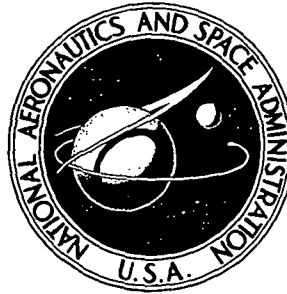


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AUGER ELECTRON SPECTROSCOPY STUDY OF  
SURFACE SEGREGATION IN THE BINARY ALLOYS  
COPPER - 1 ATOMIC PERCENT INDIUM,  
COPPER - 2 ATOMIC PERCENT TIN,  
AND IRON - 6.55 ATOMIC PERCENT SILICON

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# AUGER ELECTRON SPECTROSCOPY STUDY OF SURFACE SEGREGATION IN THE BINARY ALLOYS COPPER - 1 ATOMIC PERCENT INDIUM, COPPER - 2 ATOMIC PERCENT TIN, AND IRON - 6.55 ATOMIC PERCENT SILICON

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## SUMMARY

Auger electron spectroscopy was used to examine surface segregation in the binary alloys copper-1 at. % indium, copper-2 at. % tin, and iron-6.55 at. % silicon. The copper-tin and copper-indium alloys were single crystals oriented with the [111] direction normal to the surface. An iron-6.5 at. % silicon alloy was studied (a single crystal oriented in the [100] direction for study of a {100} surface). It was found that surface segregation occurred following sputtering in all cases. Only the iron-silicon single crystal alloy exhibited equilibrium segregation (i.e., reversibility of surface concentration with temperature) for which at present we have no explanation. McLean's analysis for equilibrium segregation at grain boundaries did not apply to the present results despite the successful application to dilute copper-aluminum alloys. The relation of solute atomic size and solubility to surface segregation is discussed. Estimates of the depth of segregation in the copper-tin alloy indicate that it is of the order of a monolayer surface film.

This study was undertaken as part of a continuing search for alloys providing superior performance as bearing materials. The results of the present study indicate potential for the copper-tin and copper-indium alloys because tin and indium tend to segregate to high concentrations at a free surface even at small bulk concentrations of the alloying element. In addition, it is possible that iron-silicon alloys also may have promise, because of the possibility of forming protective  $\text{SiO}_2$  films from both a friction and wear and a corrosion standpoint.

## INTRODUCTION

In the field of friction and wear it would be desirable to produce materials for practical applications that would reduce friction and wear and thus give improved operating

conditions and long life. In this spirit a number of Auger Emission Spectroscopy (AES) and Low Energy Electron Diffraction (LEED) studies have been performed on metal alloys in which it was found that the solute segregated at the surface in concentrations higher than existed in the bulk (refs. 1 to 3). This segregation radically altered the adhesive behavior at the metal surface (refs. 4 and 5), and therefore it is possible that both friction and wear could also be altered. There have been a number of excellent studies examining surface segregation with AES, but few have been directed towards explaining physical mechanisms (refs. 6 to 9). In references 1 to 3, it was demonstrated that the results with copper-aluminum alloys could be explained in terms of equilibrium segregation and an analysis derived by McLean for grain boundary segregation (ref. 10). The segregation in these studies was promoted by heating. It would also be desirable to have stress initiated segregation in addition to thermal segregation for practical applications. For example, in the case of bearings, if the protective coating could also be replenished by surface stress a self-healing film could be maintained even though local temperatures were too low to promote segregation. The main objective of the present studies was to gain an understanding of segregation mechanisms in order to preselect alloys in which small concentrations of solute would give a high surface coverage and greatly alter adhesion without radically affecting bulk mechanical properties. Accordingly, thermal segregation in copper-1 at. % indium, copper-2 at. % tin, and iron-6.5 at. % silicon alloy single crystals was examined using AES and LEED. A further objective of the present report was to expand the number of alloys examined and to determine the extent of applicability of McLean's analysis.

The copper-tin and copper-indium single crystals studied were oriented with the [111] direction normal to the surface. The iron-silicon alloy studied was a single crystal oriented with the [100] direction normal to the surface.

The effects of solute atomic size relative to solvent atomic size on segregation are discussed. Estimates of the thickness of the solute enriched layer are determined by a controlled sputtering experiment and observation of electron absorption by the surface layer.

## MATERIALS

The crystals studied were single crystals of copper-1 at. % indium, copper-2 at. % tin, and iron-6.55 at. % silicon. The copper alloys were above the solubility limit and the iron alloy was a solid solution of silicon in iron (ref. 11). The copper alloys were triple zone leveled with an impurity content of less than 10 parts per million and the iron alloy had an impurity level of less than 100 parts per million. Chemical analysis of the copper-indium and copper-tin alloys were performed as a result of discrepancies in the AES spectra regarding the bulk concentration. It was found that the copper-

indium alloy agreed with the suppliers analysis whereas the copper-tin alloy was 2 at. % tin rather than 1 at. % tin in agreement with the AES results.

The copper-tin alloy was rectangular in shape with a face 1.2 by 0.8 and 0.5 centimeters thick. The copper-indium crystal was a cylinder 1.3 centimeters in diameter and 0.5 centimeter thick. The iron-silicon alloy was a cylinder 0.5 centimeter in diameter and 0.5 centimeter thick.

The copper alloys were oriented in the [111] direction and the iron in the [100] direction by Laue back diffraction. The crystals were manually sawed and ground wet through 600 paper.

Each crystal was then polished with 6 micron diamond paste and given a final polish with 3 micron diamond paste. The copper alloys were then electropolished with a solution of 250 cubic centimeters of phosphoric acid, 250 cubic centimeters of ethanol, 50 cubic centimeters propanol, and 500 cubic centimeters of distilled water. The iron-silicon alloy was electropolished with a solution of 60 cubic centimeters of perchloric acid in 500 cubic centimeters of ethanol. The LEED pattern was used as further evidence of correct orientation and adequate surface preparation.

