An X-Ray Photoelectron Spectroscopy Study of Au$_x$In$_y$ Alloys

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AN X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF \( \text{Au}_x\text{In}_y \) ALLOYS

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ABSTRACT

Four gold-indium alloys have been studied by x-ray photoelectron spectroscopy. The binding energies and intensity ratios of the Au 4f7/2 and In 3d5/2 core levels were determined for the bulk alloy compositions of Au(10%In), Au3In, AuIn, and AuIn2. These values were determined for the native oxides on the materials, for the surfaces prepared by ion bombardment to remove the oxide and for surfaces scraped in-situ with a ceramic tool to expose the bulk composition. These results furnish calibration values that allow determination of the composition of thin films of this alloy system. In addition the binding energies add to the data base for understanding the effect of alloying on core level binding energies. As an illustration, these results are used to determine the composition of a series of alloy films formed by incongruent evaporation of an alloy charge.

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INTRODUCTION

The superior resistance to radiation of indium phosphide, as compared to GaAs and Si, against electron and proton bombardment has made the InP solar cell a prime candidate for use in space.\(^1\) Pure gold and gold based alloys such as Au-Zn, Au-Be, and Au-Ge-Ni are the most widely used contact metallization systems for InP solar cells.\(^2,3\) These cells are often heat treated to \(325-470^\circ\text{C}\) to reduce the metal-semiconductor specific contact resistivity to acceptable values,\(^2,3\) as well as to insure the proper adhesion of the contact to the substrate. Annealing these contacts gives rise to the formation of various Au-In phases. A Au(10% In) saturated solid solution, \(\text{Au}_3\text{In}\), AuIn, and \(\text{AuIn}_2\) are possible alloys that are formed during heat treatment by diffusion of In from the InP substrate into the Au contact.\(^4,5,6\) The formation of such alloys is intimately related to the mechanisms governing the interaction of Au with InP. To understand the contact formation mechanisms in the Au-InP system, it is therefore vital to be able to identify these phases accurately.

A simple and accurate identification of unknown Au-In alloy compositions can be made via X-ray Photoelectron Spectroscopy (XPS) if both the Au 4f\(^{7/2}\) and In 3d\(^{5/2}\) binding energies and the In/Au photoelectron intensity ratio are known. This paper provides relevant binding energies and standard values for the In/Au peak intensity ratios to allow alloy identification in both thin film and bulk samples. In addition to providing a method for identifying unknown Au-In alloys, this paper adds to the XPS data base for core level binding energy shifts in alloys and briefly addresses their interpretation.

As is known from studies of other alloy systems, the measured binding energies are not representative of the bulk values, because of the presence of a surface oxide layer which must be removed or otherwise accounted for. We used two techniques to remove the
oxide. The first was to remove the oxide by mechanically abrading the sample in-situ under UHV conditions. The oxide is either removed or buried in the abraded material, allowing measurements to be made on an oxide free surface that reflects the true binding energy (B.E.) and stoichiometry of the bulk. The abraded samples were used as standards for both absolute binding energies and stoichiometries. The second technique was to remove the oxide by ion bombardment and analyze the resulting surface. Preferential sputtering of indium during ion bombardment alters the binding energies and stoichiometry in the surface region of the alloy to values different from those of the bulk. However, after an initial transient, the ratio of indium to gold in the bombarded surface region equilibrates to a constant value. Binding energies and alloy dependent peak intensity ratios obtained from ion bombarded samples allow determination of an unknown alloy in a thin film system for which it would be difficult or impossible to remove the oxide by abrasion. Therefore, binding energies and peak intensity ratios for each alloy measured on the native oxide, the mechanically abraded surface, and the ion bombarded surface can be compared and provide a definitive determination for the stoichiometry of unknown Au-In alloys.

As was mentioned, ion bombardment of these alloys preferentially removes indium until a non-stoichiometric equilibrium is achieved. In addition to providing XPS binding energies, this study examines two artifacts of ion bombardment which can affect the equilibrium values for binding energies and peak intensity ratios. Ion beam energy affects the sputter yield of pure elements and was examined in this work by determining and comparing equilibrium values at two different ion beam energies. Also, ion beam mixing of the surface layer is commonly observed and can alter the binding energy and peak intensity within the analyzed depth. Ion mixing in the surface region was examined using angle resolved XPS.
EXPERIMENTAL PROCEDURE

I. Material Preparation

The alloys analyzed in this study were prepared by mixing pure indium and pure gold (99.999%) in weight ratios corresponding to the four room temperature stable phases Au(10%In), Au₃In, AuIn, and AuIn₂. The weight ratio for each alloy was exact to within ±0.07% of the total weight of the alloy. The alloys were then formed by melting the mixture with an electron beam in a vacuum of 10⁻⁶ torr to a molten state at beam powers well below those required for evaporation of either element. No evaporation was detected by a quartz crystal deposition monitor during the melting. The alloys were again weighed after melting to insure that no mass loss had occurred. The resulting alloys of Au(10%In), Au₃In, AuIn, and AuIn₂ were gold, pink, light silver, and darker silver in color, respectively.

