ADHESION AND FRICTION BEHAVIOR OF GROUP IV ELEMENTS GERMANIUM, SILICON, TIN, AND LEAD

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Adhesion and friction studies were conducted with thin films of the group IV elements silicon, germanium, tin, and lead ion plated on the nickel (011) substrate. The mating surface was gold (111). Contacts were made for the elements in the clean state and with oxygen present. Adhesion and friction experiments were conducted at very light loads of 1 to 10 g. Sliding was at a speed of 0.7 mm/min. Friction results indicate that the more covalently bonded elements silicon and germanium exhibit lower adhesion and friction than the more metallic bonded tin and lead. The adhesion of gold to germanium was observed, and recrystallization of the transferred gold occurred. Plastic flow of germanium was seen with sliding. Oxygen reduced, but did not eliminate, the adhesion observed with germanium and silicon.
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SUMMARY

An investigation was conducted into the adhesion and friction behavior of the group IV elements of the periodic table. The elements silicon, germanium, tin, and lead were examined as thin films \(8 \times 10^{-8} \text{ m} \ (800 \text{ Å})\) deposited by ion plating on a nickel (011) single crystal substrate. A gold single crystal pin (111) orientation contacted the film. Applied loads of 1 to 10 grams were employed, and sliding was conducted at a speed of 0.7 millimeter per minute. Surfaces were examined clean and in the presence of oxygen. LEED and Auger spectroscopy were used to monitor surface structure and chemistry.

Friction results indicate that the more covalently bonded elements silicon and germanium exhibit lower friction forces than the more metallic bonded element lead. The adhesion results show that the more covalent germanium exhibits lower adhesion than the more metallic tin. Gold was observed to adhere to germanium. Transferred gold was found to have undergone recrystallization because of frictional heating. Plastic flow of brittle germanium occurred in the sliding contact zone at the light loads employed in this investigation. Oxygen reduced, but did not eliminate, the adhesion observed with silicon and germanium.

INTRODUCTION

Where clean metal surfaces are brought in contact with themselves or other clean metals strong adhesion occurs and very high friction forces are measured (ref. 1). Under such conditions the friction coefficient becomes a meaningless term and the shear strength of a welded couple becomes more appropriate. The very strong nature of the metallic bond results from the formation of solid solution alloys or covalently bonded intermetallic compounds.
In addition to the metallic bond, a number of elements in the periodic table are bonded covalently. The elements of group IV move from the complete covalent bonding with the diamond form of carbon to the nearly complete metallic bonding with lead. Silicon, germanium, and tin lie in between.

Any attempt to measure the effects of covalent bonding on the adhesion and friction behavior of metals requires preventing the appreciable differences in the mechanical properties that exist between the covalent bonded materials and those that are metallic bonded from influencing the experiment. A measurement of the effect of the nature of the bond can be accomplished by the deposition of thin equivalent films of these materials on a common substrate. Thus, the mechanical properties of the substrate are common, and the surface bonding properties of the thin film prevail in influencing adhesion and friction.

The main objective of this investigation was to determine what effect in bond character changes of the group IV elements from covalent to metallic had on adhesion and friction. Additional observations were made as to material transfer, plastic deformation, and recrystallization. Experiments were conducted with thin films of silicon, germanium, tin, and lead. These elements were ion plated onto a single crystal nickel (011) disk surface. The mating surface in the studies was a gold (111) oriented single crystal. All experiments were conducted in vacuum at loads of the pin against the disk of 1 to 10 grams, and sliding experiments were conducted at a speed of 0.7 millimeter per minute. Scanning electron microscopy (SEM), low energy electron diffraction (LEED), and Auger emission spectroscopy were used to monitor surface structure and chemistry. Adhesion and friction were measured for the surfaces clean and in the presence of oxygen. While materials are normally in an air environment, material contact can occur through surface films; therefore, clean surface effects are important.

