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GRAIN BOUNDARY CHEMISTRY IN AL-CU METALLIZATIONS AS DETERMINED BY ANALYTICAL ELECTRON MICROSCOPY

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ABSTRACT

Al with additions of Cu is commonly used as the conductor metallizations for integrate circuits (ICs). As the packing density of ICs increases, interconnect lines are required to carry ever higher current densities. Consequently, reliability due to electromigration failure becomes an increasing concern. Cu has been found to increase the lifetimes of these conductors, but the mechanism by which electromigration is improved is not yet fully understood. In order to evaluate certain theories of electromigration it is necessary to have a detailed description of the Cu distribution in the Al microstructure, with emphasis on the distribution of Cu at the grain boundaries. In this study analytical electron microscopy (AEM) has been used to characterize grain boundary regions in an Al-2 wt.% Cu thin film metallization on Si after a variety of thermal treatments. The results of this study indicate that the Cu distribution is dependent on the thermal annealing conditions. At temperatures near the θ phase ($CuAl_2$) solvus, the Cu distribution may be modelled by the collector-plate mechanism, in which the grain boundary is depleted in Cu relative to the matrix. At lower temperatures, Cu enrichment of the boundaries occurs, perhaps as a precursor to second phase formation. Natural cooling from the single phase field produces only grain boundary depletion of Cu consistent with the collector-plate mechanism. The kinetic details of the elemental segregation behavior derived from this study can be used to describe microstructural evolution in actual interconnect alloys.

INTRODUCTION

Aluminum thin films are commonly used as the conductor metallization for ICs. As device densities increase these metallizations are required to carry larger current densities which can result in loss of reliability through electromigration failures of the Al interconnects. The addition of Cu to Al metallizations has been found to increase the time to failure due to electromigration by one or two orders of magnitude.[1,2,3] Also, Mg, Ni and O have been shown to be effective in limiting the rate at which electromigration occurs.[4] The mechanism by which these elements inhibit the electromigration failure rate is not yet fully understood.

Conventionally, electromigration is generally considered to be the result of momentum transfer from the electrons which are moving within the conductor to the ions which constitute the lattice of the interconnect material. The electron flux results in a drift of the metal ions in the conductor that eventually causes voids in the conductor followed by complete breakage of the metal interconnect. An alternate theory suggests that electromigration is a consequence of the electromagnetic term, which is usually neglected, in the diffusion equation. A number of theories have been proposed to account for the positive effects of Cu on electromigration in Al interconnects. These mechanisms all attempt to relate the electromigration behavior to the distribution of Cu within the specimen. These mechanisms are based on the observation that during electromigration copper, rather than Al, preferentially migrates toward the anode, with a resultant depletion of copper at

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the cathode. Once the Cu is depleted the Al then migrates to the anode with the concurrent formation of voids and electrical opens.[5]

One mechanism proposes that Cu atoms at, or segregated to, Al grain boundaries suppress vacancy formation and the reduced number of vacancies slows electromigration in the Al thin film.[6] A related hypothesis states that the Cu and Al react to form θ precipitates ($CuAl_2$) at the Al grain boundaries, electromigration is reduced as a result of the reduced rate of diffusion at interphase interfaces.[7] A similar hypothesis is that the θ phase at grain boundaries acts as a physical barrier to diffusion along the grain boundaries which results in reduced electromigration damage.[8] It has also been theorized that because Cu migrates preferentially to the anode, the small size of the Cu atoms enables them to diffuse without disturbing the Al lattice thereby enhancing the electromigration lifetimes.[8] Unfortunately, all of these theories have been proposed with little or no knowledge of the fine scale compositional changes which occur within the thin film during fabrication and in service. The objective of this study was to use high spatial resolution analytical electron microscopy (AEM) to determine the compositional changes that occur around grain boundaries in thin film Al-2wt%Cu alloys that had received a variety of thermal treatments that represent possible thermal profiles during IC processing..

EXPERIMENTAL PROCEDURE

Thin Film Deposition

A dielectric borosilicate glass (BSG) layer was thermally deposited on silicon wafers (15-25 Ω-cm, <100> orientation) in an atmospheric pressure chemical vapor deposition system. Films of Al-2wt%Cu were magnetron sputtered at room temperature from a single source under an argon atmosphere onto the BSG. The actual wafer temperature was approximately 100° C as a result of heating during sputtering. Films 400 nm thick were deposited. The deposited films were then heat treated under a reducing 15% H_2-N_2 atmosphere. The first heat treatment was a furnace anneal performed at 425° C for 35 minutes followed by a slow cool. The specimens were then heat treated as shown in Table I. Following the heat treatment the specimens were withdrawn from the furnace and allowed to naturally cool naturally to room temperature, which required about 1 minute.

Table 1. Heat treatment for Al-2wt%Cu on Si

		Temperature	
	200° C	300 ° C	400° C
Time	10 days	1 hr.	1 min.
	40 days	4 hr.	4 min.
	80 days	8 hr.	8 min.

Analytical Electron Microscopy

Plan view samples for AEM were prepared from the heat treated specimens. Discs 3 mm in diameter were ultrasonically removed from the Si wafer. The back side of the discs were mechanically thinned to about 50 μm . The front side of the wafer was lacquered off and the remaining Si removed by chemical dissolution in a solution of 5%HF + 95% HNO_3.

The BSG was removed by low temperature Ar^+ ion beam milling at 5 keV. This usually required about 10 minutes.

