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BONDING MATERIALS FOR MAKING CONTACTS TO p-TYPE SILICON

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The necessity for making structurally sound non-rectifying contacts to the various regions of a semi-conductor device is an ever recurring problem. The chemically deposited or electro-less nickel plate as described by Sullivan and Eigler⁽¹⁾ has been developed for making broad area contacts to lapped silicon surfaces, and can be readily adapted for use on etched n-type silicon surfaces. However, many devices including transistors cannot be made without using one or more controlled area contacts and at least one alloy or bonded contact has been necessary on all junction transistors.

Low resistance structural bonds have been made to etched n-type silicon using an antimony-doped gold bond, but the low distribution coefficients of acceptors into silicon from gold solutions⁽²⁾ produced a high resistance layer.

Satisfactory non-structural contacts have been made to etched silicon surfaces by alloying with a fine wire⁽³⁾ or a thin film of vacuum-evaporated aluminum⁽⁴⁾. Thick aluminum sections induce cracking because of a mismatch in the thermal coefficient of linear expansion. J. W. Peterson and J. H. McConville⁽⁵⁾, have used molybdenum wire on which a layer of aluminum has been electroplated for making alloy junctions to n-type silicon, with the aid of a post-alloy etch. H. W. Henkels⁽⁶⁾ used a silicon-aluminum eutectic foil to dope the n-type silicon in forming flat p-n junctions, and the foil is fused to a molybdenum or tantalum backing plate during the alloying cycle. A post-alloying etch is used.

Although our objective was limited to the formation of ohmic contacts on etched p-type silicon, we found that we could also produce alloy junctions which are quite satisfactory as emitters even without a post-alloying etch.

Similarly, there is no inherent reason which would prevent the formation of good contacts to lapped or sand-blasted silicon surfaces.

Test Specimen

The test specimen which was used to evaluate the various base plate materials is shown schematically in Figure 1. It comprised an n-type silicon wafer having (111) major faces into one face of which boron had been diffused to form a p⁺-n junction. The p-layer, having a thickness of about 0.001 inches and a surface concentration of about 10^{20} boron atoms/cm³, was placed in contact with the alloy-clad base plate which in turn had been spot-welded onto the superstructure of a solder-type, symmetrical four-pin transistor header. One wire of the header which was electro-plated with gold-antimony alloy was bent around to hold the silicon wafer securely against the base plate, and a satisfactory ohmic contact to the n-type region was obtained during the alloying cycle. After the alloying cycle, the superstructure could be sealed to protect the surfaces from subsequent contaminating influences by dropping a can into the solder trough of the header if desired. With this structure, a unitized material was simpler to use in the fabrication procedure instead of a separate solder alloy and backing plate.

A variety of base plate materials was obtained and evaluated.

Base Plate Material Variables

The pertinent variables which characterize the base plate material can be classified into three categories; first, composition of the base metal; second, the composition of the cladding material; and third, the technique of applying the cladding material to the base metal.

Base Metals

Base metals of iron, nickel, and molybdenum were investigated, using pure aluminum as the alloying film material. Aluminum-clad iron and nickel

were available from commercial sources and molybdenum samples were made to our specification.

Whenever iron was used the reverse current of the diodes was intolerably high. A typical current-voltage characteristic is shown by Diode A in Figure 2. This result is consistent with observations by Bemski⁽⁷⁾ that the minority carrier lifetime in silicon is reduced when small traces of iron are added to the system at high temperatures. The iron could be acting as a recombination-generation center in the space charge region. Good uniform mechanical bonds were not formed, and other iron-containing base metals such as kovar were not considered.

The bonding to silicon with aluminum-clad nickel was erratic, and good bonds were invariably accompanied by cracking of the silicon wafers and hence poor electrical characteristics, because of the mismatch in the coefficients of thermal expansion. Nickel was also rejected.

Occasionally, however, satisfactory bonds and electrical characteristics were obtained using early samples of aluminum-clad molybdenum, so molybdenum was chosen for further investigation. Other metals, such as tungsten, having coefficients of expansion relatively close to silicon could just as well have been used. However, molybdenum is readily available and has sufficient ductility to permit forming and manipulation in the fabrication of piece-parts for semiconductor device structures.