Each alloy ingot was sectioned and final polished with 1 micron diamond paste. The final sample size was approximately 1 x 2 x 0.2 cm. As a calibration check of the spectrometer and determination of elemental peak ratios and sensitivity factors, films of pure gold and indium vapor deposited on silicon substrates were also analyzed.

II. Sample Treatment.

All samples were analyzed using a VG ESCALAB MKII x-ray photoelectron spectrometer with VGS 5000 software used for spectrum processing. Mg Kα x-rays were used and were not monochromated. Peak areas were measured by first smoothing each spectrum with a cubic smooth over 1.2 times the full width half maximum (FWHM), subtracting a linear background, and integrating Au4f7/2 and In3d5/2 photoelectron peaks with integration limits of ± 2 eV from the peak center. Sample surfaces were analyzed normal to the analyzer at 20 eV pass energy in the constant analyzer energy mode.

Surfaces were bombarded with 2.5 keV argon ions unless noted. The ion beam was rastered over a 4 by 4 mm area with a central 1
mm diameter spot analyzed by XPS. The ion beam was calibrated using a 100 nm Ta$_2$O$_5$ anodic oxide layer on a Ta substrate. The sputter rate for the Ta$_2$O$_5$ was about 7 Å/min with a total ion current to the sample of 1 µA.

The first part of the experiment consisted of abrading several 1 mm (or larger) diameter spots on each sample. The system pressure during this procedure was 2 x 10$^{-10}$ mbar. This process, while leaving a rough surface, was effective in removing the oxide. Binding energies, peak areas, and the FWHM were then obtained and compared for photoelectrons originating from each of the various alloys.

In the next part of the experiment, the samples were repolished and depth profiles were performed on each sample with two minute ion bombardment intervals for the first twenty minutes and additional measurements at 50 and 80 minutes of bombardment. Binding energies and peak areas were measured, and the atomic ratio of In to Au was calculated at each of the bombarded depths.

The effects of ion mixing and changes in ion energy were examined. Steady state values for binding energies and peak intensities were compared for 2.5 keV and 5 keV ion bombardment on the AuIn alloy.

Ion mixing was studied using angle resolved XPS. A sample normal to the analyzer will have electrons escaping from a greater depth than a sample oriented off normal allowing nondestructive depth profiling of the analyzed depth. Peak intensities and binding energies of gold and indium were taken normal to the sample and 20, 40, 60 and 80 degrees off normal for the AuIn alloy after extended bombardment and on the AuIn$_2$ alloy before bombardment.

Finally, to illustrate the identification of unknown thin films, Au$_x$In$_y$ films were deposited on a series of Si wafer substrates by electron beam heating a single Au(10%In) charge in a graphite crucible. Indium has a vapor pressure four orders of magnitude higher than gold near the melting point of gold. This causes incongruent evaporation of the initial source charge and
results in films which are indium rich (compared to the initial charge) during early evaporations and, as indium is depleted from the evaporation charge, indium poor in later evaporations. A film 200-400 nm thick was deposited on the first Si substrate. Then, using the same Au(10%In) charge, subsequent 200-400 nm films were deposited each time on a fresh Si wafer. This furnished a series of seven samples to illustrate the evaluation of unknown thin film samples and the incongruent evaporation of one of the alloys used in this study. The first sample was not analyzed but from its color appeared to be AuIn. Samples 2-7 were analyzed before ion bombardment and after 20 min. of bombardment.

