ADHESION OF GOLD TO VARIOUS PLANES OF COPPER STUDIED WITH LEED

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

An investigation was conducted with the aid of LEED, to determine the influence of crystallographic orientation on adhesion of gold to copper. A single gold orientation contacted three planes of copper, the (111), (100), and (110) planes. Adhesion under light loads resulted in adherence of gold to all three planes of copper. This result could be correlated with theoretical considerations of adhesive and cohesive bonding forces. The gold bonded epitaxially to all three planes of copper, with the weakest force of adhesion occurring to the (111) plane of copper. While lattice strains were observed to occur in gold as a result of such adhesive contacts, no such strain was noted in the copper.
A study was conducted to determine the influence of copper orientation on adhesion in a copper-gold couple. Adhesion experiments were made in a LEED (low-energy electron diffraction) apparatus, with the surfaces being examined before and after adhesive contact. A gold (100) surface contacted three planes of copper, the (111), (100), and (110) planes. The gold specimen was 1 millimeter in diameter, and the loads applied to the gold contacting a large copper flat were from 20 to 60 milligrams. All experiments were conducted with clean surfaces at a pressure of $10^{-11}$ to $10^{-10}$ torr.

The results of the investigation indicate that copper orientation influences the adhesive forces between copper and gold. For all three planes of copper, the gold was found to adhere epitaxially. In all instances, gold transferred to the copper surface; thus, the forces required to separate the surfaces were a measure of the breaking of cohesive rather than adhesive bonds. These experimental results could be correlated with theoretical bonding forces. The weakest bonding of gold to copper was on the (111) plane.

The crystallographic orientation of metallic surfaces has been shown to exhibit a marked influence on adhesion and cohesion of metals (ref. 1). With copper in contact with itself (ref. 1), the highest atomic density plane, the (111), exhibited the least tendency to adhere to dissimilar planes of copper or to cohere to itself. The atomic arrangement of the surface thus exhibits an influence on adhesion and cohesion as it does on many other properties.

In most instances, the adherence of metal surfaces to materials other than themselves is as important or more important than self-bonding. In such contacts the forces
involved are more complex than in simple cohesion. With dissimilar metals in contact, there are the cohesive bonding forces in the two bulk metals and the adhesive forces at the interface. The adhesive forces may be very markedly influenced by atomic surface arrangement. This arrangement will influence (1) lattice stresses in the cohesively weaker of the two materials, (2) the interfacial dislocations, and (3) the electron/atom ratio.

The objective of this report is to study the adhesion of gold to three atomic planes of copper with the aid of LEED (low-energy electron diffraction) to determine the effect of copper orientation on adhesion. The adhesion experiments were conducted with a single (100) orientation of gold, and the three copper orientations examined to determine the influence of atomic plane on adhesion were the (111), (100), and the (110) planes. The copper surfaces were examined with LEED prior to contact with gold under various loads and after adhesive contact. The loads applied to a 1.0-millimeter-diameter gold flat in contact with the copper surfaces varied from 20 to 60 milligrams. All experiments were conducted in a vacuum of $10^{-11}$ to $10^{-10}$ torr after both specimen surfaces were cleaned.

**APPARATUS**

The apparatus used in these studies is shown schematically in figure 1. The single-crystal surface mounted in the center of the chamber could be rotated $360^\circ$. This rotatability allowed for the making of adhesion measurements on the crystal surface shown in figure 1, then rotating the crystal $180^\circ$ and obtaining a LEED pattern from the crystal surface in the adhesion contact area. The crystal could also be moved in the lateral and vertical directions.
The crystal specimen was supported in the chamber by means of two metal rods (insulated) which were used to resistance heat the crystal. A 100-ampere ac power supply was used for resistance heating.

