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THE SURFACE COMPOSITION OF Au-Sn ALLOYS
Determined by Auger Electron Spectroscopy

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ABSTRACT

The Auger spectra of clean and equilibrated Au-Sn alloy ingots of bulk composition ranging between 50 and 99 at% Au have been obtained. The intensity ratios of Auger peaks of various different energies were normalized by comparison with the corresponding intensity ratios from pure Au and Sn. The normalized intensity ratios are used to obtain the surface atom fractions by applying a model which takes full account of the attenuation of the Auger electrons. It is found that for a one phase alloy with overall composition of 50 at% Au there is little or no segregation at the surface, while for a one phase alloy with bulk composition of 86 at% Au there is marked segregation of Sn (surface monolayer composition of about 43 at% Au). For the alloys of bulk compositions between 50 and 86 at% Au in which both phases are present, the surface composition is given by applying the lever rule to the one phase surface compositions. For 1 at% Sn dissolved in the Au lattice there is also considerable enrichment of the surface with Sn (surface monolayer composition of about 46 at% Au). These surface compositions are related to the properties of the bulk phase diagram and are explained by the interplay of the differences in atomic size and in heats of sublimation of pure Au and Sn and of the heats of mixing of the alloys.
Introduction

The study of the surface composition of alloys has been invigorated recently due to development of techniques of electron spectroscopy. Determination of the surface phase diagram is necessary to solve many problems of catalysis, corrosion, strength of materials (i.e., related to grain boundary composition) and semiconductor devices. The ultimate goal of fundamental research in this field is to be able to predict the composition of an alloy surface given its bulk composition, thermal history and some well known information about the bulk such as the heats of sublimation of each component, the structure of the bulk phases and their free energies of mixing. It has become evident that achieving this goal will require knowledge of the surface composition of several alloy systems confirmed by a variety of experimental techniques. Most studies completed so far have been carried out on binary systems which have fairly simple bulk thermodynamic properties that can be described by the regular solution model. Somewhat less work has been carried out on systems which exhibit strong compound formation and otherwise complex bulk phase diagrams, even though many catalysts and most structural alloys have complex phase diagrams.

The complex Au-Sn system was chosen as a suitable example of this type of alloy. We have found that Sn segregates to the surface of one phase alloys containing 87 and 99 at% Au. A one phase alloy containing 50 at% Au, however, does not show evidence for segregation of Sn, but appears to have a surface composition which is nearly identical to the bulk composition. The surface of two phase alloys with bulk compositions between 50 and 87 at% Au contain both phases according to their relative abundances in the bulk, but each phase has its own constant surface
composition. These results are explained by the interplay of three physical parameters: 1) the surface free energy difference of the two components, 2) the relative sizes of the two types of atoms in the alloy and 3) the magnitude of the bond energy between unlike atoms when a compound forms. For regular solutions 1) and 2) determine the surface composition, for substitutionally ordered compounds of high binding energy 3) may override the effects of 1) and 2).

Experimental
A. Sample Preparations

Alloys of Au and Sn were prepared by melting together weighed amounts of high purity Au (6N) and Sn (4N), calculated to give the atom percent compositions given below. The sample with 99% Au was melted down in an arc furnace and was homogenized by the stirring action of the arc and by flipping the ingot several times. The remaining samples were sealed under Ar or an Ar (98%) - H₂ (2%) mixture in quartz tubes. The 50.0 at% and the 86.7 at% samples were melted at 480 and 800°C respectively, with vigorous shaking to insure thorough mixing and were then quenched in ice water. The two alloys were then homogenized at 260°C for over two weeks. The 65.0 at% Au and the 79.9 at% Au alloys were melted and remelted with vigorous shaking at 500°C and 650°C respectively and then quenched in ice water. No further homogenization was done on these samples. The 61.0 at% Au and the 75.5 at% Au were melted down but were then removed from their tubes and crushed. The resulting powder and chips were re-encapsulated and held at 650°C for several hours with occasional shaking, air quenched and then homogenized at 250-270°C for 7 days.
Following these treatments, the alloys were course ground and filed down to the desired shapes. The polycrystalline surfaces to be studied were polished with a series of Emery papers of decreasing grit size, and then final polishing was done with 1μ diamond paste on a polishing wheel moistened with kerosene. Attempts to polish the samples with .03μ alumina on a Syntron failed due to the appearance of terraces and ridges on some samples presumably due to their brittleness. To obtain consistency therefore, all samples were polished to 1μ only. The expected bulk structure and composition of the alloys was confirmed by electron microprobe, X-ray fluorescence, X-ray diffraction and optical microscopy.