RESULTS AND DISCUSSION

The intensity of a photoelectron line is given by

\[ I = n \phi \sigma y AT \]  

(1)

where \( n \) is the number of atoms per cm\(^3\), \( f \) is the X-ray flux, \( \sigma \) is the photoelectric cross-section, \( \phi \) is an angular correction factor, \( y \) is a photoelectric ground state efficiency factor, \( A \) is the area from which photoelectrons are detected, and \( T \) is the efficiency of detection of emitted photoelectrons of that energy by the analyzer and \( \Gamma \) is the mean free path.\(^8\) The product AT in equation 1 includes energy analyzer dependent terms which, in the case of a hemispherical analyzer, are approximately proportional to the reciprocal of the square root of the kinetic energy and approximately cancel with the mean free path which is proportional to the square root of kinetic energy leaving the measured intensity and peak intensity ratio dependent only on the photoionization cross-sections and atomic densities. This is not the case for other analyzers such as the cylindrical mirror analyzer (CMA) where the transmission function of the analyzer is proportional to the inverse kinetic energy.\(^9\) Therefore, sensitivity factor ratios used or compared with in this study were obtained by either correcting the Wagner empirical sensitivity factor for transmission function differences or using Scofield photoionization cross sections.
corrected for atomic densities.

Binding energies and peak areas determined from samples abraded in vacuum are reported in Table 1 along with the sensitivity factor ratio $S'$ (defined as the sensitivity factor ratio of Au 4f7/2:In 3d5/2 required to obtain the true atomic fraction). The FWHM of the Au and In photoelectron peaks reported in Table 1. varied between 0.9 and 1.2 eV. Pure elemental standards used in this study produced a sensitivity factor ratio which agreed (within 2%) with the Wagner empirically determined pure element sensitivity factor ratio. The sensitivity factors were dependent on alloy composition and considerably different from either the Wagner elemental sensitivity factors or the elemental values determined from standards used in this study. No correction was made for atomic density. Individual spectra are graphically shown in Figures 1 and 2 for all four alloys including pure Au and pure In.

Note that as the atomic percentage of In increases from alloy to alloy, the Au binding energy increases about 0.3 eV for each change in composition while the In binding energy remains approximately unchanged. This core level binding energy shift in the gold and little change in the indium was not predicted from a simple core-level electron screening calculation and the reader is referred to extensive work on core-level binding energy shifts in alloys. The measured binding energies for pure Au and pure In, as deposited on silicon substrates and after cleaning are in close agreement with the published data.

To examine the effects of ion bombardment, a depth profile was done on each sample. Peak intensities and binding energies for Au 4f7/2 and In 3d5/2 electrons were measured at each depth. The ion beam energy was 2.5 keV except for the AuIn alloy which was run at both 2.5 and 5 keV with the same total current to the sample. Indium is known to have a higher sputter yield than gold at a given beam energy. Results of ion bombardment are displayed in figure 3. Features to note are: i.) a plateau is reached in the atomic
ratio after 10 to 20 minutes of sputtering which was longer than the ten minutes required to remove the oxygen alone showing that the sputtering process continued to alter the stoichiometry after the oxide was removed, ii.) a ratio of indium to gold, as obtained on scraped samples representing the bulk, is achieved in less than 10 minutes of sputtering and before complete removal of the oxide, and iii.) sputtering at 5 keV on the AuIn alloy does not appear to alter the profile plateau obtained at 2.5 keV.

The B.E.'s for Au 4f7/2 photoelectrons from the abraded and the ion bombarded surface are plotted against the actual atomic ratio in figure 4. Values for the Au 4f7/2 B.E. on the native oxide surface could vary by 0.3 eV for a given alloy depending on the time between sample preparation and measurement. While the binding energy of indium may follow a slight trend toward lower binding energy at increased indium concentration, the difference is not large enough to distinguish alloy compositions. However, the Au 4f7/2 B.E. of figure 4 can be used in the identification of an unknown alloy. To obtain the In/Au atomic ratio in an unknown thin film alloy which can not be abraded the binding energy of Au 4f7/2 binding energy is measured on the ion bombarded surface and compared to the ion bombarded values of figure 4 reached after sputtering into the plateau region. The abraded data is highly self-consistent and abrasion is a good technique to examine the bulk-like properties of an oxidized surface provided the sample is thick enough to scrape the oxide away. Ion bombardment causes a decrease in the binding energy of the gold which is in accordance with the depletion of In observed during bombardment. To summarize, the binding energy from the abraded data can be used to determine the composition of unknown bulk samples and the binding energy from the ion bombarded films can be used as a preliminary identification of unknown thin film deposits.