## APPARATUS

A schematic diagram of the apparatus used for the LEED Auger studies is shown in figure 1. The LEED-AES apparatus is standard commercially available equipment. The stainless steel vacuum system is bakeable to 250<sup>0</sup> C and maintains a base pressure of 10<sup>-11</sup> torr. The system is pumped by sorption pumps, a titanium sublimation pump and a 0.14-cubic-meter-per-second (140-l/sec) ion pump. The crystals were conductively heated by passing a dc current through their tantalum supporting straps. Temperatures were measured with Chromel-Alumel thermocouples spot welded to the back face of the crystals.

## EXPERIMENTAL PROCEDURE

### Crystal Cleaning

Each sample was outgassed at 600<sup>0</sup> C until the base pressure in the vacuum system with all filaments heated was in the middle 10<sup>-10</sup>-torr range. Following outgassing, each sample was subjected to cleaning cycles of sputtering with 700-eV argon ions and a ~5-microampere-per-square-centimeter current density followed by heating at 600<sup>0</sup> C. A sample was then examined by AES and considered clean when the primary bulk impurity peaks of carbon, sulfur, oxygen, and phosphorous were removed from the AES

spectrum. For the iron alloy, it was not possible to completely remove the carbon contamination. Figures 2 to 4 are examples of "clean" AES traces for each alloy.

## Thermal Segregation Studies

When the alloys were clean, segregation studies were performed. The procedure used was to sputter the sample for 30 minutes at 700 eV and 5 microamperes per square centimeter, and then take AES traces spanning the entire relevant spectrum in order to establish the bulk concentration for the copper-tin and copper-indium alloys. The crystals were then annealed for 30 minutes at 600<sup>0</sup> C and following cooling to room temperature, another AES trace was taken in order to establish the room temperature surface concentration following annealing. The surficial concentration of solute as a function of temperature was then determined by observing the AES peak-to-peak amplitude in the derivative of the secondary emission energy distribution (refs. 12 and 13) at temperature following annealing.

The change in Auger peak-to-peak height as a function of temperature was determined as outlined in references 3 and 14. The temperature of the crystal was raised and the solute Auger peak-to-peak height was then determined at each of a series of increasing fixed temperatures. The same procedure was then repeated starting at an elevated temperature (approximately 600<sup>0</sup> to 700<sup>0</sup> C) and determining the solute Auger peak-to-peak height at a series of decreasing fixed temperatures. These results are later used for curve-fitting to McLean's expression for grain boundary segregation and examining the reversibility of solute surface concentration with temperature.

Since the magnetic fields from heater currents interact with the collection of the secondary electrons (ref. 2), all measurements were performed at zero heater current. When a temperature T was established, the heater current was turned off and the AES current at a given peak was determined. The crystals were sufficiently massive that the temperature did not change appreciably (5<sup>0</sup> to 10<sup>0</sup> C) during the recording time. In separate tests it was established that equilibrium of a surface concentration was established in times much shorter than the time required to obtain data.

Typical instrumental operating conditions at which data were taken are as follows: AES traces were taken at a sweep speed of 100 volts per minute, with a time constant of 100 milliseconds, and sensitivities in the 1- to 5-millivolt range on the lock-in amplifier. High sweep speeds could result in distortion of the recorded Auger peaks, since it is conceivable that the lock-in amplifier or the x, y-recorder (fig. 1) could not follow the rapid signal changes. In order to verify that the high sweep speeds were not distorting the peak shape, the same peaks were recorded at 100 and 5 volts per minute with the heater current on. The two sweep speeds produced the same height. In order

to compensate for daily changes in Auger electron gun operating conditions, all peak height data were normalized by dividing by collector current.

AES data heights can be distorted by large background slopes (ref. 13), hence the true peak height is the recorded peak minus the background. No corrections were included for changes in background on the peak-to-peak heights. These corrections were not important for the tin and indium peaks since the background was flat in these regions (figs. 2 and 3), however, with the silicon peak, it may have been a significant correction (fig. 4).

It is conceivable that changes in the Auger peak height with temperature could result from evaporation in the cases of tin and indium, because of their low melting temperature. In order to establish the importance of evaporation, a tantalum flag was placed approximately 1 millimeter from the copper-tin alloy during heating. The surface of the tantalum flag was then examined for deposition of tin using AES. It was found that, at temperatures above 500<sup>o</sup> C, the size of the AES tin peaks on the tantalum indicated that appreciable evaporation of tin was taking place.

The primary solute peaks studied were 428 and 436 eV for tin, 408 and 416 eV for indium, and 94 eV for silicon. It should be mentioned that there is a large chemical shift for oxidized silicon and the peak appears at 83 eV when oxygen is present. Changes in the 270-eV carbon impurity peaks with temperature in the iron alloy were also observed.

## Sputtering Calibration

In reference 1, a technique for estimating surface concentration referred to as the sputtering calibration was presented. In this calibration scheme it was assumed that, once the segregated surface layer of solute was removed, the solute AES peak height was representative of the bulk concentration. Therefore, a simple ratio of solute peak height after segregation to the solute peak height after sputtering for long times multiplied by the bulk concentration should give the surface concentration.

Therefore the post sputtering peak height was determined in ten separate experiments and averaged to establish the sputtering calibration AES peak height. For the copper-indium alloy, the post sputtering peak could not be resolved from the background, therefore the calibration represents a lower bound on the surface concentration. However, judging from the size of the post sputtering tin peak (fig. 2), the background for indium (fig. 3) represents approximately the correct peak height.

## Electron Attenuation Studies

In addition to the segregation studies, an attempt was made to estimate the electron transmission factor for a surface layer of tin or indium. It was noted following segregation that the copper Auger peaks decreased in height. This can result from scattering by surface layers of segregants and changes in the background secondary electron yield, or a replacement of copper atoms by tin or indium. These changes were observed for the 59-, 62-, 108-, and 940-eV copper Auger derivative peaks. Following sputtering, the clean AES spectrum was recorded. The sample was then heated permitting segregation of the solute and then allowed to cool. An AES trace of the entire spectrum was again recorded and the change in copper Auger peak height was determined. Again, all peaks were normalized to collector current.