Cladding Film Compositions

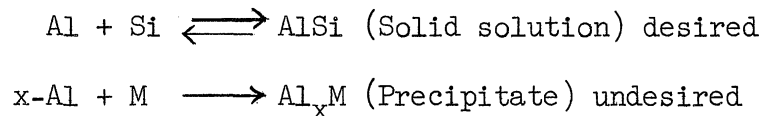
Since the cladding film must contain acceptors, the choice is almost automatically limited to aluminum or indium in their pure forms, and gallium can be used only with a carrier alloy. In our experience gold is not a satisfactory carrier alloy because of the formation of the high resistance film.*

Indium not only reacted with the molybdenum-to-molybdenum welds which were used to fabricate the test specimen, but it also imposes a maximum oper-

* See Note 1 on page 9.

ating temperature on the device of well below 150°C, so it was not considered further.

Reactions between the aluminum and the transition metals were observed in the preliminary work. These elements all react chemically with aluminum below its melting point (660°C) to form complex chemical compounds which effectively precipitate the aluminum from the system so that it is not available to form a solid solution alloy with the silicon. In effect, the aluminum is in the center of a sandwich with molybdenum on one side and silicon on the other side. Very stable compounds of the form Al_xM are known to exist, so that at equilibrium, the aluminum may not be available to dope the silicon. Perhaps as an over-simplification, it can be thought of as a reversible reaction on the silicon side which is competing with an irreversible reaction on the molybdenum side for the utilization of the aluminum.



where M is iron, nickel, molybdenum, or similar element.

Since it appeared that aluminum was necessary for good contacts, the precipitation or diffusion of the aluminum into the base plate had to be overcome to permit the formation of an alloy bond to silicon before all the aluminum was precipitated. This could be done either by interposing a barrier between the silicon and the base metal to retard the precipitation reaction or by adding another component to depress the melting temperature and/or lower the aluminum concentration. Silver was found to be satisfactory as a third component, but the overall results were not as good as those that were obtained with the aluminum-clad combinations which will be discussed in detail.

Aluminum Cladding Processes

Most processes available for cladding molybdenum with aluminum also form a thin oxide film at the aluminum-molybdenum interface. Aluminum films

obtained by (a) electroplating, (b) vacuum evaporation, (c) direct sintering, and (d) dipping into molten aluminum without a flux all formed films that were non-adherent and could be peeled off. Films applied by dipping molybdenum sheets into molten aluminum after treatment with a sodium potassium aluminum fluoride flux were non-reproducible, but very adherent; in fact, the intimacy of contact was so good that the aluminum apparently reacted with the molybdenum before the aluminum-silicon bond could be formed. A cross-section of an attempted bond to silicon using this material is shown in Figure 3 at 200 diameters. Portions of the silicon surface have definitely been dissolved, but there is no trace of the aluminum. The thin film that is visible on the molybdenum surface is probably residual silicon that has been deposited there as the aluminum diffused into the interior of the molybdenum.

Rolled-On Aluminum

Samples of molybdenum sheet having a pure aluminum film rolled onto one side were prepared to our specifications* for evaluation. These comprised .005" molybdenum sheets having .0005" of pure aluminum rolled onto one side, and were formed as the result of a substantial thickness reduction to promote the formation of atomic bonds between newly formed aluminum-molybdenum interfaces. Spectro-chemical analyses showed the materials to be very pure.

During alloying, the aluminum film dissolves enough of the silicon wafer to form an aluminum-silicon eutectic. A microscopic cross-section of an alloyed structure is shown in Figure 4 at 1500 diameters.

Several distinct phases are distinguishable in the photomicrograph. The silicon wafer has been dissolved at discrete regions over the surface, but the wetting and penetration are not uniform. During the solidification of the alloy, some of the silicon redeposited on the silicon surface, and some crys-

* From (a) Kassel Industries, Inc., 20-24 Branford Place, Newark 2, New Jersey and (b) General Plate Division, Metals and Controls Corp., Attleboro, Mass.

tallites of silicon remained suspended in the aluminum-rich phase. The grainy portion of the aluminum region is the aluminum-silicon eutectic, and apparently the aluminum in the immediate vicinity of the molybdenum surface was not melted. At the same time the aluminum thickness is sufficiently thin to avoid cracking of the silicon when alloying is carried out at temperatures around 580°C to 610°C. At lower temperatures no mechanical bonding occurs, while aluminum precipitation becomes a problem at higher temperatures.