B. Auger Measurements

The 61.0 at% Au, 75.5 at% Au, the first pure Au, and both pure Sn samples were held in the ultra-high vacuum system (base pressure, 1x10^-9 torr) using tantalum foils. However, for these samples there was occasional difficulty with Ta impurities sputtered on to the surfaces so the remaining samples were mounted with Au foil supports. The foils were bolted onto a Ta block which held the samples at an angle normal to the analyzer and the co-axial electron gun. This position simplifies the Auger intensity analysis. The Auger spectra were recorded with a Physical Electronics (Phi Model 10-150) single pass cylindrical mirror analyzer in the derivative mode and using the standard techniques. Peak to peak heights were used as a measure of the Auger intensities. A 4 keV electron beam was used and a constant modulation voltage (~2 V p-p) was used for all spectra. The samples were cleaned by sputtering with 1.5 keV Ar⁺ ions generated by a Physical Electronics (Phi Model 04-161) sputter ion gun. The samples
were heated by passing current through the samples and their supporting foils by means of a copper broad bolted to the sample mountings. The temperature of some of the samples were measured by means of a Pt and Pt-10% Rh thermocouple spot welded to the back of the samples or to their supporting foils. In addition an infra-red pyrometer was used to estimate the temperature of the remaining samples.

Results

A. Auger Intensities From Pure Au and Sn

Samples of pure Au and pure Sn were used to give reference intensities to obtain information about the surface composition of the bulk alloys. Chunks of 6N Au were melted into a button which was mashed flat, cut to size and polished, ultimately with 1μ diamond paste. Sn samples were prepared by cutting a piece from a larger 4N Sn ingot, course grinding to size and polishing, ultimately with 1μ diamond paste. The samples of Au and Sn were mounted simultaneously in the UHV system and both were sputtered and annealed until an acceptable degree of cleanliness was obtained. The troublesome impurities were carbon and oxygen on the Sn, and carbon and Sn on the Au. These impurities seemed to diffuse onto the surface from the bulk or from surrounding areas. Spectra of Au and Sn showing the maximum acceptable levels of impurities are shown in Fig. 1. All data considered were obtained from samples of this cleanliness or better.

The values desired were the intensities ratios of Au to Sn and Au to Au peaks. Upon cleaning and annealing, the intensities of three Au peaks observed at about 71 eV, 241 eV and 2024 eV (not shown in Fig. 1) and one Sn peak observed at 431 eV were measured in rapid succession. From the
intensity ratios and using the lock-in amplifiers scaling factors, the intensity ratios, \( R^{E/E'}_o \), were computed. \( R^{E/E'}_o \) = intensity of Auger peak at energy \( E \), divided by the intensity of the Auger peak at energy \( E' \). The superscript refers to ratios obtained from pure Au and pure Sn.

There are several immediately apparent sources of error in these measurements. To avoid effects due to drift in instrumental factors such as beam current, multiplier gain and modulation amplitude, only intensity ratios were used and these ratios were measured by scanning the two peaks involved in quick succession. Pure Au and Sn (and the alloys) were all polished in the same manner to minimize effects due to surface roughness. Measurements were repeated and averaged for a few different areas on the samples to further minimize effects due to roughness or any type of inhomogeneity. A source of error is introduced by the analyzer's sensitivity to the distance from the sample. This distance was set by maximizing the intensity of a 2000 eV elastic peak and was checked repeatedly. The samples were sputtered and annealed several times and the ratios remeasured again at a few different locations. After every measurement the cleanliness of the samples was rechecked. In addition to these precautions, actually two sets of pure Au and Sn samples were run and gave good agreement except the presence of some unremovable O on the first Sn sample caused a 6-8% reduction in the Sn intensities. As such the Au/Sn ratios from this first set were not used.

All of the values obtained from these various measurements were tabulated and averaged to give the final values included in Table 1. The errors given are the standard deviations of the data set and are indicative of the uncertainty introduced by the factors listed above.
B. Effects of Sputter Cleaning

The alloy surfaces were cleaned by sputtering with 1.5 keV Ar$^+$ ions. As with the pure Au and Sn the troublesome impurities were C and O, most of which seemed to come from the bulk or from diffusion from the surroundings. Spectra which show the maximum acceptable levels of impurities are given in Fig. 1. All data considered were obtained from samples of this cleanliness or better.