### Controlled Sputtering Study

It is possible to obtain estimates of the depth of the solute enriched layer by sputtering the crystal surfaces under known conditions and noting the decrease of the solute AES peak (refs. 1 and 8). Knowing the sputtering yield (number of surface atoms removed (incident ion)) and the bombarding ion current density enables one to estimate the thickness of the surface layer. The sputtering was performed at an ion energy of 400 eV and a current density of 0.25 microampere per square centimeter. The sputtering yield was assumed to be that of copper reported in reference 15.

## RESULTS

Figures 2 to 4 give the typical AES peaks for each of the alloys after sputtering and after segregation. Note that by comparing figures 2(a) and (b) that the tin Auger peak has grown markedly following heating indicating segregation has occurred. The indium Auger peak (fig. 3) also indicates that segregation has occurred. Both of these sets of data are taken at room temperature. Similar behavior was not observed with the iron-silicon alloy (fig. 4). The room temperature silicon Auger peak was the same height following sputtering and heating.

Figures 5, 6, and 7 give the thermal behavior of the AES peak-to-peak height for tin, indium, and silicon, respectively. The tin and indium spectra show weak thermal dependence, except for temperatures above 500<sup>o</sup> C where the evaporation experiments discussed in the procedure section indicated that strong evaporation should occur. The silicon AES peak (fig. 7) had strong, reversible thermal dependence. The silicon segre-



gated to the surface region at elevated temperatures and returned reversibly to the bulk as the temperature was lowered.

The results of the controlled sputtering study are presented in figure 8. The abscissa gives sputtering time and its approximate equivalence in number of layers sputtered. The ordinate gives the change in the tin AES peak height. The curve indicates that the segregant is restricted to a thin layer near the crystal surface.

Table I presents the results of the electron absorption studies. The second column gives the ratio of the copper Auger peak height following sputtering to the peak height following segregation. This ratio should be representative of the number of electrons scattered out of the energy range corresponding to the Auger peak by a surface layer of another element (e.g., tin or indium). Note that the number of electrons transmitted is energy dependent (i.e., the number of electrons scattered by the surface layer depends on energy).

## ANALYSIS OF RESULTS

### Segregation Studies

In the previous studies performed on copper-aluminum alloys (refs. 1 to 3), it was found that equilibrium segregation of aluminum had occurred and the results could be analyzed in terms of an expression derived by McLean (ref. 10) for grain boundary segregation. McLean's expression for the concentration of solute at a grain boundary is given by

$$C_d = \frac{C_o e^{Q/RT}}{1 - C_o + C_o e^{Q/RT}} \quad (1)$$

where

- $C_d$  fractional number of surface sites or grain boundary sites occupied by solute atoms
- $C_o$  fractional bulk concentration of solute
- $Q$  activation energy for segregation
- $R$  gas constant
- $T$  absolute temperature

In order to determine  $Q$  and obtain the surface coverage, using the technique of reference 2, the raw data were treated as follows. The measured Auger peak height ratio at a temperature  $T$  was divided by the peak height ratio at a temperature  $T_o$ ,

picked for convenience, and equated to the following expression:

$$A(Q, T) = \frac{Cd(T) + C_1}{Cd(T_0) + C_1} \quad (2)$$

where  $C_1$  is the sum of concentrations added for the number of layers assumed sampled by the Auger beam below the surface layer. Auger spectroscopy is sensitive to the total number of atoms in the sampled region. The experimental values of  $A$  against temperature were then curve fitted by linear regression analysis. Obtaining  $Q$  allows an absolute determination of surface concentration by knowing  $C_0$  and assuming the number of layers sampled  $C_1$ . The use of the ratio in this expression enables elimination of the need for a calibration constant relating peak height to number of atoms present which is in general unknown in AES. The properties and limitations of this curve fitting technique are presented in references 2 and 16.

## Results of Curve Fit and Sputtering Calibration

Figures 8, 9, and 10 present the resulting curve fit to equations (1) and (2). The values of  $C_1$  assumed are shown in the figures. It was found that the maximum surface concentration did not depend strongly on  $C_1$ . This curve fit gave maximum surface fractional concentrations of 0.045 for tin in copper, 0.025 for indium in copper, and 0.002 for silicon in iron.

The sputtering calibration gave a surficial concentration of 0.28 for tin in copper and 0.4 for indium in copper and 0.65 for silicon in iron at elevated temperatures. There is a marked disagreement between the sputtering calibration (ref. 1) in which the peak height after sputtering is assumed to represent bulk concentration and the curve fitting calibration.

## DISCUSSION

These are several basic conclusions that can be reached concerning these segregation studies combined with the results of references 1 and 2. The first is that segregation occurred in all cases when the samples were heated following sputtering. The second is that no one physical mechanism is adequate to explain the results of these studies. Finally, two broad categories exist for the types of segregation observed - those in which surface concentration of the solute was reversible with temperature and those in which the surface concentration of the solute depended only weakly on temperature.

A further breakdown of these results into categories can be observed. The single crystal solid solution, copper-aluminum alloys studied in references 1 and 2 and the single crystal solid solution iron-silicon exhibit equilibrium segregation; that is, reversibility of surface concentration with temperature. However, it is questionable whether McLean's model applies to iron-silicon alloy. The single crystal copper alloys which are above the solubility limit exhibit nonequilibrium segregation; that is, the segregant comes out of the bulk and appears to stay on the surface independent of temperature.

