THE DETERMINATION OF INTERFACIAL STRUCTURE AND PHASE TRANSITIONS
IN Al/Cu AND Al/Ni INTERFACES BY MEANS OF SURFACE EXTENDED X-RAY
ABSORPTION FINE STRUCTURE

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ABSTRACT

Surface extended x-ray absorption fine structure (SEXAFS) was used to investigate the interfacial conditions of Al/Cu and Al/Ni shallow buried interfaces. Previous studies using glancing angle extended x-ray absorption fine structure, x-ray reflectivity, photoemission, and SEXAFS produced conflicting results as to whether or not the interfaces between Al and Cu and Al and Ni were reacted upon room temperature deposition. In this study polycrystalline bilayers of Al/Cu and Al/Ni and trilayers of Al/Cu/Al and Al/Ni/Al were deposited on tantalum foil at room temperature in ultra high vacuum and analyzed to evaluate the reactivity of these systems on a nanometer scale. It became overwhelming apparent that the interfacial phase reactions were a function of the vacuum conditions. Samples deposited with the optimum vacuum conditions showed reaction products upon deposition at room temperature which were characterized by comparisons to standards and by least squares fitting to be CuAl_2 and NiAl_3 respectively. The results of this study showed that the reacted zone thicknesses were readily dependent on the deposition parameters. For both Al on Cu and Al on Ni as well as the metal on Al conditions 10Å reaction zones were observed. These reaction zones were smaller than that observed for bilayers of Al on Cu (30Å) and Al on Ni (60Å) where deposition rates were much higher and samples were much thicker. The reaction species are evident by SEXAFS, where the previous photoemission studies only indicated that changes had occurred. Improved vacuum conditions as compared to the earlier experiments is primarily the reason reactions on deposition were seen in this study as compared to the earlier SEXAFS studies.

INTRODUCTION

The nature of aluminum/transition metal interfaces has been of interest for a number of years since interfaces of this type play such a significant role in semiconductor devices and metal matrix composites. Interfaces of Al/Cu and Al/Ni have been studied where the interface structure and phase transitions were of primary interest [1-10]. Previous studies using glancing angle extended x-ray absorption fine structure, x-ray reflectivity, photoemission, and surface extended x-ray absorption fine structure produced conflicting results as to whether or not the interfaces between Al and Cu and Al and Ni were reacted upon room temperature deposition. Studies using glancing angle x-ray absorption fine structure (XAFS) and x-ray reflectivity of thin film bilayers of Al/Cu, showed that the interface was reacted when deposited at and below room temperature [1-4]. The reacted region was estimated to be 20-30Å in thickness. The glancing angle techniques are suited for studying Al on Cu but lack in interfacial sensitivity when the overlayer is the denser layer. It was further recognized that the first phase to form was the Al-rich CuAl_2 phase and that the presence of interfacial oxygen impeded this reaction until higher temperatures were reached. For further investigation of the interface and to investigate the nature of Cu and Ni on Al interfaces, additional experiments were necessary. For this end, both photoemission and SEXAFS were used. A photoemission study where Al/Cu was analyzed, showed that changes occurred to the base metal (Cu) electron energy distribution curve (EDC) as Al was deposited on it at room temperature [5]. This confirmed the reaction for Al on Cu but since Cu on Al was not studied this result was still not known.

For Al/Ni interfaces similar studies using glancing angle EXAFS, photoemission, and reflectivity were conducted. Al on Ni bilayer interfaces were reacted upon deposition, where NiAl_3 was the first phase formed, when the deposition was in ultra high vacuum and the thin film layers were clean. Interfaces exposed to oxygen were not reacted as studied by glancing angle XAFS and x-ray reflectivity [6-8]. The photoemission study of Ni-Al interfaces