The specimens were examined in a Vacuum Generators HB-501 dedicated scanning transmission electron microscope (STEM) which was equipped with a field emission electron source (FEG) which produced an electron probe 1 nm (FWHM) in diameter.[9] The HB-501 was also equipped with a Link Analytical AN10/95 x-ray analysis system which included a windowless energy dispersive spectrometer (EDS). The advantage to using this instrument is that the extremely small probe size allows spatial resolutions on the order of a few nm to be achieved. The Cu concentration profiles were obtained by stepping the electron probe across grain boundaries in the Al thin films oriented so that the boundaries were parallel to the electron beam. This was primarily achieved by minimizing the image width of the grain boundary. Profiles were taken across grain boundary segments which ran between θ precipitates. The electron probe was positioned automatically during the analyses by a Link software package which simplified data collection by compensating for any specimen drift during the analysis. Such computer control of the beam position allows analysis points to be taken closer together with increased accuracy of probe placement.[10]

The Cu and Al X-ray intensities obtained from the X-ray spectra were converted to compositions by the ratio technique utilizing an experimentally determined k-factor. No corrections for absorption of fluorescence were necessary in the compositions and thicknesses utilized in this study.[11]

RESULTS AND DISCUSSION

The general microstructures of the Al-2wt% thin films were quite similar and consisted of mostly equiaxed grains with θ on the grain boundaries and at most triple points. An example is shown in Figure 1 where the θ precipitates can be seen on a grain boundary in the Al-2wt% thin film sample. Cu concentration profiles were obtained from grain boundary regions between precipitates as shown in Figure 1. The profiles obtained fell into two categories: at high temperatures (400° C) relative to the θ phase solvus, grain boundary depletion of Cu was observed, at lower temperatures (200° and 300° C) the grain boundaries were significantly enriched in Cu.

400° C Heat Treatment

Specimens annealed at 425° C for 35 minutes and then slow cooled followed by heat treatment at 400° C for 1, 4 or 8 minutes exhibited classical grain boundary depletion of Cu as predicted by the 'collector plate mechanism'.[12] Solute profiles which form at grain boundaries are generally the result of the nucleation and growth of grain boundary allotriomorphs which draw solute from the surrounding matrix via the high diffusivity grain boundary which acts as a collector plate for the solute. The growing grain boundary allotriomorph then drains the solute from the grain boundary thus resulting in a depleted zone. Figure 2 shows a Cu concentration profile obtained from a Al-2wt% Cu alloy which had been held for 1 minute at 400°C. The average matrix composition remote from the grain boundary is about 0.7 wt% Cu which is lower than the initial composition of 2 wt% Cu. The grain boundary composition in this case was 0.35±0.03, although this composition will surely be an overestimate of the actual composition due to beam broadening causing some of the surrounding matrix to be fluoresced by the electron beam. Figure 3 shows a higher resolution profile across another grain boundary in the specimen heat treated at 400° C for 1 minute. The general shape of the profile is the same as shown in Figure 2. The more closely spaced analysis points now allow the shape of the profile near the grain boundary to be observed. Figure 4 shows an example of the profiles measured at a grain boundary in a specimen which was heat treated at 400°C for 4 minutes. The major difference between this profile and that shown in Figure 3 is the Cu concentration at the grain boundary. This difference is most probably due to differences in specimen thickness at the analysis points and is not due to real differences in grain boundary composition.

The collector plate mechanism predicts that longer diffusion times will allow the concentration profiles at grain boundaries to grow wider. Figure 5. shows an overlap of the profiles shown in Figure 3 and Figure 4 where it is apparent that the profile widths are not very different. In order to understand this result it was necessary to develop a thermokinetic model to simulate the concentration profiles observed in the heat treated specimens. The thermokinetic model utilizes a finite difference computer technique to model the profile development.[8] In this case the θ precipitates were assumed to be in equilibrium with the matrix, thus providing a boundary condition for the model. The grain boundary composition is assumed to be the same as the matrix composition at the precipitate/matrix interface. This assumption essentially states that the diffusivity of the grain boundary is sufficiently fast that any solute that reaches the grain boundary is immediately carried away to the precipitate. A final assumption is that below 150° C diffusion is extremely slow and further solute redistribution is negligible. The heat treatment was modeled as a hold at temperature followed by cooling of the specimen at 10° C/sec from the heat treatment temperature to 150° C. Figure 6 shows compositional profiles obtained from the thermokinetic model. The dotted curve in Figure 6 shows the expected concentration profile obtained from an isothermal hold at 400° C for 8 minutes. Note that the boundary composition is 0.83 wt% Cu. This is the equilibrium matrix/precipitate composition as given by the phase diagram. The solid curve was calculated assuming the same 8 minute hold at 400° C followed by cooling to 150°C at 10° C/minute. From these composition profiles a number of interesting observations can be made. First, the hold at 400° C, which is relatively close to the solvus temperature, results in a shallow concentration gradient near the grain boundary. The precipitation of θ at the grain boundaries occurs during this time and reduces the matrix composition substantially. The subsequent cooling from the heat treatment temperature to 150° C causes a very large concentration drop at the grain boundary. The general shape of the solid curve shown in Figure 6 should be compared with the experimental profiles shown in Figure 4. The shapes of the profiles are quite similar.

At this point it is possible to explain the observation that the concentration profile widths are similar for different hold times. The thermokinetic model shows that the effect of the hold at the heat treatment temperature is to allow the precipitation of θ precipitates on the grain boundaries in the thin film. These precipitates grow by drawing solute atoms from the matrix and thus reducing the matrix concentration of Cu. After the heat treatment time period is complete the specimen is withdrawn from the furnace and allowed to air cool. Most of the depletion of Cu at the grain boundary occurs during the cool from the heat treatment temperature. The cooling cycle is common to all the specimens heat treated at 400° C thus, all of the profile widths will be nearly the same. The experimental data indicates that the profile width is about 100 nm which is very close to the predictions of the thermokinetic model.