The fiber which contacted the single-crystal metal surface was mounted in a stainless-steel holder which was, in turn, mounted to a 1.5-millimeter-diameter stainless-steel beam. The beam was mounted in a bearing-containing yoke. At the end of the beam beyond the pivot point and opposite the fiber specimen was a small permanent magnet. Outside the chamber wall were two electromagnets. The permanent magnet and electromagnets were positioned in such a manner as to have like poles facing each other. A simple variation in the current applied to the magnets could be used to move the beam.

The current applied to the electromagnets was calibrated in terms of the force applied in the adhesion experiments. Load applied to the surfaces in contact was measured by current, as was the force required to separate the crystal surfaces.

The LEED electron optics and the vacuum system were of the standard type used by those engaged in LEED studies and is adequately described in the literature (ref. 2). It consists essentially of a beam of low-energy electrons (voltage, 0 to 450 volts) striking a crystal surface and diffracting the electrons from the outermost atomic layers. The diffracted electrons strike a phosphor screen, producing a spot pattern analogous to that obtained in conventional electron diffraction and X-ray Laue work.

MATERIALS

The crystals used in this investigation were grown from triple-zone refined metals. The specimens were all cut from single-crystal rods. The copper specimens were of 8.0-millimeter-diameter rod and were cut to a thickness of 6.0 millimeters. The flats were polished on papers to 600 grit and then electropolished in orthophosphoric acid to remove the worked surface layer. In the majority of experiments, the gold specimen which contacted the copper was 1.0 millimeter in diameter. In experiments to determine the strain in gold, copper contacted 10-millimeter-diameter gold flats. These were processed on the papers as was the copper. They were then electropolished in an aqueous solution of nitric and hydrofluoric acids.

EXPERIMENTAL PROCEDURE

The crystal specimens were mounted in the apparatus and after pumpdown and bake-out, the crystals were heated to and held at 500°C for 3 hours to allow for thorough outgassing. The temperature was decreased to 450°C, and hydrogen gas was admitted
to the chamber to remove oxygen or reduce surface oxides. Sufficient gas was admitted to raise the pressure to $10^{-6}$ torr. After 15 minutes, the system was reevacuated to $10^{-10}$ torr. The crystal was then heated to $500^\circ$ C to remove hydrogen; the pressure in the chamber after hydrogen was removed from the surface and the crystal cooled to room temperature was $1.0 \times 10^{-11}$ to $1.0 \times 10^{-10}$ torr. LEED patterns were then obtained from the clean surface.

**EXPERIMENTAL RESULTS**

**Adhesion to (111) Plane of Copper**

The LEED pattern for a clean (111) copper surface is shown in figure 2(a). Figure 2(b) shows that same surface after it was contacted by the gold specimen and the surfaces separated. Examination of the LEED pattern in figure 2(b) reveals the presence of an additional set of diffraction spots inside those for copper (111). These spots result from an epitaxial layer of gold on the copper (111) surface. The presence of gold was substantiated by solid-state mass spectrometer analysis (sensitivity ppb) of the surface layer.

The force required to separate gold from the (111) copper surface is presented in table I with other properties of this plane, as well as for the (100) and (110) planes. The force required to separate the (111) copper-gold surfaces was four times the force applied (20 mg) in making adhesive contact. It can also be seen from table I that the (111) plane is atomically the most dense plane, having the highest coordination number and, as might be anticipated from these other two properties, the greatest elastic modulus.

When the surface shown in figure 2(b) was heated to $500^\circ$ C for 30 minutes, the pattern of figure 2(c) was obtained. The presence of additional spots indicates mobility of the gold on the copper surface. When the load applied to the gold in contact with the copper surface was increased, the pattern of figure 2(d) was obtained. A further increase in the load to 60 milligrams resulted in the pattern of figure 2(e). The increase in adhesive force is believed to reflect an increase in the amount of gold transferred to the copper surface with increase in the amount of gold transferred to the copper surface with increase in load. Observations with LEED of vapor deposition of gold on the (100) surface of copper seem to substantiate that this is, in fact, what is occurring (ref. 3).