While the Au 4f7/2 binding energy alone is suitable for bulk sample identification; the uncertainty in the binding energies of fig. 4 are near ±0.025 eV and for ion bombarded samples differences
in the In/Au ratio become difficult to distinguish as the In/Au ratio drops below 1/3. Further information is necessary to determine the composition of an unknown thin film. In addition to binding energies, peak intensities were also measured. The In/Au intensity ratios determined from the ion bombarded and the scraped surfaces are plotted against the true bulk atomic ratio in figure 5. Again the abraded data is self-consistent and appears to be nearly linear with composition where deviations from linearity are possibly caused by matrix effects. The native oxide, while not displayed, appeared enriched in In or over stoichiometric while the ion bombarded surface is depleted in In or under stoichiometric. Again, the native oxide atomic ratio was dependent on the time the alloy remained in the laboratory after polishing and before analyzing. In/Au ratios for the native oxide ranged between the values for abraded samples to more than three times those values. Figure 5 provides a calibration graph for the estimation of thin film phases which can be identified by using values obtained from the ion bombarded surface and comparing them to values found in figure 4. Thus the binding energy of Au together with In/Au intensity ratios and the color of the alloy described in the experimental procedure provides a suitable confirmation of composition for unknown thin film samples.

Several issues involved in the determination of the ion bombarded steady state values of figure 3 should be addressed. Profile concentrations can change as a function of ion beam energy because the depth of an altered layer sometimes increases with ion energy and can be comparable to the XPS sampling depth on samples bombarded with 2 keV ions. Others have found, however, the atomic ratio in an ion bombarded alloy is unaffected by ion species or energy. The atomic ratio found on the bombarded surface in this study also appears to be independent of ion energy. In addition to In/Au plateaus of each depth profile, sharp changes occurred in the indium concentration as a function of time during the early indium profile for each alloy. These sharp changes in concentration as a
function of time are sometimes attributed to segregation of the alloy species occurring during preferential sputtering.\textsuperscript{16, 17}

Although an analysis of the various mechanisms of preferential sputtering, diffusion, or segregation is not done here, more can be said of the resultant surface layer obtained with or without sputtering. Angle resolved XPS provides a method of enhancing the signal obtained from the top atomic layer by analyzing the photoelectrons at a grazing exit angle to the surface.\textsuperscript{18} Table 2 shows a summary of results obtained on unsputtered AuIn and AuIn\textsubscript{2} after sputtering 80 min. Binding energies and peak areas were measured as a function of take off angle with respect to the surface normal. Peak area ratios were normalized to values found with the sample normal to the analyzer. The unsputtered AuIn alloy has an increased ratio of indium to gold and oxygen to indium in the surface region. This implies that the surface has more indium and oxygen than the underlying layers within the analyzed depth, a result which may be expected with the diffusion to the surface of cation species commonly found during metal oxidation. This was also confirmed by the corresponding decrease in the Au photoelectron binding energy which occurred with increased indium concentration in all alloys. The gold binding energy and indium to gold ratio remained the same on the sputtered samples indicating that the artifacts created by ion bombardment remain constant and continue throughout the region of analysis.

As a final addition to this study a series of unknown thin films were analyzed. Figures 4 and 5 are used to identify the unknown composition and the identification is shown in table 3. The In/Au ratio can be seen to decrease in samples 1-7 and is a result of incongruent evaporation where indium is preferentially depleted from the evaporation source. The samples from evaporations 1-7 begin at 50\% In and end at 10\% In. It thus appears that the Au/In intensity ratios as shown in figure 5 are a more accurate method of determining stoichiometry than the Au binding energy.
CONCLUSIONS

All four room temperature phases of the Au-In system have been prepared and their binding energies and Au\textsubscript{4f}/In\textsubscript{3d} peak intensity ratios measured on the native oxide, the abraded, and the ion sputtered surface. Physical abrasion is an effective method to prepare alloy surfaces to reflect bulk properties. The analysis of standards prepared in this manner has led to the ability to determine the composition of unknown thin film metalizations on solar cells. This procedure should be widely applicable in the electronic industry. Basic data on core-level binding energy shifts in alloys has also been presented adding to the current data base.
REFERENCES


TABLE 1. - BINDING ENERGIES AND PEAK AREAS FOR SAMPLES SCRAPED WITH A CERAMIC SCRAPER

[The factor $S'$ represents the normalization needed to achieve the bulk stoichiometry from the In/Au peak area ratios.]