The sputtering of the samples was always found to move the alloy surface composition away from equilibrium, as is the case for Au-Ag$^3$ and Au-Pd alloys.$^4$ Sputtering always results in an increase in the Au/Sn intensity ratios. This fact gives a means of determining temperatures at which the samples can be readily equilibrated. By annealing at a particular temperature and monitoring the Auger intensity ratios, the rate of return to equilibrium can be determined. This procedure was followed for each sample. This effect is demonstrated in Fig. 2. Generally the samples were sputtered at room temperature for 1500 to 2000 secs, resulting in an increase in $R_{71/431}$. Following sputtering the Ar was removed from the chamber and the sample was heated as quickly as possible to the desired annealing temperature. The value of $R_{71/431}$ was then recorded as a function of heating time, as shown in Fig. 2. At 150°C there is an initial rapid decrease in the value of $R_{71/431}$ with time. The intensity ratio then remains constant, within experimental error, for times long compared to the time of the initial decrease and do not change appreciably when the sample is cooled suddenly to near room temperature. This behavior is interpreted as the full equilibration of the surface composition with the bulk composition.
C. Auger Intensities from the Alloys

Having obtained the equilibrium surface composition by annealing, the heater was turned off so that the sample cooled to near room temperature while the intensities of the Au and Sn peaks were recorded. From these intensities, the intensity ratios given in Table I were obtained. To obtain these ratios, all the precautions regarding instrumental drift, sample positioning, surface roughness, etc. mentioned in considering the pure Au and Sn Auger measurements were taken. Each of the ratios given are averages of many measurements made at various positions on the sample surfaces and after various cycles of sputtering and annealing. The errors given are the standard deviations of the data sets. Values obtained for measurements for which the sample was not sufficiently clean or in which there was reason to suspect that the sample was not fully equilibrated were not included. These values were used to determine the effect of these factors on the measured values. All measurements refer to samples equilibrated at 150°C except the 99 at% Au sample which was equilibrated at 200°C.

Also given in Table I are the same intensity ratios for samples which have been freshly sputtered. The values demonstrate qualitatively the extent to which the composition of the sputtered surface varied from the surface composition in equilibrium. The ion fluxes and times of sputtering are varied for these samples and do not necessarily represent an accurate steady state sputtered composition.
Discussion

A. Properties of the Au-Sn System

Sn has a smaller surface free energy than that of Au (0.650 J/m² for Sn versus about 1.4 J/m² for Au just below their melting points⁵,⁶,⁷,⁸) and on this basis, Sn may be expected to segregate to the surface.¹ This fact may also have been deduced from the more commonly known heats of sublimation, H_{sub}, of pure Au and Sn (366 KJ/g-at versus 302 KJ/g-at for Sn⁹), since there is a general correlation between the heats of sublimation and the molar surface energy of a solid.¹ In pure fcc Au, each atom has a nearest neighbor distance of 2.88 Å.¹⁰ In bc tetragonal white Sn (the form which is stable above 286°K) each atom has four nearest neighbors at 3.02 Å and two next nearest neighbors at 3.17 Å.¹¹ This atomic size difference between Au and Sn may be expected to lead to strain induced segregation.¹² The bulk phase diagram given in Fig. 3 indicates also that there is complex bulk behavior for this system with five distinct phases forming between the composition of 50 at% Au and pure Au.⁹ The bulk structures of each of these phases have been well characterized. The δ phase which forms at 50 at% Au is a very strongly ordered phase having a hexagonal type of structure (B6 "Strukturbericht" type, isotypic with NiAs) and a heat of mixing of -15.2 KJ/g-at at 273°K.⁹,¹⁰,¹¹ The ζ phase is a hexagonally close packed lattice with Au and Sn randomly distributed on the lattice.¹³ The heat of mixing for this phase is -3.34 to -4.06 KJ/g-at at 273°K.⁹ The α phase is simply the fcc Au lattice with up to about 7 at% Sn solute mixed in substitutionally.⁹ There is also some evidence for a low temperature γ phase which forms below 160°C at 83 at% Au.¹³ The high temperature β phase¹³ is of no concern to the results discussed below.
B. Analysis of the Auger Intensities

The equilibrium Auger intensity ratios are plotted in Fig. 4 and Fig. 5. The ratios are normalized by dividing by the intensity ratios in pure Au and pure Sn. The normalized ratios in Fig. 4 are Au/Sn ratios and are plotted versus the ratio of the bulk atom fractions. If the surface composition were always equal to the bulk composition, one would expect (to a first approximation) that these normalized ratios would be equal to the ratio of the bulk atom fractions and the data points would fall upon the dashed line in Fig. 4. Deviation below the dashed line indicates enrichment of Sn in the region sampled by the Auger electrons. Such a deviation is observed for the 86.7 at% Au sample \( \frac{x_{\text{Au}}}{x_{\text{Sn}}} = 6.5 \). Also for this \( \zeta \) phase alloy, the lowering of \( \frac{R}{R_{071/431}} \) below the value \( \frac{R}{R_{02024/431}} \) is indicative of greater Sn concentration in the region sampled by the 71 eV Auger electrons. Since a 71 eV electron is established to have a lower escape depth than the 2024 eV electron in metals, this indicates segregation of Sn to the surface. Therefore, both this dispersion and the overall low values of the Au/Sn ratios for this \( \zeta \) phase alloy are strong evidence for segregation of Sn to the surface in this phase.