**Adhesion to (100) Plane of Copper**

A LEED pattern obtained for a clean (100) copper surface is presented in figure 3(a). Note the unit mesh as shown schematically in table I. Adhesive contact with gold re-
Figure 2. LEED photographs of copper (111) surface before and after adhesive contact with gold (100) surface.

(a) Clean copper (111) at 70 volts.

(b) After contact with gold (100) under 20-milligram load.

(c) Same as (b) but heated to 500°C for 30 minutes.

(d) After contact with gold (100) under 40-milligram load.

(e) After contact with gold (100) under 60-milligram load.
TABLE I. - SOME PROPERTIES OF THREE PLANES OF COPPER TOGETHER WITH MEASURED ADHESIVE FORCES TO THOSE PLANES

<table>
<thead>
<tr>
<th>Copper surface plane</th>
<th>Coordination number of surface</th>
<th>Atomic arrangement of surface unit mesh</th>
<th>Atomic number of surface, atoms/cm²</th>
<th>Elastic modulus, dynes/cm²</th>
<th>Surface energy, ergs/cm²</th>
<th>Force of adhesion to gold, a</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>9</td>
<td>![Pattern 1]</td>
<td>1.7×10¹⁵</td>
<td>19.4×10¹¹</td>
<td>2499</td>
<td>80</td>
</tr>
<tr>
<td>(100)</td>
<td>8</td>
<td>![Pattern 2]</td>
<td>1.5×10¹⁵</td>
<td>6.67×10¹¹</td>
<td>2892</td>
<td>185</td>
</tr>
<tr>
<td>(110)</td>
<td>7</td>
<td>![Pattern 3]</td>
<td>1.1×10¹⁵</td>
<td>13.1×10¹¹</td>
<td>----</td>
<td>390</td>
</tr>
</tbody>
</table>

aApplied load, 20 mg; Au (100) surface; contact time, 10 seconds.

sulted in the pattern of figure 3(b). The pattern is difficult to resolve. If the voltage is increased to 140 volts on the electron gun, the pattern of figure 3(c) was obtained. It shows again a doubling of spots indicative of epitaxial adhesion of gold to copper. When the surface of figure 3(c) was heated for 30 minutes at 200°C, the pattern of figure 3(d) was obtained. The pattern of figure 3(d) indicates mobility of the gold on the copper surface appreciably greater than that seen in figure 2(c) for the (111) plane at 500°C.

The pattern of figure 3(d) appears to reflect an incomplete rearrangement to the CuAu surface structure observed by Palmberg and Rhodin in reference 3 with vapor deposition of gold on the (100) surface of copper. In the study reported herein, it appears additional energy is required to bring about surface rearrangement to the CuAu structure because of the solid-state contact. There is also less surface coverage than observed by Palmberg and Rhodin.

The force of adhesion of gold to the (100) surface of copper is presented in table I. For a 20-milligram load, the force required to separate the surfaces was nine times the applied load. The force required to separate the gold from the (100) copper surface was greater than twice what it was to separate gold from the (111) surface. The reasons for this will be discussed later.
Adhesion to (110) Plane of Copper

The clean (110) surface of copper as seen by LEED is shown in figure 4(a). After adhesive contact with gold under a 20-milligram load, the pattern of figure 4(b) again indicates epitaxial attachment of gold to copper.

The force of adhesion of gold was greatest on the (110) plane of copper, as shown by the data of table I. On the (110) surface a force of 390 milligrams or nearly 20 times that of the applied force was measured. Table I indicates that the plane with the smallest coordination number and least number of surface atoms gave the highest force of adhesion. The adhesive force of gold to the (110) plane of copper was nearly five times that of gold to the (111) plane.
Some experiments were conducted to determine the time required to separate the gold from the copper surface. Since gold remained adhered to copper in these experiments, this consisted essentially of a tensile test on the gold. The results obtained in some of these experiments are presented in figure 5. The force to fracture the gold is plotted as a function of time to fracture. At 390 milligrams, the specimen surfaces separated very rapidly, as indicated by figure 5. As the load was decreased, the time to fracture continued to increase; at tensile forces less than 150 milligrams, no fracture of the adhered pair was obtained at times up to 6000 seconds.