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conducted by Ruckman et al. [9] showed changes to occur in the EDC of the Al when Ni films were deposited on it. These were the first results for metal on Al. Similar results were seen for Al deposited on Ni. SEXAFS would be used to study both Al on metal and metal on Al interfaces where the reaction products could be determined as opposed to only seeing changes occur as for the photoemission studies [10]. The initial finding of the SEXAFS study showed the Al/Cu and Al/Ni as-deposited interface conditions to differ in whether they were reacted or not. It was observed that Al on Cu reacted and Cu on Al did not. In the preliminary study, the Al/Ni and Ni/Al interfaces studied did not react on deposition. These results did not agree with the photoemission data where both systems showed changes to occur in the EDC's on deposition. Recall that Cu on Al was not studied by photoemission.

The present study using SEXAFS is a more extensive investigation of Al/Cu and Al/Ni interfaces where extreme care was taken to acquire optimum ultra high vacuum conditions before preparing the samples. The results show that for both systems Al/transition-metal interfaces show initial intermixing and reaction upon deposition at room temperature and that this occurs for the thin film cases where Cu and Ni are deposited on aluminum as well. It became clear that the initial reaction upon deposition was greatly effected by the contaminant nature of the interface. The results are in full agreement with that from the glancing angle XAFS and reflectivity studies and that from the photoemission studies and supersede the previous SEXAFS studies.

EXPERIMENTAL PROCEDURE

As in the preliminary study [7] thin polycrystalline films of aluminum and either copper or nickel were deposited on tantalum foil following a high temperature degassing of the foil. The samples were either metal on Al bilayers or Al-metal-Al trilayers where the metal was Cu or Ni. The initial layers of Al were deposited as thick ($\sim 100\text{\AA}$) layers to provide a good thick base with a likely smooth surface. The metal layers were deposited in the bilayer cases where the thicknesses were built up in $10\text{\AA}$ intervals to prevent heating during deposition due to prolonged deposition. In some cases thicker layers were laid down for comparison. Thicknesses were measured by a oscillating crystal thickness monitor in the SEXAFS chamber. The vacuum system after baking reached a starting level of 3×10^{-10} torr which was a significant improvement over the preliminary experiments where the starting vacuum was between $2-4 \times 10^{-9}$ torr. The vacuum remained in the 10^{-10} to low 10^{-9} torr range during deposition which was also an improvement over the earlier experiments. The time between deposition was shortened from 10-15 minutes to less than eight minutes. Cu and Ni were evaporated using 99.999% pure source materials from Al_2O_3 coated W boats. Al was deposited using 99.999% pure source material from an effusion cell with a BN crucible. Deposition rates were between 10 and $20\text{ \AA/min}$. The sources were degassed numerous times before the first samples were deposited and were repeatedly degassed before the deposition of each sample. All samples were deposited on the same tantalum substrate and were flashed off at high temperature following the SEXAFS analysis. At that time the next sample could be deposited. Auger electron spectroscopic (AES) analysis of these films showed the deposited layers to be very clean with no signs of extraneous contamination. The samples investigated in this study are summarized in Table 1 shown below.

The SEXAFS ultra high vacuum deposition/analysis chamber was wheeled into the National Synchrotron Light Source (NSLS) X-11A beamline hutch, baked out and allowed to cool before starting the experiments. The sources were degassed during the cool down period. The SEXAFS experiments of the Cu and Ni K-edges were conducted in the total electron yield mode in the SEXAFS UHV chamber. In the previous experiments [7] scans were conducted using both a grid configuration and a channeltron. In this research only the grid total electron yield configuration was used since the data showed relatively low noise levels. Most of the scans had single point glitches which were easily removed. SEXAFS scans were run less than ten minutes after the each sample was made. A number of scans were run on each sample and summed before SEXAFS analysis. The experimental data scans were deglitched by a single point removal method, the pre-edge and edge background were fit and subtracted to obtain the XAFS $\chi(k)$.