### Applicability of McLean's Analysis

At this point, it is necessary to decide whether the sputtering calibration or the curve fit to McLean's equation truly represent the surface concentration. When sputtering an alloy, there is always question regarding surface enrichment by one alloy component resulting from differences in sputtering yields (refs. 15 to 17). That is, if one component of an alloy sputters more readily than the other, surface enrichment and hence an effect indistinguishable from surface segregation can occur. In each case, however, the sputtering yields given in reference 15 coupled with the sputtering analysis of reference 16 would indicate the surface to be solute enriched following sputtering. In every case, the solute surface concentration increased with heating. Therefore, thermal segregation was definitely observed in each case. It is worth mentioning that, in references 1 and 2, where copper-aluminum alloys were studied, good agreement was obtained between the sputtering calibration, curve fit, and LEED observations for surface coverage. In the case of the copper-tin and copper-indium alloys, the LEED patterns which were the same as those presented in reference 1 gave good agreement with the sputtering calibration giving a surface coverage of 0.33.

There is a more significant reason for believing the results of the sputtering calibration rather than the curve fit. Experience with AES (ref. 18) indicates that the peak heights observed following segregation are too large to represent the surface concentrations given by McLean's analysis, whereas the post sputtering peak heights are approximately the correct size for the bulk compositions. For example, the tin and indium peaks are the same size or larger than the principal high energy copper peaks after segregation (figs. 2(b) and 3(b)) at the same lock-in amplifier sensitivities. Peaks of this size could not be representative of the bulk composition. The same principle was true for the iron-silicon alloy. The silicon Auger peaks following segregation were many times larger than could be possible for the curve fit concentration or for that matter the bulk composition of the silicon. Therefore, the sputtering calibration is used to define surface coverage for the copper-tin, copper-indium, and iron-silicon alloys. These results indicate that differential sputtering may not be important in certain alloy

systems and that sputtering to indicate bulk composition may give a reasonable and simple surface calibration scheme for certain alloys. Therefore, McLean's model does not appear to describe the observed results for these alloys since it does not predict the correct surface concentrations.

## Segregation Mechanisms

Although there are a wide variety of results some patterns still emerge. If the copper-aluminum results are compared with the copper-tin and copper-indium, the sputtering calibration indicates that segregation was much stronger in the latter in that a much higher surface concentration was obtained for a given bulk concentration increasing in the order  $(\text{Cd/Co})_{\text{Al}} = 3$ ,  $(\text{Cd/Co})_{\text{Sn}} = 14$ ,  $(\text{Cd/Co})_{\text{In}} = 40$ . In these three cases, there is a direct correlation with solute and solvent size difference and hence solubility. The copper-aluminum alloys exhibited equilibrium segregation and agreed with McLean's model. The copper-tin and copper-indium alloys demonstrate nonequilibrium segregation, that is, irreversible with temperature (or weak thermal dependence). Hence, following segregation, a transformation takes place in which return to the bulk is no longer possible indicating that the situation following sputtering was a metastable state. The iron-silicon solid solution also fits into the size pattern in that it is smaller than iron and all of the other solutes examined. It is tempting to predict on the basis of these results that the maximum segregation at room temperature will be obtained in alloys with the largest atomic size mismatch between solute and solvent and hence lowest solubility.

From the standpoint of adhesion, friction, and wear, these results are encouraging. Although a definite physical model is not yet available for the nonreversible cases, it appears that choosing alloys that have low solubility may be a reasonable criterion. These have the added attractive property that once segregation has occurred, the solute remains on the surface and there is no tendency to diffuse back into the bulk with increasing temperature as is the case with elements exhibiting equilibrium segregation. It is also possible strain may more readily promote segregation in these cases due to the large mismatch.

Preliminary studies of a copper-tin alloy (ref. 5) indicate that segregated tin reduced adhesion. Therefore, it should be possible to fabricate a number of alloys with low solubility and possibly low adhesion with solutes that have the large atomic size and are similar in chemical properties such as indium and antimony.

The single crystal iron-silicon alloy is of general interest, because it exhibited a case where the solute is at a lower energy in the bulk than on the surface. As evidence of this the solute segregated on the surface as temperature was raised and returned reversibly into the bulk as temperature was lowered (fig. 7) indicating equilibrium segregation. McLean's model, however, cannot be used to explain these results, since the

implied surface coverage is lower than can be detected with AES (fig. 10). The heights observed at high temperatures imply high coverages. At present, therefore, there is no theoretical model offered to explain the results. This alloy also presents the possibility of forming protective  $\text{SiO}_2$  surface films (ref. 19). This can be studied by oxidizing the surface at high temperature.

### Thickness of Segregated Surficial Layer

Figure 11 represents the results of a controlled sputtering study on the copper-tin alloy performed in order to estimate the thickness of the surface layer. For equilibrium segregation, the film thickness should be limited to a few layers near the surface (ref. 20). The crystal was sputtered at 400 eV with argon ions at a current density of 0.25 microamperes, and the sputtering yield was assumed to be that of copper (ref. 17). This calibration indicates an approximate thickness of the surface film of one or two layers. Therefore, although equilibrium segregation does not occur, the thickness of the surface film is limited to a few layers near the surface (ref. 1).

The electron absorption studies give further evidence for this conclusion and indeed indicate that the segregated tin or indium lie on the surface as speculated in reference 1 for the aluminum layer. If segregation occurred by replacement of copper atoms by indium or tin atoms, it would be expected that all of the copper-Auger peaks would decrease uniformly. As can be seen in table I, the attenuation of the copper Auger electrons depends on energy. This is the result that would be expected for a film of tin or indium on top of the alloy surface. In fact, the fraction of electrons transmitted has the correct energy dependence (low energy electrons are attenuated more strongly than high energy ones). Again as in reference 1, LEED results for copper-tin and copper-indium support these results. It appears that the segregated layer, therefore, is composed entirely of solute.

### CONCLUDING REMARKS

The results of the present studies indicate that, in all alloys studied in this report and previous work by Ferrante and Buckley, surface segregation occurs. At present equilibrium segregation was only observed in single crystal solid solutions. McLean's analysis for equilibrium grain boundary segregation does not apply to the alloys studied in this report. There is a correlation between the atomic size difference, between solute and solvent, and the degree of solute segregation. The larger the solute atom relative to the solvent, the higher the degree of surface segregation. In the case of the iron-silicon alloy, silicon is at a lower energy in the bulk than on the surface, since silicon segregates at high temperatures and returns to the bulk at low.