**MATERIALS**

The silicon and germanium used were 99.999 percent in purity. The tin and lead were 99.99 percent in purity. These elements were ion plated (ref. 2) onto a nickel single crystal substrate of the (011) orientation having a purity of 99.99 percent. This orientation was selected because it has a high surface energy promoting a greater adhesion of the film to the substrate. Nickel single crystal wafers 8.0 millimeters in diameter and 4.0 millimeters in thickness were cut from the nickel single crystal rod. Parallel slices were cut out of the rod and the orientation of the wafers or disk flats was within ±2° of the (011) orientation.

The gold crystal pin which made contact with the disks was 99.999 percent in purity. The pin had a 2.0-millimeter radius on the end of a 3.0-millimeter-diameter cylindrical crystal. The (111) plane was parallel to the contacting or sliding interface to within ±2°.
APPARATUS

The apparatus used in this investigation was a vacuum system capable of measuring adhesion, load, and friction and capable of Auger and LEED surface analyses. The mechanism for measuring adhesion, loading, and friction is shown schematically in figure 1.

A gimbal mounted beam projects into the vacuum system. The beam contains two flats machined normal to each other with strain gages mounted thereon. The end of the rod contains the gold single crystal pin specimen. The load applied by moving the beam toward the disk was measured by the strain gage. The adhesion force, that is the force necessary to separate the pin and disk after being loaded together, is measured in the direction opposite to that of bond application by the same strain gages.

Tangential motion of the pin along the disk surface is accomplished through the gimbal assembly. Under an applied load the friction force is sensed by the strain gage normal to that used to measure load.

Almost any load measuring sensitivity can be achieved by properly thinning the flats in the beam. In the present study full scale deflection on a conventional strip chart recorder resulted from a 10 gram load, adhesion, or friction force.

Multiple wear tracks could be generated on the disk specimen surface by the translational motion of the disk or pin. Pin sliding was in the vertical direction of figure 1.

The vacuum apparatus in which the components of figure 1 were contained also had a LEED diffraction system and an Auger spectrometer. The electron beam of both could be focused on any disk site desired. This was accomplished with a disk manipulation device.

The vacuum system was a conventional vacsorb and ion pumped system capable of readily achieving pressures of $1.33 \times 10^{-8}$ newton per square meter ($10^{-10}$ torr) as measured by a nude ionization gage within the specimen chamber. Sublimation pumping was also used for more rapid achievement of the ultimate pressure desired.

EXPERIMENTAL PROCEDURE

The nickel single crystal wafers or disks were cut with a wire saw. The (011) flats were polished on metallurgical papers down to 600 grit, and the surfaces were electropolished in orthophosphoric acid. The group IV elements were ion plated onto the nickel disks. The thickness of the films was measured with an optical interference microscope.

The specimens were then mounted in the adhesion and friction apparatus. The system was evacuated and baked out. The ambient pressure before the commencement of each experiment was $1.33 \times 10^{-8}$ newton per square meter ($10^{-10}$ torr). The sur-
faces were then characterized by examination with LEED (low energy electron diffraction) and Auger emission spectroscopy. Adhesion or sliding friction experiments were conducted on surfaces which had been sputter cleaned by ion bombardment and with surfaces selectively contaminated with oxygen until the surface was saturated.

The disk surface was sputter cleaned by ion bombardment with argon ions at 1000 volts with an argon pressure of 10 micrometers. After ion bombardment the surfaces of the specimens were annealed by heating.

In the adhesion experiments the contact time was held constant at 1 minute after application of the load through the gimbal assembly. Load appeared continuously on the recorder. Sliding was commenced after 1 minute of contact under load in friction experiments. The distance of sliding was 7.0 millimeters. After sliding the load was removed and the force to fracture adhesive junctions, when adhesion occurred was measured.

RESULTS AND DISCUSSION

It is highly desirable when measuring surface effects and separating the bulk effects examined in adhesion and friction studies to keep surface films as thin as possible. There is, however, a minimum thickness below which uniform films can no longer be maintained and deposited species begin to form in islands. As a general rule this thickness is about $6 \times 10^{-8}$ meter (600 Å) (fig. 2).