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Table 1

Al-Cu and Al-Ni Bilayers (BL) and Trilayers (TL)

<u>Designation</u>	<u>Sample description</u>
Cu10BLa and b*#	10Å Cu on 100Å Al.
Cu20BL	20Å Cu on 100Å Al w/Cu deposited in two 10Å layers.
Cu30BLa	30Å Cu on 100Å Al w/Cu deposited in three 10Å layers.
Cu30BLb	30Å Cu on 100Å Al w/Cu deposited in one 30Å layer.
Cu30TLa and b	100Å Al/30Å Cu/30Å Al.
Cu50TL	100Å Al/50Å Cu/30Å Al.
Ni10BLa and b	10Å Ni on 100Å Al.
Ni20BLa	20Å Ni on 100Å Al w/Ni deposited in two 10Å layers.
Ni20BLb	20Å Ni on 100Å Al w/Ni deposited in one 20Å layer.
Ni30BL	30Å Ni on 100Å Al w/Ni deposited in three 10Å layers.
Ni30TLa,b, and c	100Å Al/30Å Ni/40Å Al.

*Samples with a, b, and c indicates that these samples were deposited more than once.

#All samples were prepared with vacuum conditions in the 10^{-9} - 10^{-10} torr range with times between depositions of less than eight minutes.

For comparison, transmission XAFS of CuAl, CuAl₂, NiAl, NiAl₃, Cu and Ni were run. This data serves as standards for comparing with the chi data. Previous glancing angle EXAFS and SEXAFS studies showed that interface mixing and reactions are easily distinguished when comparing to standards of Cu, CuAl, CuAl₂, Ni, NiAl, and NiAl₃ [1-4, 6-8, 10]. An interface that is not reacted strongly resembles that of the metal phase (Cu or Ni). In some cases the amplitude of the XAFS will be reduced due to disorder from grain boundaries or from grain boundary diffusion of the metal into the Al layer. When an interface is reacted the $\chi(k)$ is altered toward lower k. A partially reacted interface (either very short range or incompletely reacted across the interface) will have features in low k that approach that of the metal-Al phases (where the metal is either Cu or Ni) and features in high k that resemble that of the metal phase. Interfaces that exhibit intermixing significantly resemble that of the metal-Al phases yet may be reduced in amplitude for reasons already mentioned. This approach is well accepted and will be the primary basis for indicating reactions. Results will be presented in terms of $\chi(k)$ and $k\chi(k)$ in this paper. To further support the findings based on $\chi(k)$ results near edge data for some of the samples and standards will also be given. Near edge data shows from a comparative basis whether or not the interface is reacted or if the sample resembles that of the parent metal. Discussion will also be given as to findings from least squares fitting of the SEXAFS data. This will also support the findings shown here as $\chi(k)$ and $k\chi(k)$.

RESULTS AND DISCUSSION

The preliminary experiments using SEXAFS [10] showed that the Al on Cu reacted but that the Cu on Al did not. It was also observed that the Al on Ni and the Ni on Al were not initially reacted even though glancing angle EXAFS and photoemission had shown otherwise. The earlier SEXAFS data had samples prepared in a vacuum chamber with a base pressure of $2-4 \times 10^{-9}$ torr. That played a significant role in the condition of the transition zone of the Al-

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metal interfaces. The present SEXAFS experiments were conducted where the starting vacuum conditions were an order of magnitude better (3×10^{-10} torr).

Figure 1 shows the results from SEXAFS analysis of Cu foil, two different samples of 10Å of Cu on Al (Cu10BLa and b), CuAl₂, and CuAl. The first Cu/Al sample deposited (Cu10BLa) was slightly reacted where the contribution from Al neighbors can be seen at low k. At higher k the $\chi(k)$ has features like that of Cu. Cu10BLb is further reacted and the Al neighbor contributions to the spectrum are overwhelming to the point that there are no indications of remaining Cu. Figure 2 shows similar results for the Ni on Al samples where the $\chi(k)$'s for Ni foil, two samples of 10Å of Ni on Al (Ni10BLa and b), NiAl₃ and NiAl can be seen. Here it is observed that the Ni on Al interfaces are reacted upon deposition. Also for the Ni on Al samples, the first sample is less reacted than the second. For both the Ni and Cu cases it is expected that the continued degassing of the source materials prior to deposition of the samples was the reason for this result.