The alloys studied seem promising as bearing materials in that the copper alloys being nonreversible and having high segregation could give stress initiated segregation and the iron alloys may form protective  $\text{SiO}_2$  films.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, July 24, 1972,  
502-01.

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TABLE I. - ELECTRON  
SCATTERING BY A TIN  
OR INDIUM LAYER FOR  
AN ELECTRON OF A  
GIVEN INCIDENT

ENERGY<sup>a</sup>

Electron energy, eV	Tin	Indium
	Electron trans- mission coef- ficient	
59	0.682	0.555
62	.725	.595
108	.747	.62
940	.902	.936

<sup>a</sup>The fact that the number of electrons collected depends on energy following segregation indicates that a surface film of the segregant scattering electrons is incident on the layer.

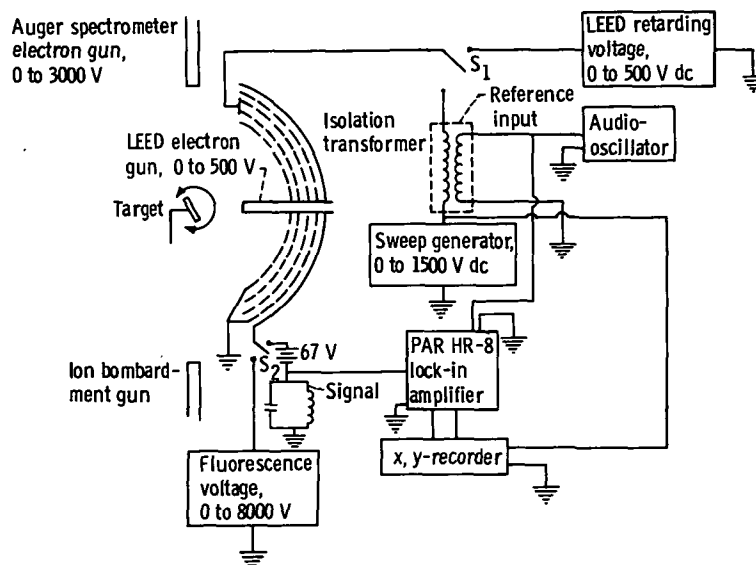


Figure 1. - Schematic of LEED AES apparatus.



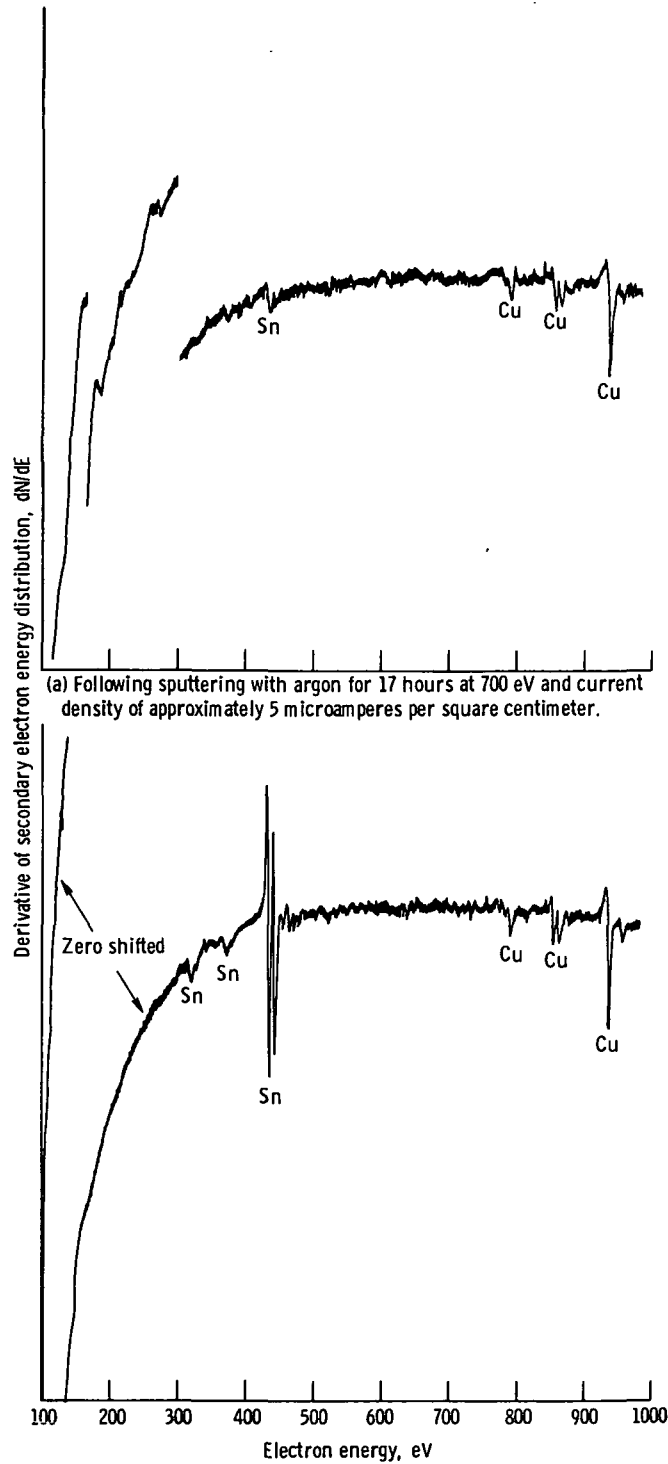


Figure 2. - AES spectrum for copper-2 at. % tin.