Silicon is highly covalent in bond character with lead being principally metallic in the nature of its bonding. Germanium is principally a covalent material with some metallic nature. Tin exists in two crystalline forms - the gray tin having the diamond like structure exists below 18° C and the white tin with the body centered tetragonal structure exists above 18° C which reflects its mixed bonding character partially covalent, partially metallic (ref. 4).

Because of their mixed nature the adhesion and friction behavior of tin and germanium were measured and compared. An Auger spectrum for the tin film on the surface is presented in figure 3. Adhesion forces measured for gold to tin and gold to germanium are presented in figure 4. An examination of figure 4 indicates a stronger adhesive bonding of gold to tin than of gold to germanium. At all the applied loads the resulting measured adhesive force was higher for tin. The penetration of the tin film believed to occur at high loads accounted for the marked increase seen in figure 4 for the force of adhesion. The film thickness of both materials was $8 \times 10^{-8}$ meter (800 Å).

The adhesive forces measured in figure 4 are markedly less than those usually observed with the transition metals such as the substrate nickel. Adhesion data for the gold to the nickel surface without the film is presented in figure 5. The data of figure 5
indicate very strong adhesive bonding of gold to nickel. Note that the adhesion force scales in figures 4 and 5 are different by an order of magnitude. Even at the highest measured adhesive value for tin (0.8 g at 8.0 g load) the force was an order of magnitude less than seen for nickel (8.0 g at 8.0 g load). This may be due in part to the partially covalent bonding behavior of tin.

Friction behavior was markedly different for the two elements. This is reflected in the actual friction traces presented in figure 6. In figure 6(a) the germanium shows a sharp spike on the left where sliding began due to static friction. The actual friction trace is, however, very smooth with no evidence for stick-slip behavior. With germanium the friction trace is unlike that normally seen for metals. Silicon behaved in a manner similar to germanium, and thus reflected the difference between covalent and metallic bonding in adhesion.

In contrast, figure 6(b) shows for the tin film a marked stick-slip behavior with a continuous increase in friction force when moving from the start of sliding at the left to the end of sliding at the right of the figure. The results of figure 6(b) are as anticipated for metallic bonding across the interface.

If the nickel crystal is heated to evaporate some of the tin (500°C, above the melting point of tin), an elementally mixed surface film such as that reflected in the Auger spectrum of figure 7 can be obtained. Adhesion and friction measurements on such a film result in adhesion and friction values between those for tin and nickel.

If repeated passes are made of the gold pin over the same germanium surface, the friction coefficient decreases as indicated by the data of figure 8. This change is believed to be due to a plastic deformation and texturing of the germanium. Evidence for this plastic deformation is presented in figure 9.

In figure 9(a) the wear track on the germanium film is shown. Because of the brittle nature of the germanium, some of the germanium broke away from the surface and exposed the nickel substrate. In the center of the wear track where the gold pin was in contact the germanium underwent plastic flow as evidenced by the wavey flow lines seen in the wear track transverse to the sliding directions. Gold adhered to the germanium surface; that section of the track is magnified in the photograph in figure 9(b).

The germanium surface with the adhered gold in figure 9(b) is composed of a cluster of individual crystallites. The source of this cluster of individual crystallites was the gold single crystal pin. The only way the cluster could form is as a result of interfacial recrystallization of the gold. Thus, the gold achieved a sufficiently high temperature to recrystallize. Recrystallization temperature is a function of the strain. Since wear particles are generally highly strained, the recrystallization temperature was most likely at its minimum.

The energy dispersive X-ray analysis (EDAX) of the wear track shown in figure 9(a) revealed the elemental map presented in figure 9(c) for germanium and in figure 9(d) for
nickel. The presence of germanium in the wear track can be seen by the vertical path of white dots in figure 9(c). The location where the germanium broke away exposed the nickel can be seen in the map for nickel in figure 9(d).

The adhered cluster of gold shown in figure 9(b) is mapped elementally for gold in figure 9(e) and shows that gold has definitely transferred to the surface. The cluster of white dots corresponds to the gold crystallites.