**ABRADED SAMPLES**

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>AREA NO.</th>
<th>Binding Energy (eV)</th>
<th>PEAK INTENSITY</th>
<th>Actual Atomic Ratio</th>
<th>Normalization Factor</th>
<th>$S'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(In) (In=10%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 1</td>
<td></td>
<td>84.20 eV</td>
<td>443.95 eV</td>
<td>0.270</td>
<td>0.111</td>
<td>0.41</td>
</tr>
<tr>
<td>- 2</td>
<td></td>
<td>84.25 eV</td>
<td>443.95 eV</td>
<td>0.287</td>
<td>0.111</td>
<td>0.39</td>
</tr>
<tr>
<td>- 3</td>
<td></td>
<td>84.20 eV</td>
<td>444.00 eV</td>
<td>0.267</td>
<td>0.111</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave. 0.41±0.02</td>
</tr>
<tr>
<td>Au$_3$In</td>
<td>- 1</td>
<td>84.50 eV</td>
<td>444.00 eV</td>
<td>0.674</td>
<td>0.333</td>
<td>0.50</td>
</tr>
<tr>
<td>- 2</td>
<td></td>
<td>84.55 eV</td>
<td>444.00 eV</td>
<td>0.774</td>
<td>0.333</td>
<td>0.47</td>
</tr>
<tr>
<td>- 3</td>
<td></td>
<td>84.55 eV</td>
<td>444.00 eV</td>
<td>0.710</td>
<td>0.333</td>
<td>Ave. 0.47±0.04</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave. 0.719±0.055</td>
</tr>
<tr>
<td>AuIn</td>
<td>- 1</td>
<td>84.80 eV</td>
<td>443.85 eV</td>
<td>1.86</td>
<td>1.000</td>
<td>0.54</td>
</tr>
<tr>
<td>- 2</td>
<td></td>
<td>84.80 eV</td>
<td>443.90 eV</td>
<td>1.83</td>
<td>1.000</td>
<td>0.55</td>
</tr>
<tr>
<td>- 3</td>
<td></td>
<td>84.80 eV</td>
<td>443.90 eV</td>
<td>1.84</td>
<td>1.000</td>
<td>Ave. 0.54±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave. 1.84±0.02</td>
</tr>
<tr>
<td>AuIn$_2$</td>
<td>- 1</td>
<td>85.15 eV</td>
<td>443.85 eV</td>
<td>3.93</td>
<td>2.000</td>
<td>0.51</td>
</tr>
<tr>
<td>- 2</td>
<td></td>
<td>85.15 eV</td>
<td>443.85 eV</td>
<td>3.92</td>
<td>2.000</td>
<td>0.51</td>
</tr>
<tr>
<td>- 3</td>
<td></td>
<td>85.10 eV</td>
<td>443.85 eV</td>
<td>3.81</td>
<td>2.000</td>
<td>0.53</td>
</tr>
<tr>
<td>- 4</td>
<td></td>
<td>85.20 eV</td>
<td>443.85 eV</td>
<td>3.87</td>
<td>2.000</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave. 3.88±0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave. 0.52±0.01</td>
</tr>
<tr>
<td>Pure Gold and Indium</td>
<td></td>
<td>83.95 eV</td>
<td>443.65 eV</td>
<td>1.183</td>
<td>1.000</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(CLEANED BY ION BOMBARDMENT)</td>
</tr>
</tbody>
</table>

Wagner sensitivity factor ratio from bulk elemental values and corrected for the hemispherical analyzer transmission. $(S_{Au}/S_{In})^{10}$ 0.86
TABLE 2. - BINDING ENERGIES AND PEAK AREAS AS A FUNCTION OF ANGLE FOR UNSPUTTERED AUIN AND AUIN$_2$ AFTER 80 MINUTES OF SPUTTERING

[No oxygen was detected on AuIn$_2$ at any angle.]

<table>
<thead>
<tr>
<th>ANGLE</th>
<th>AuIn ALLOY WITH NATIVE OXIDE (ratios normalized to 0°)</th>
<th>Au B.E.</th>
<th>In B.E.</th>
<th>In/Au RATIO</th>
<th>In/O RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td></td>
<td>84.75</td>
<td>444.4</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>20°</td>
<td></td>
<td>84.70</td>
<td>444.6</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>40°</td>
<td></td>
<td>84.70</td>
<td>444.6</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>60°</td>
<td></td>
<td>84.60</td>
<td>444.8</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>80°</td>
<td></td>
<td>84.55</td>
<td>444.9</td>
<td>1.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