Attention should also be called to the data in Table I for the 99 at% Au sample which is not plotted in Fig. 4. Here also the normalized ratios \( \frac{R_{071/431}}{R} < \frac{R_{0241/431}}{R_{02024/431}} < \frac{R_{02028/431}}{R} < 99 \), which is evidence for segregation of Sn in this \( \alpha \) phase alloy.

For the 50% at% Au sample (\( \delta \) phase) by contrast, the different energy Au peaks give very little dispersion and the points lie close to the dashed line indicating that the surface composition is possibly identical to the
bulk. For the two phase samples with composition between 50 and 86.7 at% Au, the intensity ratios vary smoothly between the one phase values.

In Fig. 5 the normalized Au/Au ratios are plotted versus bulk composition. Again, because of the difference in escape depths, \( \lambda \) (generally accepted as \( \lambda_71 < \lambda_241 < \lambda_2028 \)) variation of the normalized ratios from the value 1.0 may be interpreted as surface segregation. For the \( \zeta \) phase alloy (86.7 at% Au), the lowering of both ratios \( R/R_71/241 \) and \( R/R_71/2024 \) below the dashed line, and the trend \( R/R_71/241 < R/R_71/2024 \) are evidence for segregation of Sn to the surface. The same is true for the \( \alpha \) phase (99.0 at% Au) sample. For the \( \delta \) phase alloy (50 at% Au), the data would seem to indicate an enrichment of the surface in Au, but this is not consistent with the normalized ratios being less than 1.0 in Fig. 4. The two phase alloys again have intensity ratios varying quite smoothly between those of the \( \delta \) and the \( \zeta \) phases.

To attempt to estimate the extent to which the indicated segregation may be taking place, a model for the intensity of Auger emission may be used.\(^{3,16,17}\) In this model, the intensity of an Auger peak at energy \( E \), \( I_E \), is given by

\[
I_E = I_p \left( \sigma_i P_A \frac{\rho_i}{4\pi} \right) \sum_{i=1}^{\text{layers}} \rho_i x_i r_i \exp\left(-\frac{(i-1)d}{\lambda E \cos \theta_0}\right) \quad (1a)
\]

\[
\equiv K(E,\ldots) \sum_{i=1}^{\text{layers}} a_i x_i \quad (1b)
\]

Here \( I_p \) is the incident electron current, \( \sigma_i \) is the ionization cross section of the excited species, \( P_A \) is the probability of an Auger event occurring after ionization, \( \Omega \) and \( T \) are the solid angle and transmittance of the analyzer, \( \rho_i \) and \( x_i \) are the atomic density and the atomic fractions of the emitting species in the \( i \)th layer, \( r_i \) is the backscattering factor,
d is the interlayer spacing, $\lambda_E$ is the escape depth of an electron of energy E in the solid, and $\theta_0$ is the angle of acceptance of the analyzer. The first expression is broken down into a sum of intensities from each layer, $a_i x_i$, where the coefficients $a_i$ can be calculated from (1a). For pure Au or Sn the expression becomes

$$I_E^0 = I_p \left( \sigma_I^0 p_A^0 \frac{\Omega}{4\pi \ T} \right) \sum_{i=1}^{\text{layers}} \rho_i^0 r_i^0 \exp\left(-\frac{(i-1) d_i^0}{\lambda_E^0 \cos \theta_0} \right)$$

Using expressions 1 and 2 and the definition restated by (3),

$$R/R_{E/E'}^0 = \frac{I_E}{I_{E'}} \left/ \frac{I_E^0}{I_{E'}^0} \right.$$  

the values for the normalized ratios $R/R^0$ of some hypothetical surface configurations can be calculated and compared with the data. More details are given in the Appendix.

This was done using the parameters given in Table II. The expressions 1) and 2) can really only apply to close packed surface planes (i.e., planes in which each atom has six nearest neighbors in the plane) since it is assumed that every layer fully attenuates the layers below it. In pure Sn and in the $\delta$ phase, there are no close packed planes. Nevertheless, these expressions were applied to the most densely packed planes in the solid, as derived from the crystal structure and lattice parameters of the crystals. If we neglect matrix effects, then the normalization results in a cancelling of the terms $I_p \left( \sigma_I^0 p_A^0 \frac{\Omega}{4\pi \ T} \right)$, and the values of $\lambda_E$ are constant for all bulk compositions.

The results of these calculations are shown for two hypothetical surface configurations. The first configuration is for a surface in which there is no segregation in the $\delta$ (50 at% Au) or the $\zeta$ (86.7 at% Au) phase alloys. For the two phase alloys it is assumed that the two unsegregated phases are present at the surface according to their relative abundances in the bulk, that is, according to the lever rule. The result is given by the dashed-dotted curves
in Fig. 4 and 5. The fact that these curves are different than the dashed lines is due entirely to the fact that the δ and ζ phase and each of the two references all have different crystal structures so that a_i/a_i^0 in Eqns. 1) and 2). Also because of this there is, even for this unsegregated configuration, a very slight difference between the calculated normalized intensity ratios for the different energies involved. The dispersion is too slight to show up in Fig. 4 but it does appear in Fig. 5.