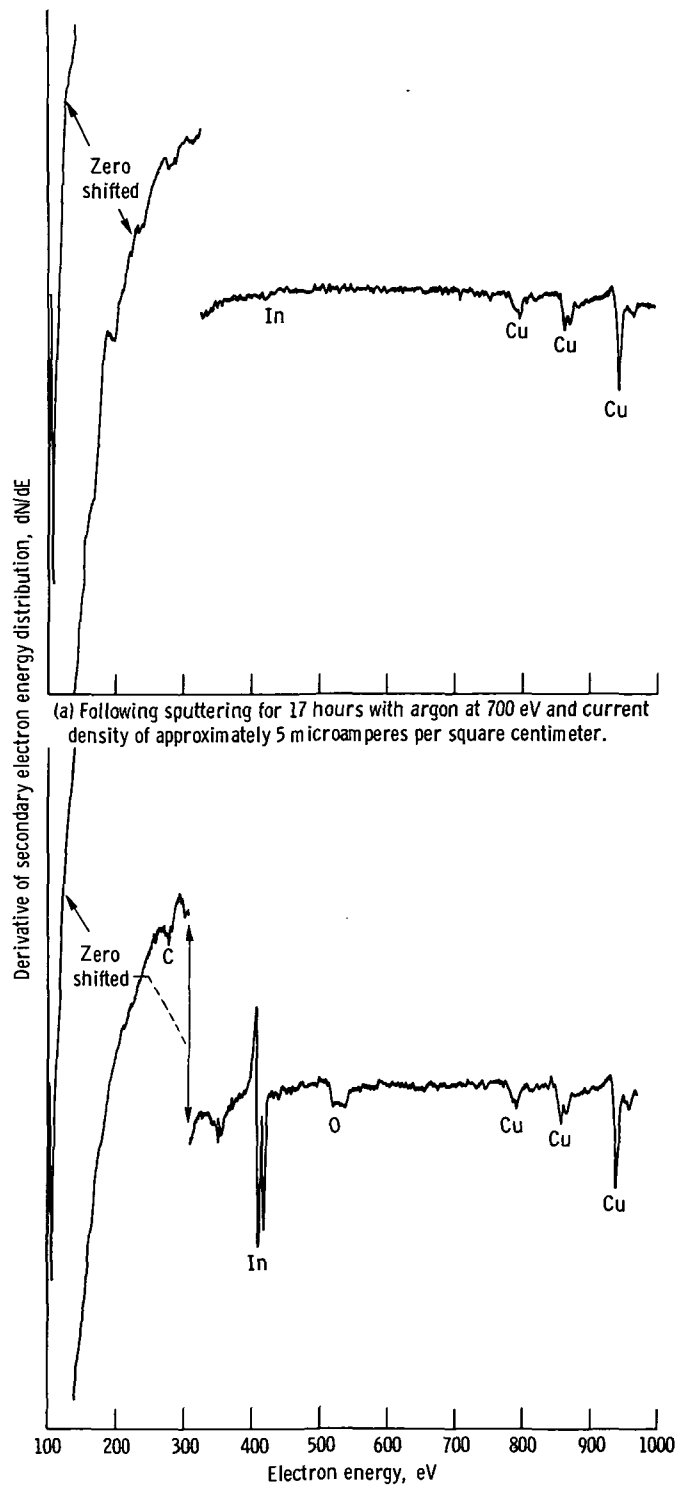


Figure 3. - AES spectrum for copper-1 at.% indium.

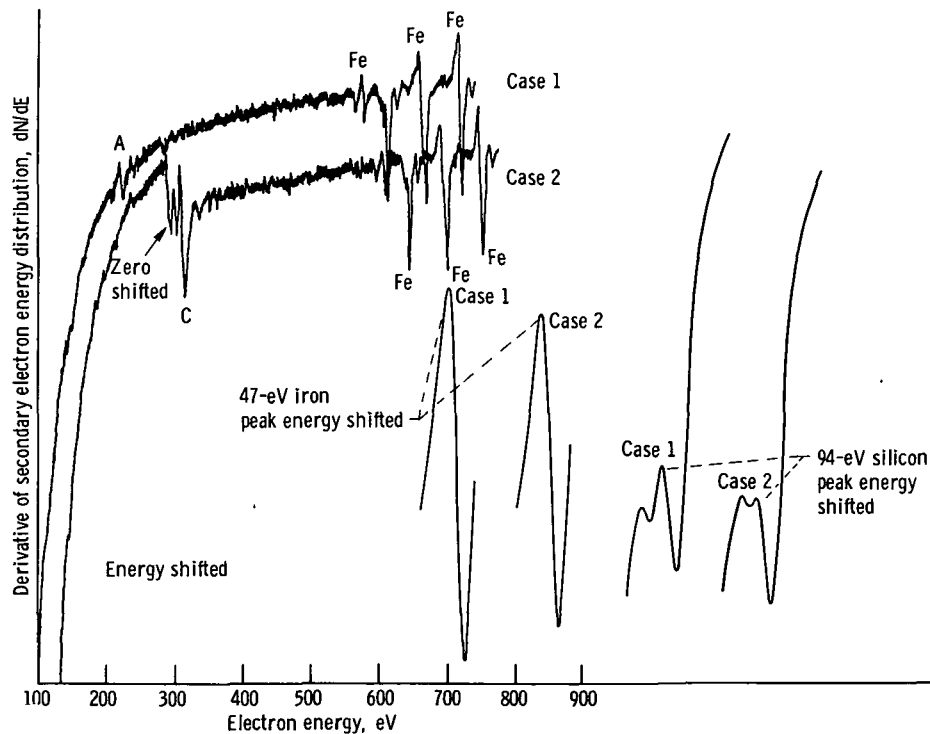


Figure 4. - AES spectrum for iron-6.55 at.% silicon. Case 1: Following sputtering with argon for 17 hours at 700 eV and current density of approximately 5 microamperes per square centimeter. Case 2: Following heating at 400° C for 30 minutes and cooling to room temperature.