200 and 300° C Heat Treatments

The results from the heat treatments performed at 200 and 300° C were significantly different than those obtained at 400° C. The grain boundaries in the specimens heat treated at 200 or 300°C exhibited substantial enrichment of Cu as opposed to the depletion observed in those specimens heat treated at 400° C. Figure 7 is a Cu concentration profile obtained from a specimen treated at 300° C for 2 hours. The grain boundary composition is about 1.4 wt% Cu while the matrix adjacent to the grain boundary contains about 0.3 wt% Cu. Figure 8 is a similar profile obtained from a specimen which had been heat treated at 200° C for 10 days. The grain boundary composition in this case is nearly 1.8 wt % Cu while the matrix composition is about 0.1 wt % Cu which is lower than that observed at 300° C. It is readily apparent that the collector plate mechanism will not explain the behavior observed at the lower heat treating temperatures. The Cu enrichment could be due to segregation of Cu atoms to grain boundaries in Al or the elevated Cu concentration at the grain boundaries may be due to the formation of an extremely narrow film of θ ($CuAl_2$) at the grain boundary. The width of the grain boundary film may be assessed from the width of the profile shown in figure 9 where the analysis points were taken at intervals of 2.5 nm. Here the width of the enriched region is between 5 and 7 nm. which may indicate that a thin layer of θ phase has formed at the grain boundary. The decrease in the matrix composition with decreasing heat treatment temperature is an indication that equilibrium has been reached between the composition of the grain boundary and the matrix, which also supports the theory that the grain boundaries consist of a thin layer of θ. Further characterization of this thin film is underway and will be reported at a later date.

IMPLICATION TO ELECTROMIGRATION

These results indicate that there are at least two different Cu distributions that can occur in the Al-2wt% thin film metallizations used in this study. At high temperatures relative to the θ solvus, grain boundary depletion of Cu occurs by the collector plate mechanism. At lower temperatures, grain boundary enrichment of Cu probably occurs in the form of a thin layer of θ at the boundaries. The two different behaviors make a choice of mechanisms for Cu reduction in electromigration failure rates difficult. The hypothesis that the presence of grain boundary precipitates inhibits the grain boundary diffusion does not appear to be valid since the grain boundary precipitates act as sinks for Cu and drain Cu from the grain boundaries. Therefore, the amount of Cu in the boundary itself is relatively low and close to the precipitate/ matrix composition predicted by the phase diagram. It is possible that at lower temperatures where the collector plate mechanism is no longer operating that the Cu enrichment of the grain boundaries either due to segregation or precipitation of thin layers of θ may serve to reduce the electromigration failure rate. More work needs to be performed in this area to answer this question.

It is apparent that electromigration tests performed at high temperatures will characterize a microstructure and elemental distributions that do not exist at lower temperatures. Thus, accelerated electromigration tests conducted at high temperatures may not be valid for actual component service conditions. To determine if these tests are valid the actual operating temperature must be determined and a suitable microstructure tested at these temperatures in order to adequately determine the effect of Cu on the electromigration lifetimes of thin film metallizations.

CONCLUSIONS

This study has examined the spatial distribution of Cu in thin film Al-2wt %Cu metallizations that had undergone a series of different heat treatments. The specific conclusions are:

1. At 400° C Cu depletion of the grain boundaries occurs due to the operation of the collector plate mechanism.

2. At temperatures of 200 and 300° C Cu enrichment of the grain boundaries occurs which may be due to the formation of a thin layer of θ at the grain boundaries.

3. As a result of the two different Cu distributions observed in these specimens it is important to perform electromigration tests of the microstructures that are present during service.

4. The thermokinetic model can accurately predict the Cu distribution in thin film metallizations heat treated at relatively high temperatures.

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FIGURE CAPTIONS

Figure 1. Bright field transmission electron microscope image of a typical grain boundary with θ precipitates in an Al-2wt% Cu thin film metallization.

Figure 2. Cu concentration profile across a grain boundary in the Al-2wt% Cu alloy held at 400° C for 1 minute.

Figure 3. High resolution Cu concentration profile measured across a grain boundary in the Al-2wt% Cu alloy held at 400° C for 1 minute.

Figure 4. Cu concentration profile measured across a grain boundary in the Al-2 wt% Cu alloy held at 400° C for 4 minutes.