A second hypothetical surface configuration is presented in which the δ phase was assumed to be unsegregated (x_1=x_2=...=x_b) while the ζ phase was assumed to have x_{Au}^ζ = .40 but x_2=x_3=...=x_b = .367. The two phase alloy surfaces were then assumed to be given by applying the lever rule to the calculated intensity ratios of the unsegregated δ and the segregated ζ phases. The results are shown in Figs. 4 and 5 as solid curves. In Fig. 4 there is a marked difference between the values calculated for R/R_{71/431} and for R/R_{2024/431} which is due principally to the segregation of the ζ phase. In Fig. 5 there is also a wide dispersion between the calculated values of R/R_{71/241} and R/R_{71/2024} due to the same cause.

This second model fits quite well the data for the ζ phase, and it reproduces the general trend of the data for the two phase region. The fit is not perfect and is worse on the δ side. However, the calculation serves to show that the segregation of Sn which is evident in the ζ phase may be as great as 60 at% Sn in the top layer of a solid composed of only 13 at% Sn. It should also be pointed out that this composition (40 at% Au) does not exist in the bulk phase diagram and so may be thought of as an independent surface phase.

For the 50 at% Au sample, the data points in Fig. 4 are between the
dashed line and the dashed-dotted curve. Again, both the curve and the line result from assuming the surface composition to be equal to the bulk, but arise from different assumptions about the coefficients \( a_i \) and \( a_j \) in Eqs. (1) and (2). On the other hand, these equations might be expected to apply only to close packed surface planes of which there are none in Sn or the \( \delta \) phase. There is for this sample a slight dispersion in the normalized Au/Sn intensity ratios with the more surface sensitive ratio indicating slightly more Au. This dispersion is related to the dispersion shown in Fig. 5 for this \( \delta \) phase alloy. These inconsistencies make it difficult to state a definite surface composition, but the surface composition appears to be nearly identical to that of the bulk for the \( \delta \) phase alloy.

The effects of backscattering have also been left out of this discussion. As discussed in ref. 3 and in analogy with Au-Ag alloys since Au is the stronger backscatterer, the effect of alloying Sn into an Au matrix would be that of lowering the intensities of the Au peaks and increasing that of the Sn peaks. This would result in a depression of the Au/Sn intensity ratios. The extent and energy dependence of this poorly understood effect is not known.

C. The Surface Composition

The \( \delta \) Phase (50 at\% Au)

The Auger data seems to indicate that the surface composition is identical to that of the bulk for this alloy. This seems surprising at first since due to the lower surface energy of pure Sn, it is expected that Sn should segregate to the surface. This contradiction can be explained by consideration of the bulk structure of the \( \delta \) phase alloy.
This alloy is very strongly ordered and remains so up to the melting point. If surface segregation is to take place, this order must be defeated by interchanging Au and Sn atoms. For this alloy then it appears that the ordered lattice is stable enough to be energetically favored over the disordered state brought about by surface segregation.

In work done by Bouwman et al., the surface composition of a PtSn alloy which has the same structure as the δ phase AuSn alloy was studied and in that case they found by that there was segregation of Sn to the surface. For this alloy apparently the tendency for Sn to segregate to the surface is strong enough to bring about the disordering. For the AuCu systems, which form ordered compounds at about 25, 50 and 75 at% Au, the long range ordering is weak enough that it breaks up before the melting point is reached. Fain and McDavid found surface segregation of Au, the component believed to have the lower surface energy, for films of a wide bulk composition range.

It would be ideal to be able to predict these results by comparing quantitatively the tendency for the alloy to remain ordered and the tendency for segregation to occur. The driving force for segregation may be expected to be related to the difference between the surface energy of the pure components, or to the difference in their heats of sublimation. The tendency of the alloy to order should be related to $\Delta H_m^A$, the heat of mixing of the alloy, or better to $\Omega = \frac{\Delta H_m^A}{\frac{x^A}{x^B}}$, where $x^A$ and $x^B$ are the atom fractions of the two components in the alloy. The ratio $|H_{sub}^A - H_{sub}^B| / |\Omega|$ may be of use in predicting whether segregation takes place in an alloy. This ratio is 1.05 for AuSn. For PtSn, the heat of mixing at 298°K is -58.6 kJ/g-at, which gives a value for this ratio of 1.13.
This larger ratio indicates that for PtSn the tendency towards segregation is somewhat greater than for the AuSn alloy, in agreement with the experimental results.

