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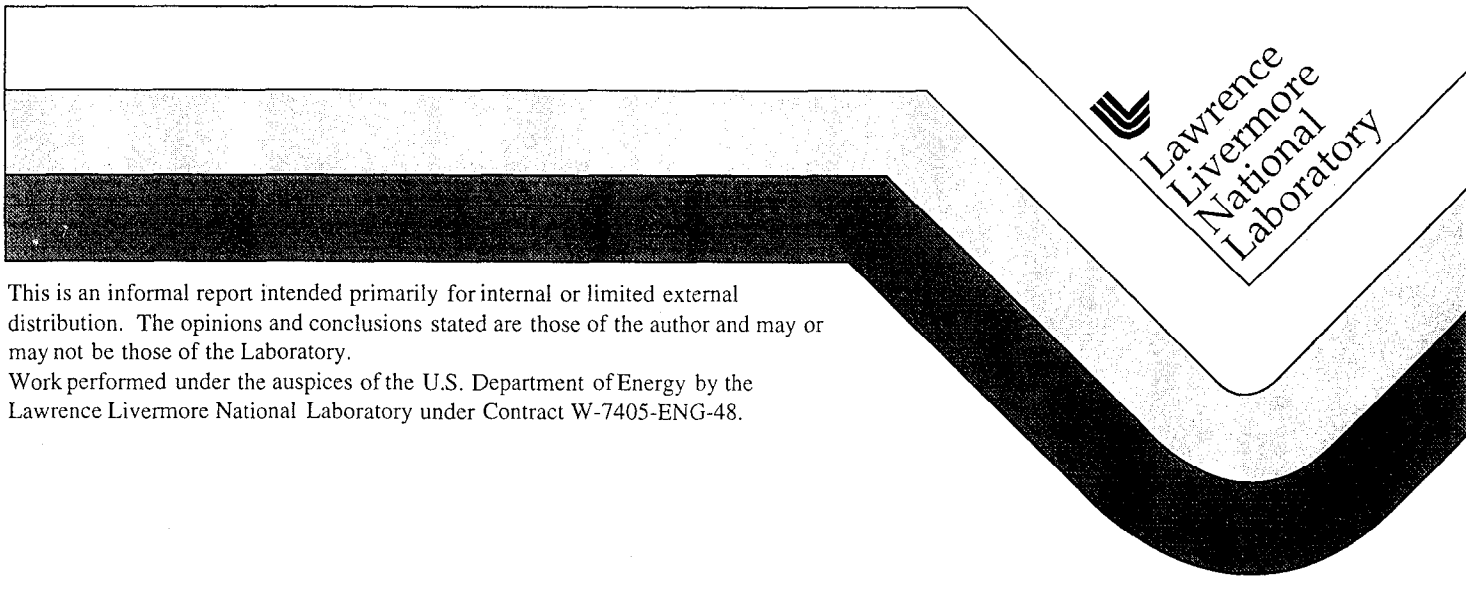

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INTERFACIAL ELECTRONIC CHARGE TRANSFER AND DENSITY OF STATES IN SHORT PERIOD Cu/Cr MULTILAYERS

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INTRODUCTION AND BACKGROUND

Nanometer period metallic multilayers are ideal structures to investigate electronic phenomena at interfaces between metal films since interfacial atoms comprise a large atomic fraction of the samples. The Cu/Cr binary pair is especially suited to study the interfaces in metals since these elements are mutually insoluble, thus eliminating mixing effects and compound formation and the lattice mismatch is very small. This allows the fabrication of high structural quality Cu/Cr multilayers that have a structure which can be approximated in calculations based on idealized atomic arrangements. The electronic structure of the Cu and the Cr layers in several samples of thin Cu/Cr multilayers were studied using x-ray absorption spectroscopy (XAS). Total electron yield was measured and used to study the white lines at the Cu L_2 and L_3 absorption edges. The white lines at the Cu absorption edges are strongly related to the unoccupied d-orbitals and are used to calculate the amount of charge transfer between the Cr and Cu atoms in interfaces. Analysis of the Cu white lines show a charge transfer of 0.026 electrons/interfacial Cu atom to the interfacial Cr atoms. In the Cu XAS spectra we also observe a van Hove singularity between the L_2 and L_3 absorption edges as expected from the structural analysis. The absorption spectra are compared to partial density of states obtained from a full-potential linear muffin-tin orbital calculation. The calculations support the presence of charge transfer and indicate that it is localized to the first two interfacial layers in both Cu and Cr.