The strong adhesion of gold to strongly covalent silicon has been observed with simple vapor deposition of gold to freshly cleaned silicon (ref. 5). The interfacial adhesive bond of the gold to the silicon was so strong that it could not be removed without damaging the silicon. The presence of oxygen on the silicon surface reduced the adhesion of gold to silicon. Oxygen was therefore adsorbed onto the germanium surface to determine if germanium behaved in a manner similar to silicon. An Auger spectrum for oxygen adsorbed onto germanium is presented in figure 10. The oxygen peak is seen among the germanium peaks. The presence of oxygen on germanium reduced the adhesion of gold to germanium.

Silicon with its highly covalent bond character and lead with its highly metallic nature were compared next. An Auger spectrum for the silicon film after sputter cleaning and heating to anneal is presented in figure 11.

Friction forces measured for both lead and silicon in contact with gold are presented in figure 12. Metallic bonded lead exhibits higher friction forces at various loads than was observed with covalent silicon at all loads. The films of lead and silicon were both \(8 \times 10^{-8}\) meter (800 Å). The friction trace for silicon was very much like that observed for germanium, while that for lead was much like that observed for tin in figure 6.

As already mentioned, gold adheres very strongly to clean silicon (ref. 5) in spite of the difference in bond character of silicon and gold. With lead, the gold interacts at the interface to form intermetallic compounds (ref. 6). The formation of interfacial intermetallic compounds implies a strong adhesive bonding of gold to lead; in fact, strong adhesive forces were measured in the present study. Whether what gives rise to the strong bonding of gold to silicon is metallic, ionic, or covalent is not known.

In reference 5 it was indicated that in the presence of oxygen gold did not adhere to silicon. Oxygen was therefore adsorbed on both silicon and lead films to determine its effect on friction. An Auger spectrum for the oxidized lead film is presented in figure 13.

Friction force measurement results from oxygen on silicon and lead films are presented in figure 14 together with data for clean surfaces. The upper two curves of figure 14 are for clean lead and silicon. The data points for the oxygen on lead fall very close to the curve for the clean silicon. These points are below those shown for clean lead. The lowest friction forces are for oxygen on silicon.

The presence of oxygen purportedly eliminates the adhesion of gold to silicon (ref. 5). The results of figure 14 would indicate that in sliding this is not the case. The
friction forces presented in figure 14 are sufficiently high to imply adhesion during sliding.

The experimental results presented herein indicate that for films of the group IV elements on a common substrate adhesion and friction are less for the covalently bonded elements than for the metallic bonded metals in contact with a metal. The cohesive binding energies for silicon and germanium are greater than those for tin, lead, and the gold pin as shown by the data of table I. The stronger the interatomic bonding within the element the more closely the valence electrons are held to the nucleus. The covalent bond character of the group IV elements is due to the sp³ hybrid formation. In this study, the electron pair bonds are strongest in silicon and become weaker with the other elements. The electrons become less and less of a valence type and tend to resemble free electrons more and more when moving from silicon to germanium to tin and finally to lead.

Valence electrons require a greater degree of specificity in interfacial electron compounds than is required with free electrons. Thus, bonding can be expected to occur more readily with free electron elements.

The good adhesion resistance of germanium was recognized in early engineering studies (ref. 3). These early observations were, however, not related to bonding.

CONCLUSIONS

Based on the experimental results presented herein, when gold is in contact with films of the group IV elements the following conclusions are reached:

1. Germanium, the more covalently bonded element of group IV, showed lower adhesion than the more metallic tin; likewise, the more covalent silicon showed lower friction than the metallic lead.

2. Gold adhered to group IV elements with weaker binding forces than those measured for gold in contact with the nickel substrate.

3. The adhesive transfer of gold to germanium was observed in sliding.

4. While germanium is normally very brittle, it flowed plastically in sliding under the very nominal loads employed in this study.