Typical small area p-n junction characteristics are shown by Diodes B and C in Figure 2. The differences in reverse current around 0.1 microamperes are thought to arise from varying degrees of background contamination from the process. Minority carrier lifetimes⁽⁸⁾ measured on these diodes by a junction recovery method, were found to be in the range of from 50 to 100 millimicroseconds.

Penetration Control: Silicon-Aluminum-Clad Molybdenum

Although these results were quite satisfactory and reproducible, the penetration into the silicon wafer might be undesirable for some applications. With a 0.0005" thick film of aluminum as the alloying agent, the depth of penetration into the silicon at 600°C would be about 0.0001". This penetration could be reduced by using a silicon-aluminum eutectic as the alloying medium. Accordingly a composite structure was made to our specifications by the rolling-on process described previously, comprising a molybdenum sheet 0.008" thick onto one side of which an aluminum film .0005" thick containing nominally 12% silicon had been applied.* During rolling the molybdenum developed a mica-like striated structure, and separations were observed inside the molybdenum sheet. In all probability this rolling texture is not inherent in the material and could be eliminated, as it was not present on the pure aluminum-clad material.

* From Kassel Industries, Inc. 20-24 Branford Place, Newark 2, New Jersey

The alloying characteristics of this material were found to be substantially different from the pure aluminum material. It was impossible to form an alloy bond between the aluminum-silicon and the silicon even by heating to temperatures in excess of 700°C. These observations were corroborated in the work with the silver carrier alloy. When as little as 4% silicon was added to a silver-aluminum eutectic solution, the resulting alloy would not wet spontaneously to the silicon wafers.

Although the experiments with aluminum-silicon clad molybdenum were carried out in a different furnace using flat plates instead of the formed plates as shown in Figure 1, the consistency of the results with the alloys containing silicon seems to indicate that the test specimen configuration and alloying furnace are of secondary importance. Since the surface properties of the system are such that wetting would not occur spontaneously, the use of a flux was indicated.

Wetting

By using various fluxes we were able to obtain uniform wetting of the Al-Si-clad molybdenum to the silicon slices with a minimum of penetration. In all cases the fluxes used were made from elements which either were acceptors in silicon or were substantially inert, electronically. Lithium, for example, was avoided since it acts as a donor when introduced interstitially into silicon⁽⁹⁾. Although several fluxing agents were tried, the best results seemed to be obtained by painting the eutectic film with a dilute solution of boric acid in denatured alcohol immediately prior to assembling the wafer stack for alloying. Anhydrous ethyl sodamide was also used successfully, but its effectiveness decreased as the solution absorbed moisture from the atmosphere.

A photomicrograph of a boric acid-fluxed bond is shown at 500 diameters in Figure 5. The alloying was carried out at about 675 - 700°C in an atmosphere of anhydrous, de-oxidized nitrogen for an alloying time of 5 to 10 minutes. At

lower temperatures an apparent bond forms since the boric oxide acts as a glassy cement, but the bond can be ruptured by boiling in water for a few minutes. Bonds made in the alloying temperature range were mechanically sound, and on rupture, either the molybdenum was separated, or the silicon was pulled out of the silicon wafer in the vicinity of the bond.

In making relatively large area contacts, it is desirable that the specimen should be cooled at a rate no greater than about 5°C per minute. If substantially faster cooling rates are used, the differential thermal expansions of the system are sufficiently great to induce cracking in the silicon wafers. Observations made at the corners of the specimens (silicon-eutectic-flux interfaces) indicate that the wetting angle has been reduced considerably in comparison with the silicon-aluminum-gas interfaces.

These diodes did not have electrical characteristics quite as good as those shown in Figure 1, presumably because it was not possible under the experimental conditions used to stabilize the ambient atmosphere around the junction with a hermetic seal subsequent to the time of alloying.