At loads less than that required for fracture, the tensile stress must be below the elastic limit of the weakest region in the couple, and fracture will not occur. If the stress is increased to a value where the junction area will yield plastically, fracture and separation occur after some period of time. Figure 5 shows the intercepts of the elastic and plastic regions of the curve. From figure 5 it can be said that, at loads in excess of 150 milligrams, the gold below the surface contact in the microjunctions is behaving plastically; while at loads less than 150 milligrams, it is elastic.

The elastic limit of gold is well known. From the intercept value of figure 5, it should be possible to determine real contact area. Such a determination yields a contact area $1/185^{th}$ that of the apparent area (area defined as that of the 1 mm diam contacting fiber). It must be stressed that the yielding and fracture discussed here, in light of the LEED patterns, is occurring in the outermost atomic layers and the terms do not apply to bulk behavior.
Figure 5. - Time required to rupture cohesive bonds in gold. Adhesion of gold (100) to copper (110); contacting load, 20 milligrams for 10 seconds; ambient pressure, $10^{-10}$ torr; temperature, 20°C.

Figure 6. - Change in current intensity with adhesion of gold (100) surface to various planes of copper. Load, 20 milligrams; contact time, 10 seconds; beam incidence, (00).
Concentration of Gold on Copper After Adhesive Contact

The current intensity at some specific voltage on the LEED screen will be decreased by the adherence of a foreign material to the copper crystal surface (refs. 4 and 5). Figure 6 shows a decrease in current intensity for both the (111) and (100) surfaces. On the (110) surface the intensities were nearly the same before and after adhesive contact. This would indicate that the amount of gold transferred was greatest on the (110) surface. The reason for this is that, when the deposited material covers enough of the surface, the gold peak intensity will emerge with its own intensity, which may be as great as that of the initial copper peak. In studies with varying loads on the gold contacting these three surfaces, the intensity curve went through a minimum as load was increased. The explanation for this may well be that, as discussed in references 4 and 5, epitaxial deposition of metal to the surface at small concentrations results in a decrease in the copper peak intensity. At some thickness, a new peak will develop for the epitaxially deposited metal; and, when the film is sufficiently thick (three monolayers of nickel in ref. 5), the peak intensities may be those of the deposited metal.

Adhesion of Copper to (100) Plane of Gold

If gold is transferred to copper in the adhesion experiments, the question arises as to whether this is a two-way process; that is, is copper also transferred to gold? Experiments were therefore conducted with the (100) copper surface making contact with a (100) surface of a gold flat. Figure 7(a) shows the LEED pattern for the clean gold surface at two different voltages. Figure 7(b) shows that same surface after it had been

![Figure 7](C-69-1088)

(a) Clean gold (100) at 65 volts.  (b) After contact with copper (100) under 20-milligram load.

Figure 7. - LEED photographs of gold (100) surface before and after adhesive contact with copper (100) surface.
contacted by a 1-millimeter-diameter copper (100) under a 20-milligram load. Strain has taken place in the surface of the gold. Note that while the gold (100) surface has undergone strain at 20 milligrams, the copper (100) surface in figure 3(c) had not. Analysis of the gold surface did not reveal the presence of copper. The gold surface in figure 7(b) was heated above its annealing temperature to substantiate that strain had occurred. The pattern of figure 7(b) was obtained before heating.

DISCUSSION

Theoretical Considerations

In a copper-gold ordered alloy the distribution of copper and gold atoms for a CuAu composition are as shown in figure 8(a). There is a uniform distribution of copper and gold atoms in each of the two layers. Each copper atom has for its neighbor a gold atom.