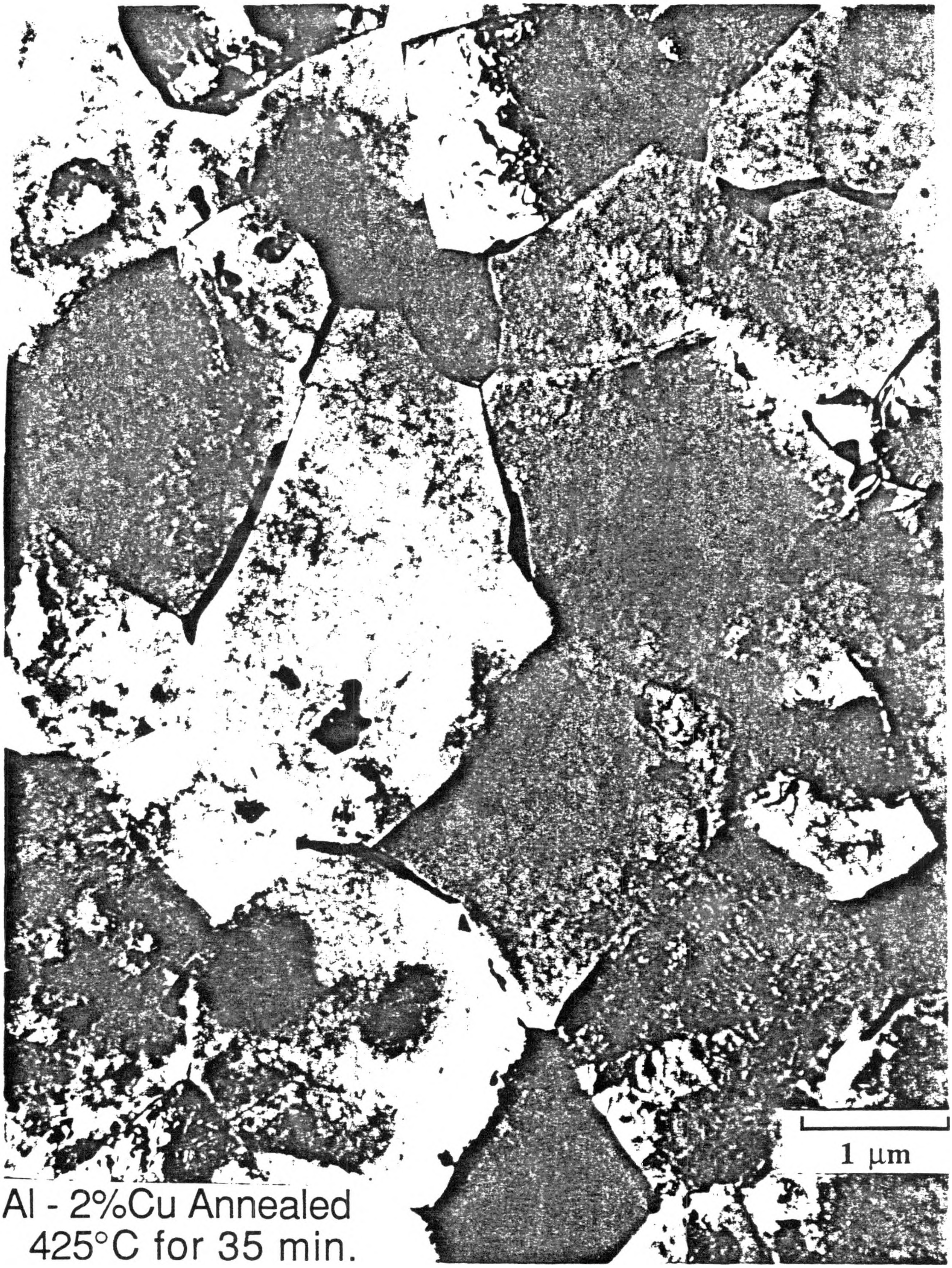
Figure 5. Overlap of Figures 3 and 4 to demonstrate the similarity of the profile widths for the specimens held at 400° C for 1 and 4 minutes.

Figure 6. Cu concentration profiles calculated by the thermokinetic model.The dotted curve shows the concentration profile expected after an isothermal hold at 400° C for 8 minutes. The solid curve shows the calculated concentration profile expected after an isothermal hold at 400° C followed by slow cooling (10°C/sec) to 150° C.

Figure 7. Cu concentration profile across a grain boundary in a Al-2wt% Cu alloy heat treated at 300° C for 2 hours.

Figure 8. Cu concentration profile across a grain boundary in a Al-2wt% Cu alloy treated at 200° C for 10 days.

Figure 9. High resolution concentration profile measured across a grain boundary in a sample heat treated at 200° C for 10 days. The analysis point spacing was 2.5 nm.



Al - 2%Cu Annealed
425°C for 35 min.