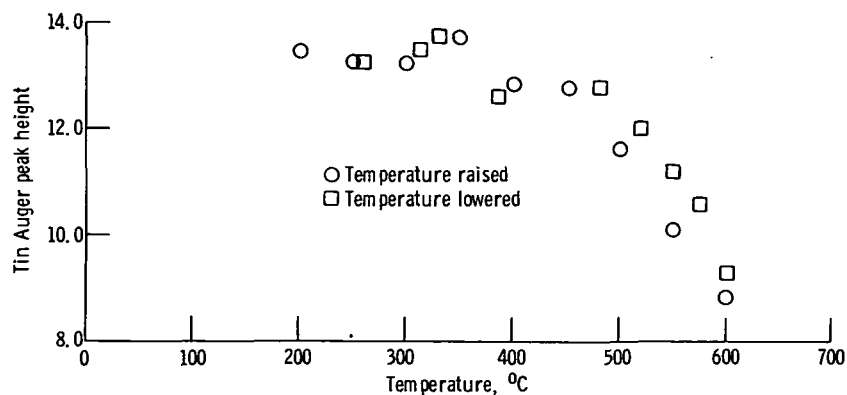


Figure 5. - AES tin peak-to-peak height normalized to collector current for copper-2 at.% tin against temperature.

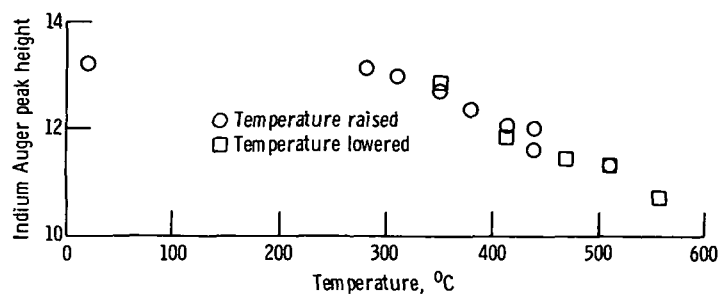


Figure 6. - AES indium peak-to-peak height normalized to collector current for copper-1 at.% indium against temperature.

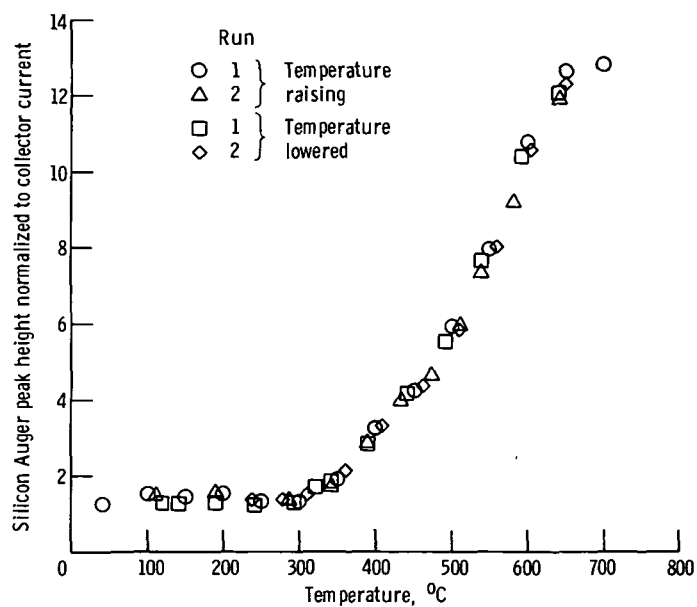


Figure 7. - AES silicon peak-to-peak height normalized to collector current for iron-6.55 at.% silicon (single crystal) against temperature.

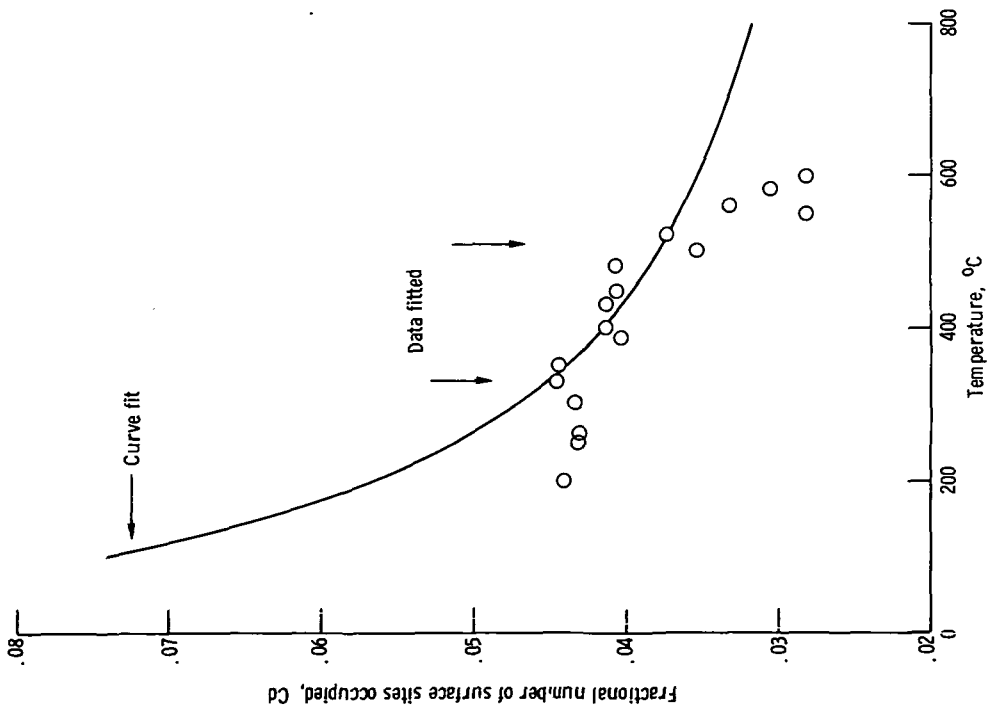


Figure 8. - Curve fit of data in figure 5 for copper-2 at 2 at.% tin to equations (1) and (2) giving fractional number of surface sites occupied against temperature for activation energy for segregation  $Q = 1014$  calories per mole and sum of concentrations added for number of layers assumed sampled  $C_1 = 0.02$ .