The point of this discussion is to indicate that the strength of bonding between unlike atom pairs in the alloy is of importance in predicting the surface composition. Qualitative information about this effect can be obtained from the alloy heats of mixing, but much theoretical and experimental work is necessary before this effect will be fully understood.

The \( \zeta \) Phase (86.7 at% Au)

For the \( \zeta \) phase alloy, contrary to the \( \delta \) phase alloy, there is no long range ordering in the bulk and all lattice points are equivalent whether occupied by Au or Sn.\(^{13}\) For this alloy the value of \(|H^A_{\text{sub}} - H^B_{\text{sub}}|/|r|\) ranges from 2.07 to 2.21 at 273°K, which is larger than for the \( \delta \) phase alloys of Au-Sn and Pt-Sn. Here then it is expected to be easier for the Sn to segregate to the surface of the alloy. As described above, the Auger intensity data for this sample is consistent with there being a monolayer of only about 40 at% Au sitting on top of the bulk. More exact calculations and consideration of the uncertainties in the data and in the escape depths listed in Table II, leads to a value of 43±10 at% Au for this first layer composition.\(^{2}\)

It should be pointed out that this composition does not exist in the bulk phase diagram and as such, the layer may be thought of as a distinct surface phase. It would be of interest to study the structure of this surface phase by a technique such as LEED.

There are possibly two driving forces causing this segregation. The first is the fact that pure Sn has a lower surface free energy than Au. Secondly, the effects of lattice strain might also enter, since the Sn...
is somewhat dilute in a lattice where the nearest neighbor distance (2.91 Å) is smaller than that in pure Sn (3.01 Å). Segregation of Sn to the surface sites where there are fewer nearest neighbors can relieve this strain. This solid state effect which is often ignored in regular solution theories of surface segregation, has been cited as a driving force for segregation in other dilute alloys. Any theory that predicts the surface composition of alloys must take both effects into account.

The Two Phase Alloys

The samples with bulk compositions between 61 and 80 at% Au, consist of both the δ and ζ phases present simultaneously. The trend of the Auger intensity data indicates that both phases are present on the surface in the same relative proportions as their abundances in the bulk, i.e., according to the lever rule. This trend is not so clear in Fig. 4 and 5 because of the poor fit of theory to experiment for the δ phase alloy. In Fig. 6, the trend is more clearly demonstrated. In this case, rather than using the Auger intensity model given above, the lever rule is applied directly to the experimental Auger intensities of the δ and ζ phase alloys. The resulting curves must trivially pass through the one phase data points, but the good agreement of the two phase data with these curves indicates that the surface composition is given by the lever rule applied to the segregated ζ phase and the unsegregated δ phase. This eliminates the possibility that one surface active phase is coating the surface in a manner similar to the cherry model proposed by Sachtler.

The possibility that the γ phase (shown in Fig. 3) is present has been ignored in this discussion. It is difficult to say how the existence of the phase would alter these conclusions without preparing and studying a
The α Phase (99 at% Au)

The Auger data for this alloy indicates strong segregation of Sn to the surface. Using the intensity model described earlier, and the parameters of Table II, the data was found to be consistent with a monolayer surface composition of 46±10 at% Au covering the bulk composition of 99 at% Au.² Here again the driving force for segregation is due partly to the lower surface free energy of Sn, but in this case possibly the more important driving force is the relief of lattice strain caused by the large Sn atoms dissolved substitutionally in the Au lattice.

In summary, the surface composition of clean and equilibrated alloys with bulk composition between 50 and 100 at% Au have been determined by Auger electron spectroscopy. Sn is found to segregate to the surface of mono-phase substitutionally disordered alloys such as the α and the γ phase alloys. Both the lowering of the surface free energy and reduction of lattice strain are recognized as driving forces for the segregation. For an alloy composed of the single strongly ordered δ phase (forming at 50 at% Au) the tendency to remain ordered overcomes the tendency for Sn surface segregation giving rise to the same surface and bulk compositions. In alloys consisting of two phases (the δ and γ phases), the surfaces of crystallites of each phase behave independently and there is no tendency for one phase to preferentially cover the surface of the sample.

Acknowledgment

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References

Figure Captions

Fig. 1 - Derivative Auger spectra of pure Au, pure Sn and two representative alloys demonstrate the maximum acceptable levels of C and O impurities.

Fig. 2 - Annealing curves demonstrate the effects of heating sputtered alloys. The most surface sensitive Au/Sn intensity ratio is plotted as a function of annealing time after sputtering for various different temperatures.