Fig 1 photo

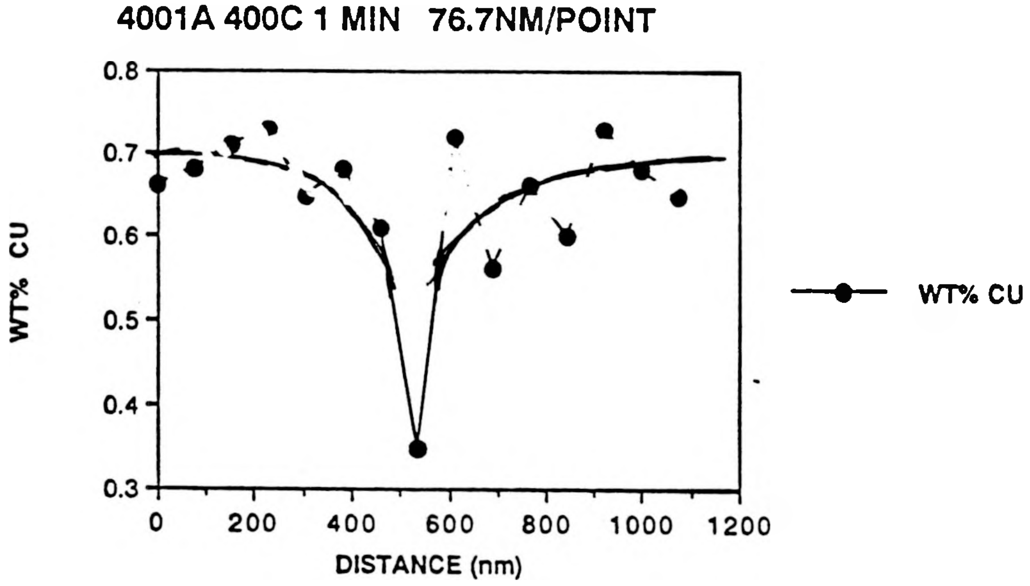


Fig #2

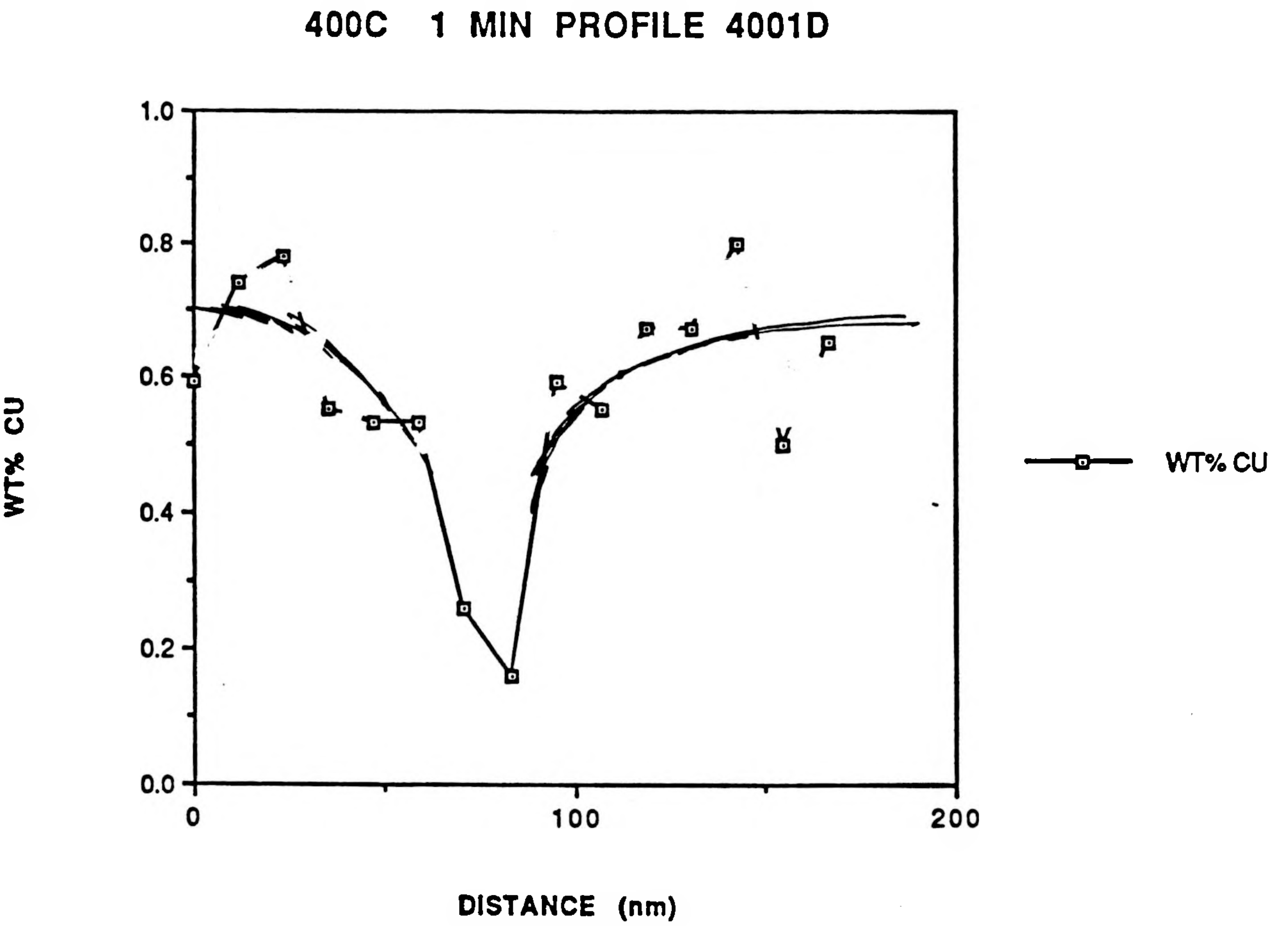

400C 1 MIN PROFILE 4001D
1.0
0.8
0.6
0.4
0.2
0.0
WT% CU