EXPERIMENT

All the Cu/Cr multilayer films studied were fabricated by DC magnetron sputtering. Base pressures were typically 10^{-7} torr; argon sputter gas at a pressure of about $2x10^{-4}$ torr was used. In these samples all layers were designed to have an integer number of monolayers (ML), where the thickness of a monolayer was calculated using bulk structures (FCC and BCC). Expected growth directions ([111]-Cu and [110]-Cr) of the constituent elements were also assumed. Table I presents the samples prepared for this study and their structural characteristics.

Table I. Cu/Cr Bilayers of Varying Periods

Bilayer Thickness of Cu/Cr [ML]	Bilayer Thickness of Cu/Cr [Å]	Bilayer Period [Å]	% Cu in bilayer
		Cr (110)	0
3/6	6.25/12.89	19.14	32.6
6/8	12.53/16.31	28.84	43.4
3/3	6.25/6.44	12.69	49.2
6/6	12.53/12.89	25.42	49.3
8/8	16.66/16.31	32.97	50.5
5/5	10.43/10.19	20.63	50.57
8/6	16.66/12.89	29.55	56.4
6/3	12.53/6.44	18.97	66.1
		Cu (111)	100

Table I. Set of Cu/Cr samples studied. The samples were designed with the layer thicknesses shown and fabricated using independently measured Cu and Cr deposition rates.

Total Electron Yield (TEY) x-ray absorption experiments were conducted at Beamline 8-2 of the Stanford Synchrotron Radiation Laboratory (SSRL). Data was acquired after annealing the sample at progressively higher temperatures in order to remove oxygen contamination from the sample surface. An optical pyrometer monitored the annealing temperature which was kept below 600 C. Details of the experiment setup are presented in another paper[1].

RESULTS AND DISCUSSION

A major complicating factor in x-ray absorption is oxide contamination, which occurs when samples are in ambient atmosphere. Here, scans were taken after progressively higher temperature anneals to determine just when the oxide signals[4] disappeared. For Cu_5/Cr_5, the data taken at 300 C and higher temperature anneals removed the oxide signatures. At 300 C, features not directly related to the oxide were preserved. Higher temperature anneals distorted these features. Figure 1 shows how the Cu spectrum evolves upon annealing, starting with a slight shoulder due to the CuO and a relatively large absorption peak due to the Cu_2O. There is also one broad peak between the L_3 and L_2 absorption edges, indicative of a BCC symmetry point, where the DOS increases (van Hove singularity). The spectrum change is continued by the disappearance of the shoulder and a slight decrease in intensity of the absorption peak at about 300 C. Higher temperatures show the spectrum gradually becoming more like that for annealed Cu_5/Cu_5 or bulk Cu, and at the final annealing temperature of 500 C, the spectrum clearly shows the three peaks in the L_3 edge that is the distinct signature for FCC Cu.

On the DOS calculations, two methods were used.[5] The first is the full-potential linear muffin-tin orbital (FP) method[6,7], which employs a localized basis that provides a convenient framework for projecting out individual atom- and angular momentum-resolved partial densities of states (DOS). The partial DOS were calculated using a Mulliken decomposition as described by Hoffman[8] and McMahan[9] . The FP method makes no shape approximation to the crystal potential, whereas methods based on the atomic sphere approximation (ASA) assume that the potential is spherically symmetric about each atom. The second method, although less accurate, is the atomic sphere approximation, linear muffin-tin potential method, which works reasonably well for close-packed systems and provides an alternate means of obtaining the partial DOS. Therefore, ASA calculations were carried out to cross-check the FP results. The ASA method is the one used by Ebert, et. al.[10] in their study of $L_{2,3}$ x-ray absorption of Cu multilayers.