Conclusion

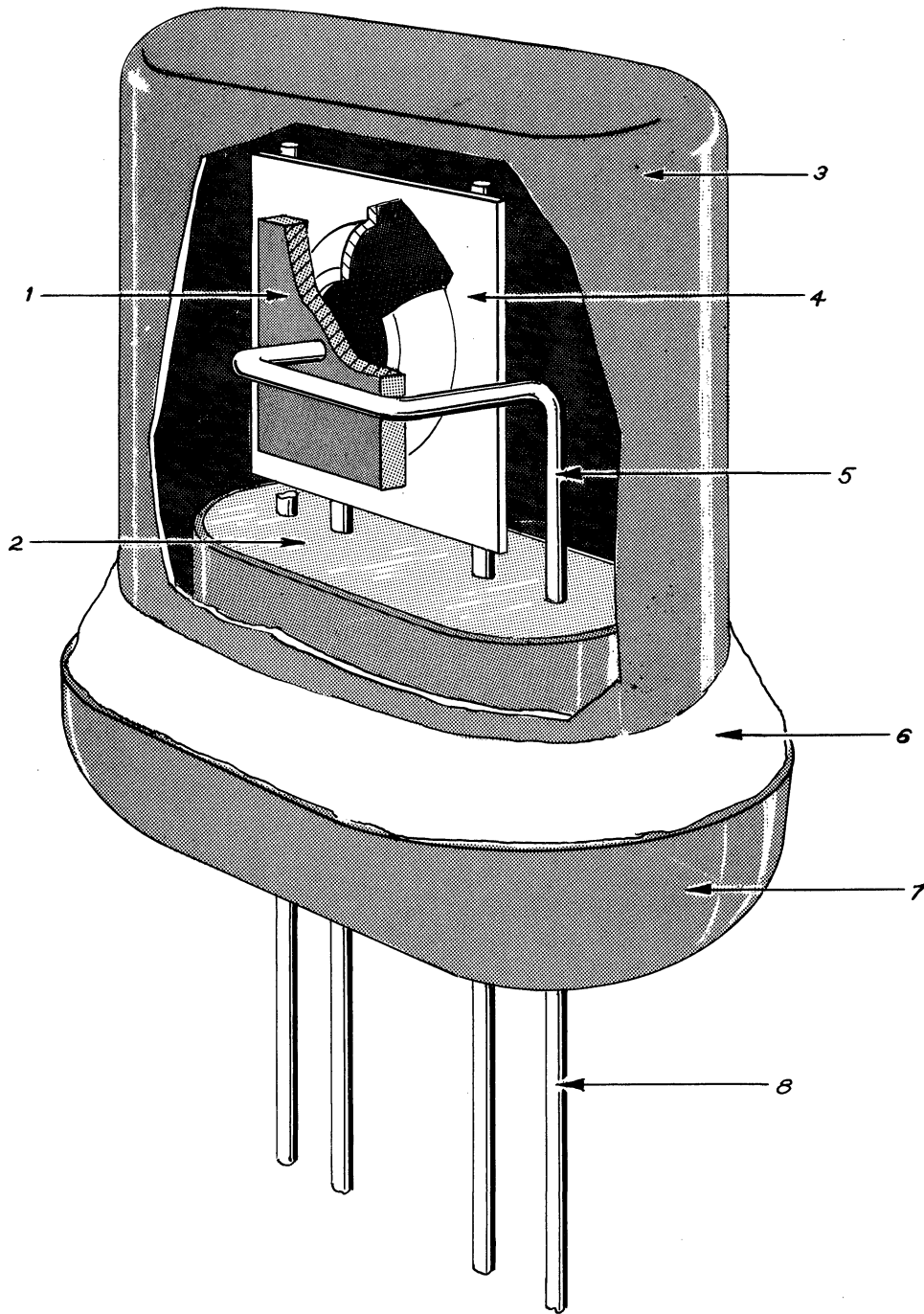
Wafers of p-type silicon have been bonded successfully to alloy-clad molybdenum to form structurally sound ohmic contacts. Molybdenum has been used as the base plate material because its coefficient in linear expansion is reasonably well-matched to that of silicon and introduces no deleterious elements into the p-n junction structure during processing. Bonding agents of pure aluminum or aluminum-silicon eutectic were applied to the molybdenum sheet by rolling accompanied by a substantial thickness reduction to promote the formation of atomic bonds between newly formed aluminum-molybdenum interfaces. The silicon bonding temperature cycle must be carried out in either an inert or reducing atmosphere. The maximum temperature is limited by the reaction of aluminum with the molybdenum and the cooling rate is limited by the necessity for relieving stresses in the bimetallic structure without inducing fracture. When silicon is added to the aluminum bonding material, considerably more stringent alloying conditions must be used to obtain a satisfactory bond.

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REFERENCES

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Note 1. In reviewing this manuscript, M. Tanenbaum reports that he has been able to make satisfactory contacts to p-type silicon using gold doped with boron or gallium.