0
100
200
DISTANCE (nm)
WT% CU

Fig 3

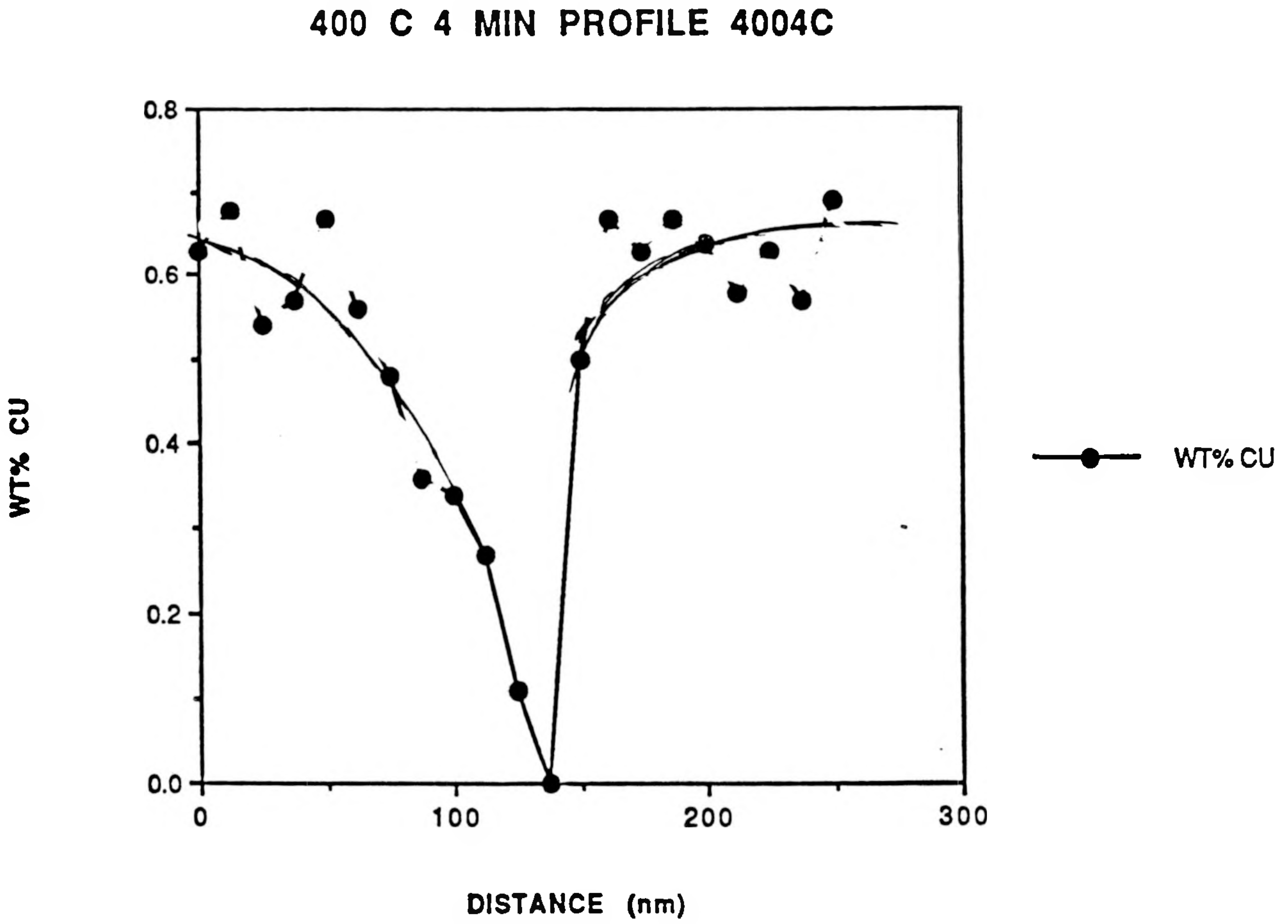

400 C 4 MIN PROFILE 4004C
WT% CU
0.8
0.6
0.4
0.2
0.0
0
100
200
300
DISTANCE (nm)