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**Figure 8.** - Atomic arrangement and lattice bonding.
This structure appears to be developing on the surface shown in figure 3(d) and was observed in reference 3 with vapor deposition of gold onto copper. Figure 8(b) represents the atom arrangement of figures 2(b), and 4(b). Each atom is bounded on three sides by like atoms. Across the interface, adhesive bonding occurs.

Since gold remains on the copper surface after adhesion experiments, the gold-to-gold cohesive bonds must be weaker than either the interfacial adhesive bonds of figure 8(b) or the copper-to-copper cohesive bonds. The experimental results should then agree with calculations of these various bonds. Reference 6 gives equations for such bond force calculations. The equation for cohesion is

\[ \sigma_{\text{cohesion}} = \frac{\langle C_{11} \rangle}{\beta} \]

where

- \( \sigma_{\text{cohesion}} \): cohesive strength, dynes/cm\(^2\)
- \( C_{11} \): average elastic stiffness
- \( \beta \): constant

and

\[ \langle C_{11} \rangle = \frac{C_{44} - \frac{d}{5} (2C_{12} + C_{11})}{C_{44} + C_{12} - 2 \frac{d}{5}} \]

where

\[ d = 2C_{44} + C_{12} - C_{11} \]

and \( C_{44}, C_{12}, \) and \( C_{11} \) are elastic constants which are readily available in the materials science literature for both gold and copper.

If the appropriate values are put into the equations for copper and gold, the cohesive strength for copper is \( 2 \times 10^{11} \) dynes per square centimeter. For gold the cohesive strength is \( 4.73 \times 10^{10} \) dynes per square centimeter. Thus, it should be easier to break the gold bonds. Using elastic constants for copper-gold alloy from reference 7, an adhesive bond force of \( 5.72 \times 10^{10} \) dynes per square centimeter is obtained.

From a theoretical consideration of bond forces, it might be anticipated that the weakest bonding would occur in the gold. This agrees with the experimental observations reported herein.
Adhesion Mechanism

Epitaxial deposition of one metal onto another has been observed in a number of investigations (refs. 4 and 8 to 11). It has been observed for inorganic crystals (ref. 12) and in oxides on the parent metal (refs. 13 and 14). Thus epitaxial adhesion in this investigation is not an unprecedented observation. The interesting observation herein is that it occurs when two solid surfaces make contact. The patterns presented herein are believed to reflect epitaxial adherence of gold to copper. The concept of what constitutes epitaxy has been a subject of discussion by those engaged in LEED studies for some time. The interpretation presented herein is essentially the same as that observed by Taylor in reference 4 with the deposition of copper on tungsten. There exists extremely good correlation between what was observed with gold contacting copper in this study and the characteristics of the patterns observed by Taylor for copper on (110) tungsten in reference 4.

It is of interest to consider what brings about such atomic registry in the two interfacial layers. Gold and copper are atomically mismatched in their lattice by about 12 percent. The mismatch can be accommodated for by two processes which occur with adhesion: (1) lattice coherency strain (fig. 8) and (2) the generation of misfit dislocations (fig. 9). The subject of accommodation of lattice mismatch to achieve epitaxy has been very thoroughly examined in the literature. The work of Van der Merwe has lent considerably to the understanding of the phenomenon (refs. 15 to 19); some additional work has been done by others (refs. 20 to 23).

Based on the literature cited, a plausible explanation for the epitaxial attachment observed herein may be as follows. As the gold makes contact with the copper surface, lattice strain takes place in the weaker of the two metals, namely the gold. This may be seen with the aid of the schematic of figure 8(c). In figure 8(c), as the gold makes contact with the copper the gold atoms of the outermost atomic layer are drawn to the lattice sites of the copper. This produces a strain several atomic layers deep in the gold. The depths to which gold atoms are strained will depend upon the degree of misfit (refs. 15 to 19). Van der Merwe (ref. 16), in considering lattice mismatch to about 10 percent, indicates lattice strain to a depth of 10 monolayers.

