this hypothesis to be tested by anomalous dispersion measurements. Satellite peak intensities were observed as the incident x-ray energy was scanned through the Cr K absorption edge at 5.988 keV. Bragg peak intensities are proportional to the square of the atomic scattering factor f, which can be written as

$$f = f_0 + f' + if''$$

where f_0 is the high frequency limit of f, f' is the dispersion correction, and f'' is the contribution due to absorption. Anomalous dispersion arising from the resonant interaction of the x-rays with the Cr K shell electrons[10–12] should cause a reduction in the intensity just below the K absorption edge as f' becomes large and negative.[13] This reduction was observed in the satellite intensity measurements, as illustrated in Fig. 2 (inset). The intensity due to substrate peaks as well as background regions between Bragg peaks and far removed from the satellites showed no changes correlated with the Cr K edge, whereas the bcc Cr peaks exhibited the same pronounced dip. These results confirm that the satellites must be due to scattering from Cr atoms.

Another possible cause of the satellites is the existence of bcc Cr domains with a [110] orientation normal to the surface, since the bcc (110) interplanar spacing of Cr is the same as the fcc (200) interplanar spacing of Au [Fig. 1(c)]. Such domains, however, would also produce other {110} reflections in off-normal directions which should be readily detectable. A thorough search revealed only peaks which were much weaker than the satellites and which also exhibited no dispersion at the Cr K edge. (These weak diffraction features were probably due to {200} reflections from very small misoriented Au domains.) This null result leaves [110] bcc Cr domains as an unlikely explanation for the satellite data.

After establishing Cr atoms as the source of the satellite scattering and ruling out [110] bcc Cr domains, the presence of an expanded fcc Cr phase initiated at the fcc Au epitaxial interface remains as the most plausible explanation. While perhaps it would not be surprising if the interplanar spacing of one or two Cr monolayers would be perturbed by an epitaxial Au(100) interface, the expansion by a factor of $\sqrt{2}$ for a distance of 25 Å would appear to yield a highly unstable structure. The specimens were maintained at liquid nitrogen temperatures after fabrication to inhibit the transformation of such metastable phases, although the satellite peaks were still observed after several days of x-ray measurements at room temperature.

A factor which may contribute to the stability of a metastable fcc phase is the presence of a small amount of interdiffused Au, coming from either the substrate or the thin overlayer. Although anomalous dispersion showed that Cr atoms made a significant contribution to the satellite scattering, the presence of Au in the Cr layer can by no means be ruled out. We also note that there is at least one intermetallic compound[14] reported for the Au-Cr binary alloys, a cubic structure with 20% (atomic) Cr and a lattice constant of 4.04 Å. Such a compound could be responsible for the observed satellites if two conditions are satisfied: The structure has the same lattice constant as the Au substrate, and the diffracting domains have a uniform thickness of 25 Å. The number of Cr atoms per unit volume in the intermetallic phase, however, is only about 15% of the density in the stable bcc Cr phase. It would not seem likely that a Cr film would react to form the intermetallic phase with the reduced Cr density while retaining its 25 Å thickness.

We believe that a metastable phase of fcc Cr with the same lattice constant as fcc Au is the most plausible explanation of the observed data. Direct determination of this structure from the positions of the Bragg peaks is impossible, because of the perfect coincidence with the Au substrate peaks. Alternative hypotheses based on a 25 Å Au overlayer or [110] bcc Cr epitaxy have been ruled out.