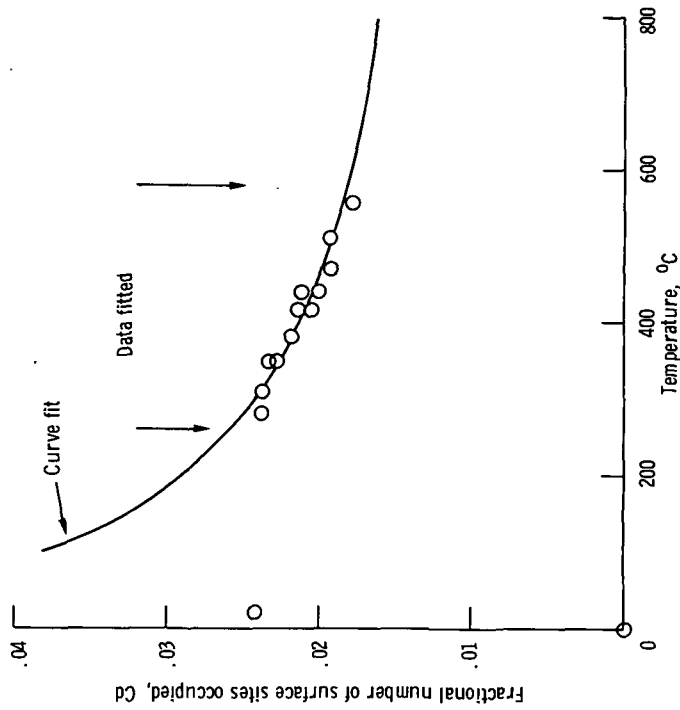


Figure 9. - Curve fit of data in figure 7 for copper-1 at 1 at.% indium to equations (1) and (2) giving fractional number of surface sites occupied against temperature for activation energy for segregation  $Q = 1016$  calories per mole and sum of concentrations added for number of layers assumed sampled  $C_1 = 0.01$ .

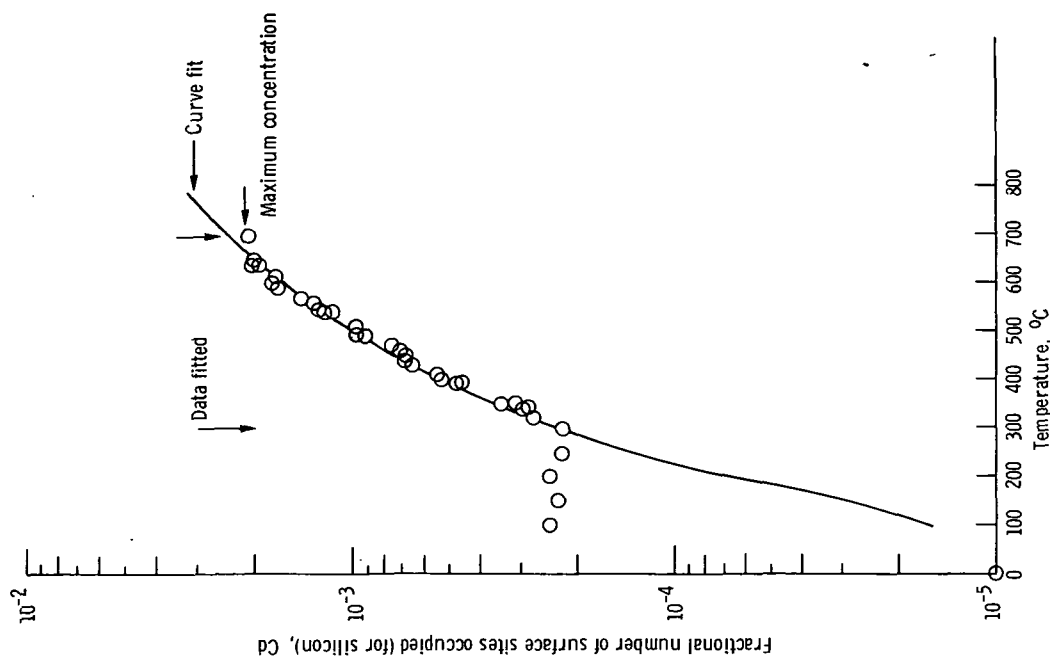


Figure 10. - Curve fit of data in figure 9 for iron-6.55 at. % silicon to equations (1) and (2) giving fractional number of surface sites occupied against temperature for activation energy for segregation  $Q = -6600$  calories per mole and sum of concentrations added for number of layers assumed sampled  $C_1 = 0$ .

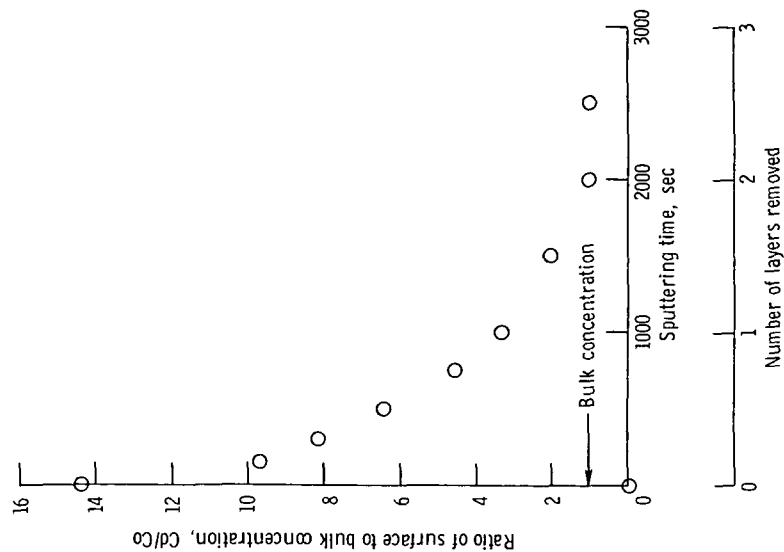


Figure 11. - AES tin peak-to-peak height normalized to collector current for copper-2 at. % tin against sputtering time and calibrated in number of layers.

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