Figure 9. Accommodation of lattice mismatch in copper-gold contact with misfit dislocations.
The large strains produced in the lattice cannot be completely accommodated by simple atomic shift, and interfacial dislocations are generated to satisfy large atomic strains. The generation of interfacial dislocations with epitaxy has been firmly established (refs. 8, 9, 11, 16, and 17). The mechanisms for the generation of such dislocations may be seen with the aid of figure 9. With adhesion of the gold to copper, if an assumption is made that one pair of copper-gold atoms match with zero strain (the center lines of fig. 9), the amount of lattice strain will continue to increase in each successive row of atoms outward from the zero strain condition. At some point the strain will be too great to be accommodated by the lattice and an interfacial, or misfit, dislocation will develop. A pair of such dislocations are shown in figure 9, with the spacing between them indicated as b. The presence of such misfit dislocations has been observed with electron microscopy by Mathews (ref. 11) for gold in contact with palladium, silver, and platinum; the lattice mismatch for the couples is 4.4, 0.1, and 3.5 percent, respectively. Since misfit dislocations are generated at these conditions of mismatch, there is little doubt that they must also exist for the copper-gold system where there is an even greater lattice mismatch.

The amount of atomic mismatch is going to be influenced greatly by the atomic plane. Since the atomic arrangement will differ (see table 1), it might be anticipated that the number of copper-to-gold bonds formed across the interface will be influenced by the orientation. Construction of models might show this effect.

If what has been said with respect to the results of this investigation is correct, it ought to be possible to predict the behavior of various face-centered-cubic metal couples. That is, some insight into what surface will transfer to another surface ought be predictable. A consideration of the cohesive strength equations for metals indicates some relation to such things as interatomic distance and even valence electrons (ref. 24). These properties can be related to a mechanical property whose values are readily measurable, namely the elastic moduli as shown in figure 10.

As might be anticipated, the smaller the interatomic distance, the stronger the bonding and the greater is the resistance to elastic deformation. Similarly, the greater the number of valence electrons available for interatomic bonding, the greater the elastic moduli.

A consideration of the elastic moduli of each of the metals in the couple and the alloy or compound formed at the atomic interface should indicate whether the metals will separate without transfer or with transfer and also which metal will transfer. That is, some approximation of which surface will adhere to the other may be obtained from the relation of elastic moduli; the material with the lower elastic modulus adheres to the high modulus material. This assumes that any alloy or compound formed at the interface will be more resistant to deformation than either parent metal. Additional experiments have been conducted to further establish this hypothesis. For example, as might be predicted
from figure 10, copper was found to adhere to nickel with breaking of cohesive copper bonds, and gold was found to adhere to nickel with breaking of cohesive gold bonds.

**SUMMARY OF RESULTS**

Based on the adhesion experiments conducted in this investigation, with gold contacting three crystallographic planes of copper, the following conclusions are made:

1. With the adhesion of gold to a copper surface, separation resulted from the breaking of gold cohesive bonds. The gold cohesive bonds were weaker than the adhesive copper-to-gold bonds or the copper cohesive bonds. These results correlate with what might be anticipated from a consideration of bonding forces.

2. At the small contact forces used in this investigation, gold adhered to the (111), (100), and (110) planes of copper in an epitaxial manner.

3. The force of gold adhesion to the planes of copper was in the order (110) > (100) > (111).

4. From the data obtained for the time to fracture adhesive junctions, some concept of real contact area could be obtained.
5. The LEED patterns gave no evidence of strain in the copper planes as a result of adhesive contact. The gold did, however, undergo strain.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 27, 1969,
129-03-13-09-22.

REFERENCES


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