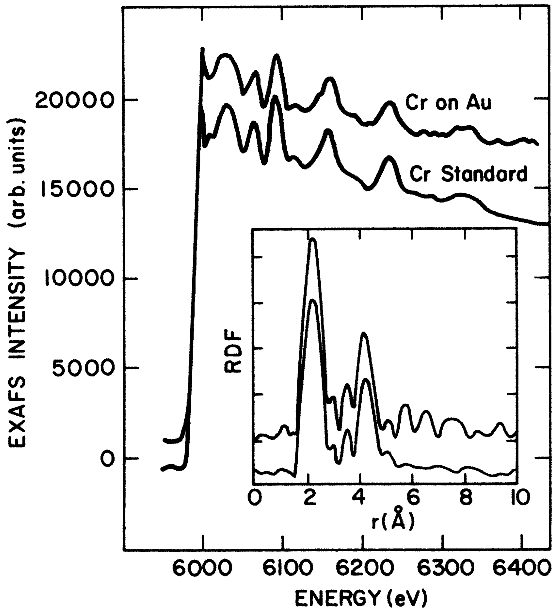

FIG. 3. Fluorescence EXAFS spectrum for 25 Å Cr on Au (upper curve), and transmission EXAFS for a pure Cr foil (lower curve). Inset: Fourier transforms of EXAFS data, approximately corresponding to radial distribution functions for the Cr/Au sample (upper) and the Cr foil (lower).

As mentioned above, the experimental station at CHESS permitted convenient measurements of EXAFS spectra. Figure 3 shows a Cr fluorescence EXAFS spectrum from the specimen with the most pronounced satellite peaks, along with transmission EXAFS from a standard Cr foil. The Fourier transforms of these data are also shown, which yield curves roughly equivalent to radial distribution functions.[15] Although there may be some effect due to the presence of fcc Cr and the Cr/Au interfaces (in addition to the somewhat poorer signal-to-noise ratio for the Cr/Au data), the principal features of the transforms are nearly identical, indicating that most Cr atoms are in a bcc environment. The diffraction data from the same specimen, however, revealed greater peak intensity from the fcc satellites than from the bcc Cr reflections. This apparent conflict between EXAFS and diffraction results can be explained by noting that diffraction is primarily sensitive to domains with long range order, while EXAFS senses the immediate local environment of the absorbing atom. For this specimen, the diffraction data indicate that the fcc phase is a major fraction of the large epitaxial Cr domains, while EXAFS reveals that most Cr atoms are in bcc environments, presumably fine-grained.

III. DISCUSSION

A thorough study of the epitaxy and electronic structure of Cr grown on Au (100) was conducted by Zajac *et al.*[16] Their samples differed from ours primarily in that Cr was deposited at an elevated temperature to improve the epitaxy, as monitored by low energy electron diffraction (LEED). Photoemission measurements showed that the electronic properties of the epitaxial Cr layer were closely related to those of bcc Cr. Although their LEED measurements were generally consistent with either fcc or bcc structures, the usual bcc Cr structure was adequate to explain their LEED, photoemission, and electron energy loss data. They also extend a hypothesis for the observed superconductivity in Cr/Au systems based on the presence of amorphous or highly disordered Cr. We agree with those authors that a reconciliation of our results requires an alternative explanation of the observed fcc Cr satellites. We have described above how the most likely alternatives fail to explain the x-ray data.

IV. CONCLUSIONS

These measurements indicate the existence of an expanded fcc phase of Cr at an epitaxial Au(100) interface, extending for a thickness of 25 Å for the samples prepared for this study. We cannot rule out the possibility that some Au may have diffused into the Cr layer during film growth, which may stabilize the fcc phase. By combining diffraction, anomalous dispersion, and EXAFS data, we conclude that a preponderance of the Cr is probably in a microcrystalline bcc environment, but that substantial epitaxial fcc Cr domains have been formed.

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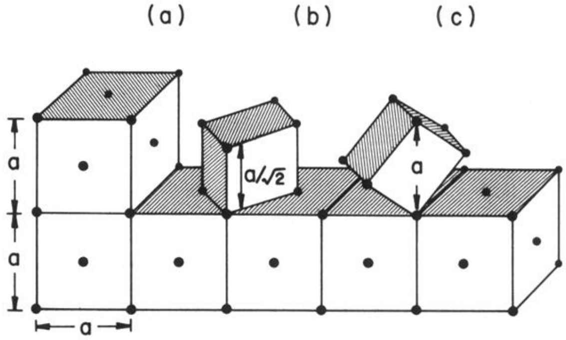

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