5. Gold was observed to recrystallize at the interface in the transfer of gold to germanium.

6. Oxygen reduced adhesion with covalent germanium and silicon but did not eliminate it.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 7, 1975,
506-16.
REFERENCES


TABLE I. - COHESIVE BINDING ENERGIES

<table>
<thead>
<tr>
<th>Element</th>
<th>Cohesive energy</th>
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<tr>
<td></td>
<td>J/g atom</td>
</tr>
<tr>
<td>Silicon</td>
<td>4.48×10⁵</td>
</tr>
<tr>
<td>Germanium</td>
<td>3.72</td>
</tr>
<tr>
<td>Gold</td>
<td>3.66</td>
</tr>
<tr>
<td>Tin</td>
<td>3.01</td>
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<tr>
<td>Lead</td>
<td>1.96</td>
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</tbody>
</table>

*Ref. 7 and 8.*
Figure 2. - Friction force as function of load for ion plated thin film of germanium on nickel single crystal (011) face. Slider, gold (111); temperature, 23°C; pressure, 1.33x10^-10 newton per square meter (10^-10 torr); sliding velocity, 0.7 millimeter per minute.

Figure 3. - Auger spectrum for 8x10^-8 meter (800 Å) tin film present on nickel (011) surface.
Figure 4. - Force of normal adhesion for gold (111) to nickel crystal (011) faces with $8 \times 10^{-8}$ meter (800 A) film of tin and germanium. Sputter cleaned film surface; temperature, 23°C; pressure, 1.33 x $10^{-10}$ newton per square meter ($10^{-10}$ torr).

Figure 5. - Force of adhesion as function of applied load for gold (111) surface contacting clean nickel (011) surface. Ambient pressure, 1.33 x $10^{-8}$ newton per square meter ($10^{-10}$ torr); temperature, 23°C.
Figure 6. Friction traces for \(8 \times 10^{-8}\) meter (800 Å) films of geranium and tin films ion plated onto nickel (011) surface. Load, 1 gram; sliding velocity, 7.0 meters per minute; temperature, 23°; pressure, 1.33 \(\times 10^{-8}\) newton per square meter (10^{-10} torr).

Figure 7. Auger spectrum for original tin film \(8 \times 10^{-8}\) meter (800 Å) thick on nickel (011) surface heated to 500° C to evaporate the film.
Figure 8. - Coefficient of friction for gold (111) surface sliding on $8 \times 10^{-8}$ meter (800 Å) film of germanium ion plated onto nickel (111) surface as function of number of sliding passes. Load, 1.0 gram; sliding velocity, 0.7 millimeter per minute; temperature, 23°C; ambient pressure, $1.33 \times 10^{-10}$ newton per square meter (10^-10 torr).
Figure 9. - Scanning electron micrographs of wear track on germanium film on nickel (011) substrate. Rider, gold (111) single crystal.
(c) EDAX of germanium. X1500.

(d) EDAX of nickel. X1500.

Figure 9. - Continued.
(e) EDAX of gold. X6000.

Figure 9. - Concluded.

Figure 10. - Auger spectrum for adsorbed film of oxygen on 8x10^{-8} meter (800 Å) germanium film present on nickel (011) surface.
Figure 11. - Auger spectrum for 8x10^{-8} meter (800 Å) silicon film present on nickel (011) surface.

Figure 12. - Friction force as function of load for gold (111) surface sliding on ion plated 8x10^{-8} meter (800 Å) thick films of lead and silicon on nickel (011) single crystal. Sliding velocity, 0.7 millimeter per minute; temperature, 23 °C; pressure, 1.3x10^{-5} newton per square meter (10^-10 torr).
Figure 13. - Auger spectrum for oxygen adsorbed to $8 \times 10^{-8}$ meter (800 Å) lead film present on nickel (011) surface.
Figure 14. - Friction force as function of load for lead and silicon films with adsorbed oxygen. Sliding velocity, 7.0 millimeters per minute; temperature, 23°C; pressure, 1.33x10^-10 newton per square meter (10^-10 torr).
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