WT% CU

Fig 4

overlap of 400C for 1 min and 4 min profiles 4001B and 4004C

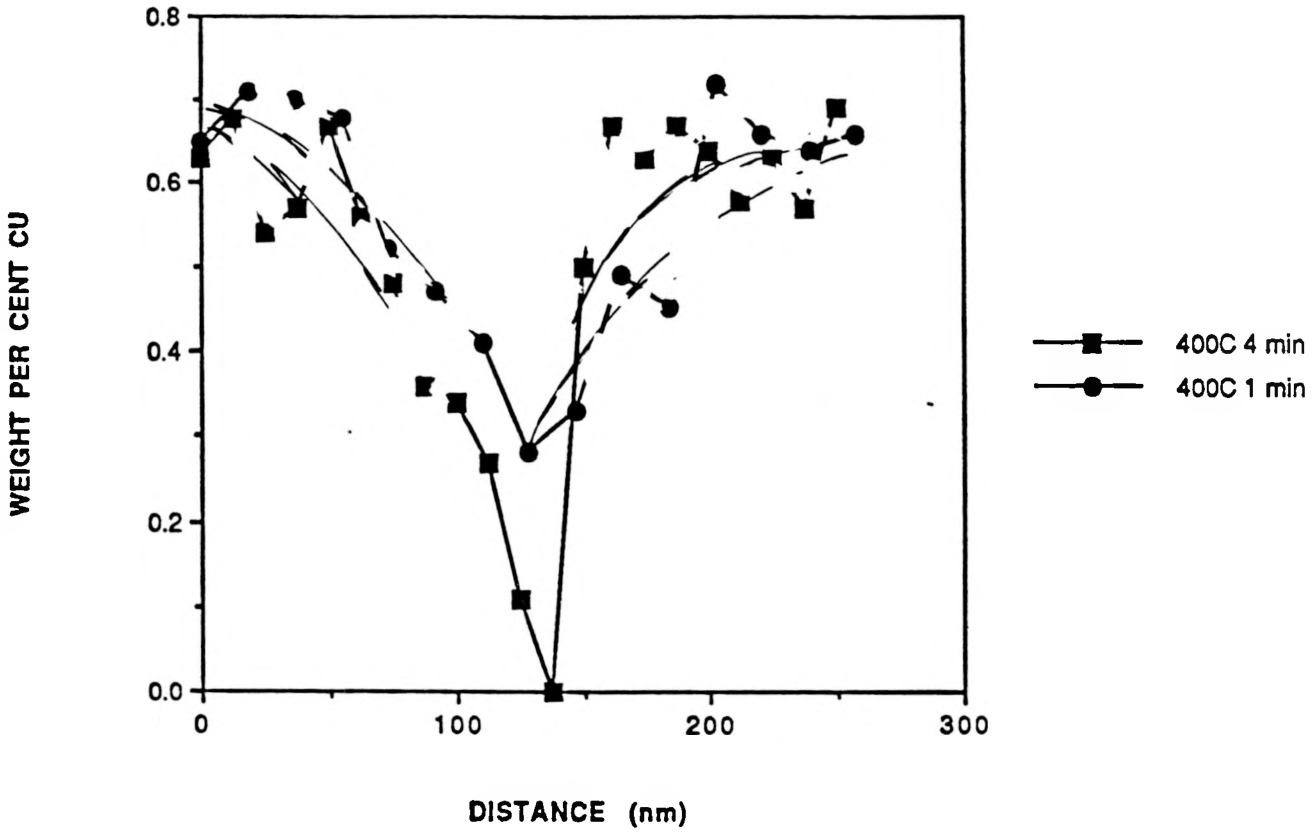
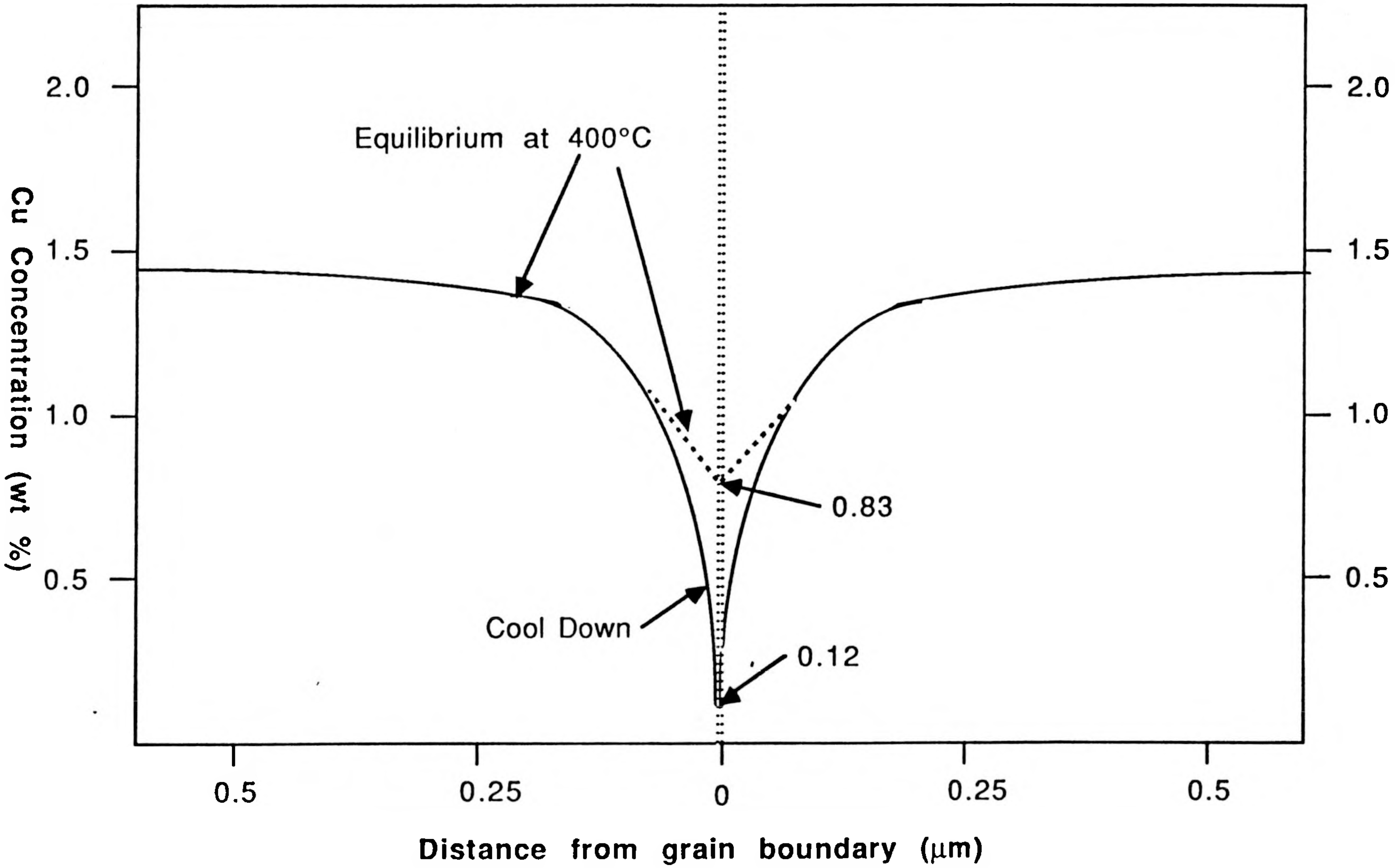