Figure 3 for the Ni on Al samples shows that when an additional 10Å of Ni is deposited, where the sample becomes Ni20BL, the spectrum is dominated by the Ni-Ni contributions and compares with the Ni foil and no longer with the NiAl₃. Similar results were observed for Cu on Al. For both Cu on Al and Ni on Al the reaction is limited to less than 10Å as compared to that seen by glancing angle EXAFS for Al on Cu where the reaction was considered to be 20-30Å. The reaction seen for Al on Ni was seen to be as much as 60Å. For the specimens studied in this research the deposition times and deposition rates are significantly less than of the thick bilayers used in the glancing angle XAFS and x-ray reflectivity studies. The sensitivity is better for both SEXAFS and glancing angle XAFS than that of Rutherford Backscattering spectroscopy (~100Å) as used by other investigators in similar studies [11-12].

The interface of the Al on the metal were also studied using SEXAFS. The results from the Al/Cu/Al samples (Cu30TLa and b and Cu50TL) can be seen in Figure 4 where the Cu30TL samples are strongly reacted and the Cu50TL sample shows a contribution from Cu-Cu interactions. This indicates that the Al/Cu reactions are very shallow for both Cu on Al and Al on Cu. As observed in Figure 3, when more metal is deposited to the metal layer on the metal on Al sample, the metal-metal contributions start to dominate. This effect is not observed for the Cu30TL samples since the overlayer Al on Cu reacted interface XAFS dominates the spectrum. As for the Cu50TL sample the overlayer Al/Cu interface is reacted yet the presence of more Cu is observed in the XAFS. Similar results were observed for the Al/Ni/Al trilayers (Ni30TLa, b, and c).

For the thin film samples significant amplitude reductions can be seen, and as the thin films get thicker, these reductions go away. This is seen in the SEXAFS experiments and in Figure 3 for the Ni20BL sample. There are two possible reasons at this time why the amplitude reductions are seen, that being metal diffusion into the Al grain boundaries which produce little XAFS due to a high degree of disorder in the grain boundary environment, and a high degree of disorder in the thin metal film due to the small grain size [6].

As in the previous SEXAFS study of the Al/Cu and Al/Ni as deposited thin films, x-ray absorption near edge structure (XANES) results will be presented to confirm the conditions of the interface systems which were shown in the $\chi(k)$ results. Figure 5 is a plot of the total electron yield vs. photon energy (XANES) for Cu10BLa, Cu30TLb, Cu50TL, and Cu foil. The scans from the Cu10BL and Cu30TL specimens strongly resemble each other. Previous experiments have shown that these edge features are similar to that of CuAl₂ where the knee and edge peak features are washed out as compared to that for Cu [10]. The scan for Cu50TL resembles that of Cu where the knee and edge peak features are observable. The XANES for the Cu50TL specimen is dominated by the Cu-Cu contributions. The Al-Ni results are similar although the edge features for Ni are not as pronounced as that seen for the Cu edge. To support the findings as have been seen for the Al-Ni specimens least squares fitting using the EXCURVE program have been conducted [13]. Table 2 shown below is a compilation of preliminary EXCURVE results. For the Ni10BLb, Ni20BLa, Ni20BLb, and Ni30BL specimens two shell fits were run where Ni and Al neighbors were considered. If the films are Ni + NiAl₃ then $n(\text{Ni})/12 + n(\text{Al})/8 = 1$. It appears that for the thicker films the Ni-Al distance may be increasing closer to that of NiAl (2.50Å) although the errors become larger (as seen in the value of the Debye-Waller constant) for the small Al contributions. These results are all consistent with an approximately 10Å reacted region which is much small than the case of Al on Ni when deposited as a thick bilayer and analyzed by glancing angle XAFS and x-ray reflectivity.