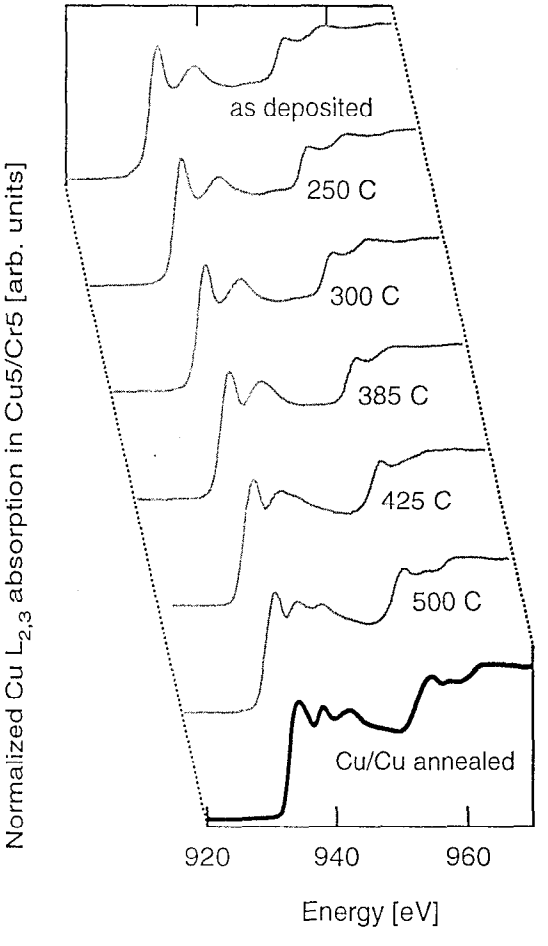

Figure 1. Cu spectra from Cu_5/Cr_5 as it is annealed progressively to higher temperatures. For clarity, the axes are shifted for each spectrum. For comparison, the annealed Cu_5/Cr_5 is shown at the bottom.

Integrating the DOS up to the Fermi energy gives 11 electrons, but integrating just the d-band DOS gives 9.89 electrons instead of the 10 electrons normally associated with the full d-band of Cu. This

amount of unoccupied d-states make is possible to observe the white lines in the near-edge x-ray absorption of Cu.

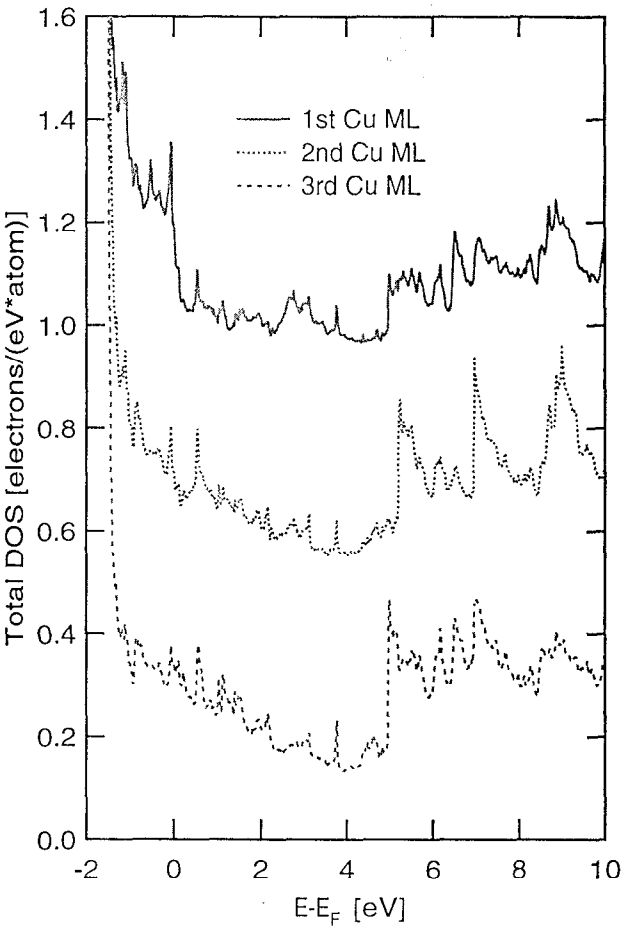

Figure 2. Total DOS of the individual Cu monolayers (plots are offset by 0.4 and 0.8 in the vertical axis for clarity.).