Fig. 3 - The Au-Sn bulk phase diagram. (From Ref. 9)

Fig. 4 - Three different experimental Au/Sn normalized intensity ratios are plotted versus the ratio of the bulk atom fractions. The line (----) has a slope of unity. The curve (-.-.-.-.) gives the values for all three ratios calculated from equations 1) and 2) in the text, assuming no segregations. Upper and lower solid curves (-----) are calculated for $R/R^0_{2024/431}$ and $R/R^0_{71/431}$ respectively for a configuration exhibiting segregation of Sn in the $\zeta$ phase. (see text)

Fig. 5 - Two different experimental Au/Au normalized intensity ratios are plotted versus bulk composition. The upper and lower curves (-- - - -) are calculated for $R/R^0_{71/241}$ and $R/R^0_{71/2024}$ respectively for a configuration from equations 1) and 2) in the text assuming no segregation. The upper and lower curves (-----) are calculated for $R/R^0_{71/241}$ and $R/R^0_{71/2024}$ respectively for a configuration exhibiting segregation of Sn in the $\zeta$ phase. (see text)
Fig. 6 - The experimental intensity ratios are plotted as in Figs. 4 and 5. The curves are obtained by applying the lever rule to the experimental intensity ratios of the \( \delta \) and \( \zeta \) one phase alloys.
Table I

**Annealed Values**

<table>
<thead>
<tr>
<th>at% Au</th>
<th>(R_{71/431})</th>
<th>(R_{241/431})</th>
<th>(R_{2024/431})</th>
<th>(R_{71/241})</th>
<th>(R_{71/2024})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Au &amp; Sn</td>
<td>.558±.016</td>
<td>.068±.014</td>
<td>.0395±.0016</td>
<td>9.73±.18</td>
<td>13.97±.62</td>
</tr>
<tr>
<td>50.0</td>
<td>.505±.013</td>
<td>.0500±.0010</td>
<td>.0316±.0010</td>
<td>10.10±.14</td>
<td>15.99±.42</td>
</tr>
<tr>
<td>61.0</td>
<td>.667±.016</td>
<td>.0683±.0013</td>
<td>.0487±.0008</td>
<td>9.71±.11</td>
<td>13.60±.50</td>
</tr>
<tr>
<td>65.0</td>
<td>.657±.016</td>
<td>.0678±.0025</td>
<td>.0490±.0023</td>
<td>9.69±.19</td>
<td>13.41±.40</td>
</tr>
<tr>
<td>75.5</td>
<td>.782±.033</td>
<td>.0835±.0020</td>
<td>.0640±.0020</td>
<td>9.35±.20</td>
<td>12.20±.30</td>
</tr>
<tr>
<td>85.7</td>
<td>.931±.084</td>
<td>.1050±.0090</td>
<td>.0870±.0084</td>
<td>8.83±.19</td>
<td>10.69±.36</td>
</tr>
<tr>
<td>99.0</td>
<td>1.640±.030</td>
<td>.1860±.0030</td>
<td>.1540±.0020</td>
<td>8.79±.09</td>
<td>10.62±.27</td>
</tr>
</tbody>
</table>

**Sputtered Values**

<table>
<thead>
<tr>
<th>at% Au</th>
<th>(R_{71/431})</th>
<th>(R_{241/431})</th>
<th>(R_{2024/431})</th>
<th>(R_{71/241})</th>
<th>(R_{71/2024})</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>.838</td>
<td>.0969</td>
<td>.0729</td>
<td>9.11</td>
<td>12.13</td>
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<tr>
<td>61.0</td>
<td>1.25</td>
<td>.127</td>
<td>.0903</td>
<td>9.76</td>
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<tr>
<td>65.0</td>
<td>1.03</td>
<td>.114</td>
<td>.0829</td>
<td>8.98</td>
<td>12.5</td>
</tr>
<tr>
<td>75.5</td>
<td>2.31</td>
<td>.241</td>
<td>.169</td>
<td>9.62</td>
<td>13.7</td>
</tr>
<tr>
<td>79.9</td>
<td>6.05</td>
<td>.622</td>
<td>.430</td>
<td>9.67</td>
<td>14.27</td>
</tr>
<tr>
<td>85.7</td>
<td>5.34-11.78</td>
<td>.555-1.21</td>
<td>.422-833</td>
<td>9.60</td>
<td>13.78</td>
</tr>
<tr>
<td>99</td>
<td>24.8-51.8</td>
<td>2.63-4.73</td>
<td>1.91-3.72</td>
<td>9.43</td>
<td>13.31</td>
</tr>
</tbody>
</table>
Table II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal Face</th>
<th>Atom Density, $\rho_1$ †</th>
<th>Interlayer Spacing, $d_1$ †</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>(100)</td>
<td>.108</td>
<td>2.910</td>
</tr>
<tr>
<td>$\delta$ phase</td>
<td>(110)</td>
<td>.097</td>
<td>2.157</td>
</tr>
<tr>
<td>$\zeta$ phase</td>
<td>(001)</td>
<td>.135</td>
<td>2.38</td>
</tr>
<tr>
<td>$\alpha$ phase*</td>
<td>(111)</td>
<td>.139</td>
<td>2.354</td>
</tr>
<tr>
<td>Au</td>
<td>(111)</td>
<td>.139</td>
<td>2.354</td>
</tr>
</tbody>
</table>

$\lambda_{71} = 4\pm1$ Å
$\lambda_{241} = 8\pm2$ Å
$\lambda_{431} = 12\pm2$ Å
$\lambda_{2024} = 30\pm5$ Å

$r_1 = 1$ (no backscattering effects)
$\theta_0 = 42^\circ$

* For these purposes the lattice parameters of the $\alpha$ phase may be assumed to be equal to those of the pure Au.