AuIn$_2$ ALLOY BOMBARDED 80 MIN. NO OXYGEN

<table>
<thead>
<tr>
<th>ANGLE</th>
<th>AuIn$_2$ ALLOY BOMBARDED 80 MIN. NO OXYGEN</th>
<th>Au B.E.</th>
<th>In B.E.</th>
<th>In/Au RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td></td>
<td>84.80</td>
<td>443.85</td>
<td>1.00</td>
</tr>
<tr>
<td>20°</td>
<td></td>
<td>84.85</td>
<td>443.85</td>
<td>1.1</td>
</tr>
<tr>
<td>40°</td>
<td></td>
<td>84.85</td>
<td>443.85</td>
<td>1.1</td>
</tr>
<tr>
<td>60°</td>
<td></td>
<td>84.85</td>
<td>443.85</td>
<td>1.2</td>
</tr>
<tr>
<td>80°</td>
<td></td>
<td>84.80</td>
<td>443.85</td>
<td>1.0</td>
</tr>
</tbody>
</table>

TABLE 3. - RESULTS OF THE ANALYSIS OF THIN FILM Au-In ALLOYS DEPOSITED IN SEQUENCE ON SILICON SUBSTRATES

[Evaporations were done using the same original charge of Au (10% In).]

<table>
<thead>
<tr>
<th>EVAPORATION NO.</th>
<th>ANALYSIS CONDITIONS</th>
<th>Au B.E.</th>
<th>In/Au PEAK RATIO</th>
<th>IDENTIFIED INDIUM/GOLD RATIO FROM Au B.E.</th>
<th>FROM In/Au PEAK RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NOT ANALYZED</td>
<td>(FROM THE COLOR IT APPEARED TO BE AuIn)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>SPUTTERED</td>
<td>84.40</td>
<td>0.524</td>
<td>0.333-1.000</td>
<td>0.71</td>
</tr>
<tr>
<td>3</td>
<td>SPUTTERED</td>
<td>84.10</td>
<td>0.188</td>
<td>0.111-0.333</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td>SPUTTERED</td>
<td>84.10</td>
<td>0.188</td>
<td>0.111-0.333</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>SPUTTERED</td>
<td>84.05</td>
<td>0.130</td>
<td>0.111-0.333</td>
<td>0.22</td>
</tr>
<tr>
<td>6</td>
<td>SPUTTERED</td>
<td>84.05</td>
<td>0.099</td>
<td>0.111-0.333</td>
<td>0.18</td>
</tr>
<tr>
<td>7</td>
<td>SPUTTERED</td>
<td>84.05</td>
<td>0.084</td>
<td>0.111-0.333</td>
<td>0.16</td>
</tr>
</tbody>
</table>

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Au$_3$In = Au(In)$_{10\%}$

FIGURE 1. - Gold 4f$^{7/2}$ binding energy as a function of composition. Note the 0.3 eV shift from pure gold to Au(10%In) and each subsequent increase in indium concentration.

FIGURE 2. - Indium 3d$^{5/2}$ binding energy as a function of alloy composition. All alloys are within a 0.2 eV window in binding energy with no apparent trend.

FIGURE 3. - Indium to gold peak intensity ratio as a function of bombardment time with 2.5 keV argon ions for each of the four alloys and AuIn bombarded at 5 keV. Plateau values for AuIn$_x$, AuIn$_2$, Au$_3$In, and Au(10%In) are 1.6, 0.69, 0.18, and 0.067 respectively.

FIGURE 4. - Binding energy of Au 4f$^{7/2}$ electrons as a function of alloy composition for the abraded and the ion bombarded surface.
**Figure 5.** Indium to gold intensity ratio as a function of alloy composition for the abraded and ion bombarded surface. Note the abraded surface, representative of the bulk stoichiometry, shows the ion bombarded surface to be under stoichiometric.
Four gold-indium alloys have been studied by x-ray photoelectron spectroscopy. The binding energies and intensity ratios of the Au 4f7/2 and In 3d5/2 core levels were determined for the bulk alloy compositions of Au(10%In), AuIn, AuIn2, and AuIn2. These values were determined for the native oxides on the materials, for the surfaces prepared by ion bombardment to remove the oxide and for surfaces scraped in-situ with a ceramic tool to expose the bulk composition. These results furnish calibration values that allow determination of the composition of thin films of this alloy system. In addition the binding energies add to the data base for understanding the effect of alloying on core level binding energies. As an illustration, these results are used to determine the composition of a series of alloy films formed by incongruent evaporation of an alloy charge.