In addition to bulk Cu, the total DOS of the multilayer Cu_5/Cr_5 was calculated using the FP method, where the 5 Cr monolayers were taken to have the same structure and lattice parameter as bulk Cr (BCC, a=2.884 Å). The 5 Cu monolayers, however, were taken as BCC with a lattice parameter of 2.829 Å, leading to a 2% lattice mismatch at the interface. The x-ray diffraction data of Cu_5/Cr_5 other unpublished results[11] point to a BCC Cu structure and the specific lattice parameter value.

From the calculations, it is possible to separate the total DOS of individual monolayers in the multilayer in addition to computing the total DOS for the whole multilayer. Shown in Figure 5 are the total DOS for each of the Cu monolayers in the multilayer — the first Cu monolayer is the one right next to Cr, and the second Cu monolayer is the second closest monolayer to the Cr. Integrating the total DOS of the first Cu monolayer gives 10.85 electrons/atom, which is less than the full 11 electrons/atom expected for bulk Cu. The second Cu monolayer has 10.89 electrons/atom, which is also less than for bulk Cu, but the third Cu monolayer has 11 electrons/atom, which is identical to the value for bulk Cu. The same calculations are done for the Cr monolayers, and the results show that the Cr monolayer next to Cu has 6.17 electrons/atom, the next closest has 6.07 electrons/atom, and the third closest has 6.01 electrons/atom, which is identical to the 6 electrons/atom expected for bulk Cr.

The change in charge count relative to the bulk is greatest for the monolayers right at the interface, and the evidence point to charge transfer flow from Cu to Cr — the first Cu monolayer loses 0.15 electrons/atom, while the first Cr monolayer gains 0.17 electrons/atom. The second monolayers also show a net charge transfer — Cu gains 0.11 electrons/atom, and Cr loses 0.07 electrons/atom.

Figure 2 shows that in the first Cu monolayer, there is a sharp rise in the DOS at the Fermi energy. This is possibly due to electron states that characterize a bond introduced at the interface between Cu and Cr, and is where some of the charge transfer occurs. It is reasonable to expect that when there is charge

transfer between Cu and Cr at an interface, the transferred charge gets localized close to the Fermi level since it is at the outermost electron levels where the interaction takes place. The same type of feature in the DOS of the first Cr monolayer is observed and is even more pronounced. In the region of the Fermi energy there is a sharp peak, which decreases for the second Cr layer, and finally disappears for the third Cr layer. The progressive weakening of the peak as the Cr monolayer gets farther from Cu indicates that it is associated with the interface. The figure also shows that in the unoccupied states from the Fermi level to about 2 eV above it, the general shape of the DOS remains the same. As previously discussed, the first Cu ML has a shoulder right below the Fermi energy. But with a typical average difference (absolute value, point-to-point) of 0.03, the curves are similar for all three monolayers in that energy region. In another study[11], we describe and use a technique to calculate the charge transfer from the x-ray absorption. The method uses the fact that the general shape of the DOS from the Fermi energy to about 2 eV above it is similar for the bulk and the monolayers. There, the calculated charge transfer was 0.026 electrons per interfacial atom.

SUMMARY

In unannealed samples of Cu/Cr of varying period and Cu composition, the x-ray diffraction scans show one reflection peak, indicating one structure throughout the multilayer. In the Cr rich samples, the BCC Cu has a lattice parameter nearly equal to that of Cr. In the Cu_5/Cr_5 sample, annealing to 500 C decomposes the multilayers into bulk-like Cu and Cr. TEM shows well-defined layering of Cu and Cr in a columnar structure in as deposited samples. Analysis of the XAS data show a charge transfer of about 0.03 electrons per interfacial atom, which we believe provides the enhanced bonding at the interface and promotes wetting of Cr by Cu.

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