Figure 1. SEXAFS $\chi(k)$ also labeled $\chi(k)$ for Cu Foil, Cu10BLa and b where (a) is slightly reacted and (b) is further reacted, CuAl₂ and CuAl. The slightly reacted sample has features similar to Cu Foil and the reacted sample is similar to CuAl₂.

Figure 2. SEXAFS $\chi(k)$ also labeled $\chi(k)$ for Ni Foil, Ni10BLa and b, NiAl₃, and NiAl. Ni10BLa is slightly reacted and has features similar to Ni Foil. The Ni10BLb sample is further reacted and is similar to NiAl₃.

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Figure 3. SEXAFS $k\chi(k)$ for NiAl_3 , 10Å of Ni on 100Å Al (Ni10BL), 20Å Ni on 100Å Al (Ni20BL), and Ni Foil. For the Ni20BL the Ni-Ni contributions start to dominate.

Figure 4. SEXAFS $\chi(k)$ also labeled $\chi(k)$ for Cu30TLa, Cu30TLb, and Cu50TL. The interface reaction is dominate for the Cu30TL samples yet Cu-Cu contributions are evident in the Cu50TL sample.

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Figure 5. Comparison of XANES of Cu10BLb, Cu30TLa, Cu50TL and Cu foil where Cu10BLb and Cu30TLa are very similar and favor the CuAl₂ phase. Cu50TL is dominated by Cu-Cu contributions and is similar to that of Cu foil.

Table 2

Least Squares Fitting Results for 10, 20, and 30 Å of Ni on Al as compared to Ni and NiAl₃

Specimen	Neighbor Type and no.	1st Shell Dist. (Å)	Debye-Waller
Ni	Ni, n = 12	r = 2.49	ss = .0055*
NiAl ₃	Al, n = 8	r = 2.46	ss = .007
Ni10BLb	Al, n = 7.2	r = 2.46	ss = .0145
	Ni, n = 1.1	r = 2.48	ss = .0065
Ni20BLa	Al, n = 3	r = 2.49	ss = .0075
	Ni, n = 7	r = 2.48	ss = .006
Ni20BLb	Al, n = 4.4	r = 2.49	ss = .0075
	Ni, n = 9.9	r = 2.48	ss = .007
Ni30BL	Al, n = 2.5	r = 2.53	ss = .007
	Ni, n = 9.8	r = 2.49	ss = .007

*The Debye -Waller factor for face centered cubic Ni is a relatively low value since the near neighbor configuration about each Ni atom is well ordered.

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CONCLUSIONS

In this research, extensive SEXAFS experiments were conducted on interfaces of Al/Cu and Al/Ni where the samples were deposited at room temperature. These experiments showed new results over the previous experiments since the vacuum conditions were improved by an order of magnitude. It was observed that these interfaces whether they be Al on Cu or Cu on Al were highly reactive and that Al rich phases formed in $\sim 10\text{\AA}$ transition zones. Similar results were seen for the Al/Ni samples. The results as seen in comparisons of $\chi(k)$ and XANES data show that these interfaces were reacted upon room temperature deposition. Further proof of the interface reactions and the phases that occurred were obtained by least squares fitting. The reaction can easily be impeded by the presence of small amounts of contamination. The contamination is likely to be oxygen in these cases. Of further interest were the results which showed that the level of the reaction was highly dependent on the cleanliness of the source materials. This further indicated that the reaction is strongly impeded by the presence of even the lowest level of contaminant. It is reasonable to consider that when the oxygen is not present in the interface that Al on metal and metal on Al react equally and that there is not a preferred deposition direction as to the level of the reaction. Although experimental conditions may cause other conclusions to be drawn since the more reactive Al surface is more sensitive to the ambient environment than either Cu or Ni.

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