† The density and interlayer spacing were taken to be the same in every layer of an alloy, even if there was segregation.
APPENDIX

As further clarification of the use of the intensity model, a numerical calculation of some values of the curves in Fig. 4 is given. The quantity $\xi_E$ is defined according to equation A.1, from which A.2 follows. Using Eqns. (1)

$$
\xi_E = \frac{I_E}{I^0_E}
$$

A.1

$$
\frac{R}{R^0_{E/E'}} = \frac{I_E}{I^0_E} / \frac{I^0_{E'}}{I^0_E} = \frac{I_E}{I^0_E} / \frac{I^0_{E'}}{I^0_E} = \xi_E / \xi_{E'},
$$

A.2

and (2) from the text, A.3 is obtained. A.4 follows from

$$
\xi_{E'} = \frac{K(E,...)}{K^0(E,...)} \begin{array}{c}
\sum_{i=1}^{\infty} a_i x_i \\
\sum_{i=1}^{\infty} a^0_i
\end{array}
$$

A.3

$$
\xi_E = \frac{\sum_{i=1}^{\infty} r^0_i \rho_i \exp\left(-\frac{(i-1) d^0}{\lambda_E \cos \theta_0}\right) x_i}{\sum_{i=1}^{\infty} r^0_i \rho_i \exp\left(-\frac{(i-1) d^0}{\lambda_E \cos \theta_0}\right)}
$$

A.4

A.3 if it is assumed that there are no matrix effects and if the definition of $a_i$ and $a^0_i$ are inserted. For a monolayer configuration it is assumed that in the alloy $x_2=x_3=...=x_b$. In the calculations given in the text it was also assumed that $\rho_i$ and $r_i$ are actually independent of the layer depth so that $\rho_i=\rho$ and $r_i=r$. Then from A.4 the expression A.5 is obtained. The sums in A.5 can

$$
\xi_E = \frac{r \rho}{r^0 \rho} \begin{bmatrix}
x_1 + x_b \sum_{i=2}^{\infty} \exp\left(-\frac{(i-1) d}{\lambda_E \cos \theta_0}\right) \\
\sum_{i=1}^{\infty} \exp\left(-\frac{(i-1) d^0}{\lambda_E \cos \theta_0}\right)
\end{bmatrix}
$$

A.5
be evaluated by using the properties of the geometric series which yields A.6.

\[ \xi_E = \frac{r \rho}{r_0 \rho_0} \left[ x_1 + x_b \left( \frac{\exp\left(-\frac{d}{\lambda_E \cos \theta_0}\right)}{1 - \exp\left(-\frac{d}{\lambda_E \cos \theta_0}\right)} \right) \right] \]

As an example the values of \( \xi_{71} \) and \( \xi_{431} \) (the normalized intensities of the Au(71eV) and the Sn(431eV) Auger peaks) will be calculated for the \( \zeta \) phase alloy. Using the parameters in Table II for the \( \zeta \) phase and for pure Au and Sn, A.6 leads to A.7.

\[ \xi_{71} = \frac{r}{r_0^{Au}} \left[ .530 \ x_1^{Au} + .432 \ x_1^{Au} \right] \]

\[ \xi_{341} = \frac{r}{r_0^{Sn}} \left[ .343 \ x_1^{Sn} + 1.139 \ x_1^{Sn} \right] \]

The values for the normalized intensity ratios \( R/R_{71/431}^0 \) can be obtained from A.7 by using A.2. For the \( \zeta \) phase sample \( (x_b = .367) \) if a top monolayer composition of \( x_1^{Au} = .40 \) is assumed, then from A.7 it is calculated that \( R/R_{71/431}^0 = 1.63 \) if the backscattering is neglected. This value is plotted in Fig. 4 as a point along the solid curve. Other ratios can be calculated in this same manner and the procedure can be extended to more than a surface monolayer. It is also, of course, possible to reverse the procedure and use the experimental intensity ratios to calculate a surface monolayer composition.
Fig. 1
Fig. 2

86.7 at.% Au

- △ - 105°C
- ○ - 150°C

50.0 at.% Au

- ▽ - 75°C
- △ - 100°C
- □ - 125°C
- ○ - 150°C

Time, seconds
Fig. 3
Fig. 4
Fig. 5
Fig. 6
This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.