Fig 5

Fig 6 — TK model

Al-2%Cu 400°C for 8 minutes



6

[illegible] 5

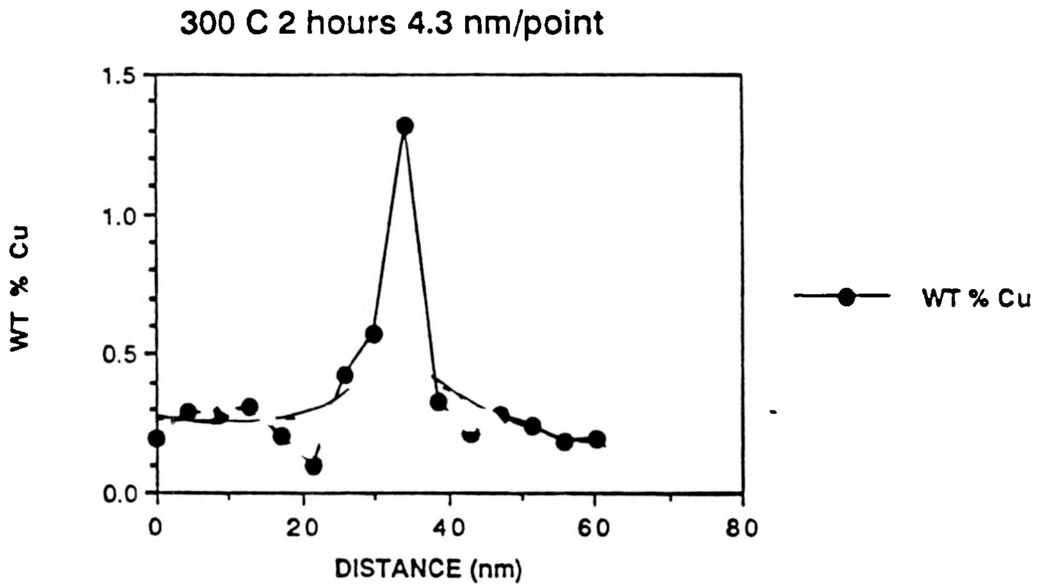

300 C 2 hours 4.3 nm/point
WT % Cu
1.5
1.0
0.5
0.0
0
20
40
60
80
DISTANCE (nm)
WT % Cu

Fig 7

200C 10 ~~HOURS~~ days 3.6NM/POINT 2001C

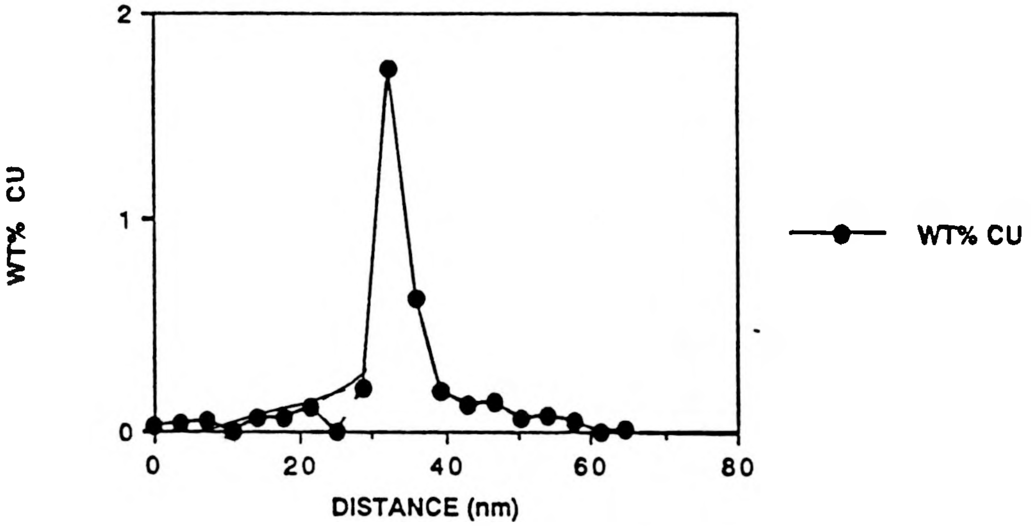
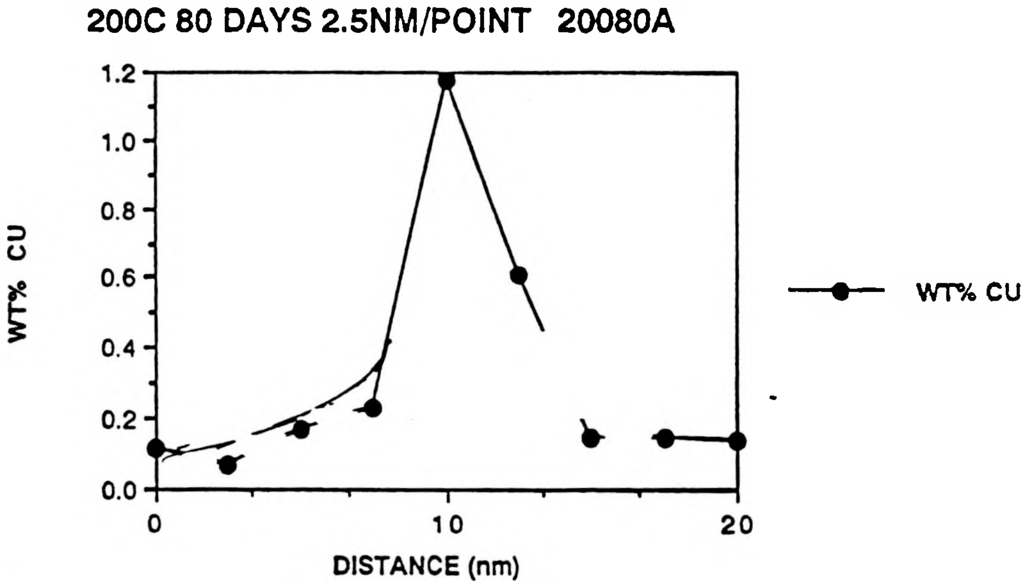


Fig 8



200C 80 DAYS 2.5NM/POINT 20080A

Fig 9