1- SILICON WAFER WITH
DIFFUSED JUNCTION

2- GLASS

3- GOLD PLATED CAN

4- EMBOSSED ALLOY
CLAD BASE PLATE

5- Au-Sb ELECTROPLATE
ON THIS PIN

6- Sn-Ag EUTECTIC
SOLDER

7- KOVAR EYELET

8- MOLYBDENUM PINS

**Figure 1. SEALED DIODE TEST SPECIMEN USED FOR EVALUATION OF BASE PLATE MATERIALS
PLATE MATERIALS**

D. R. MASON
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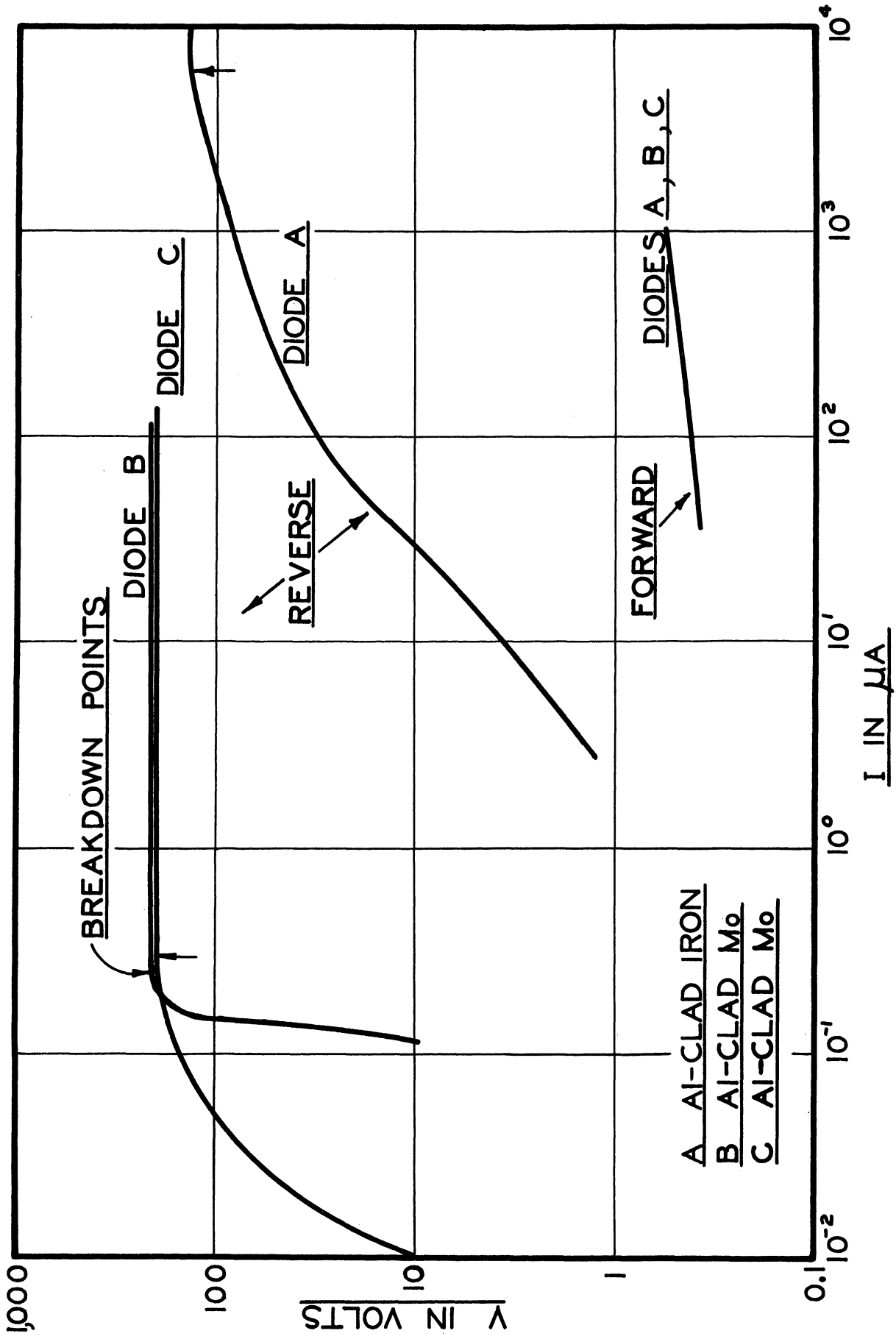


Figure 2. Rectification Characteristics of Diodes Made with Aluminum-Clad Base Plate Materials

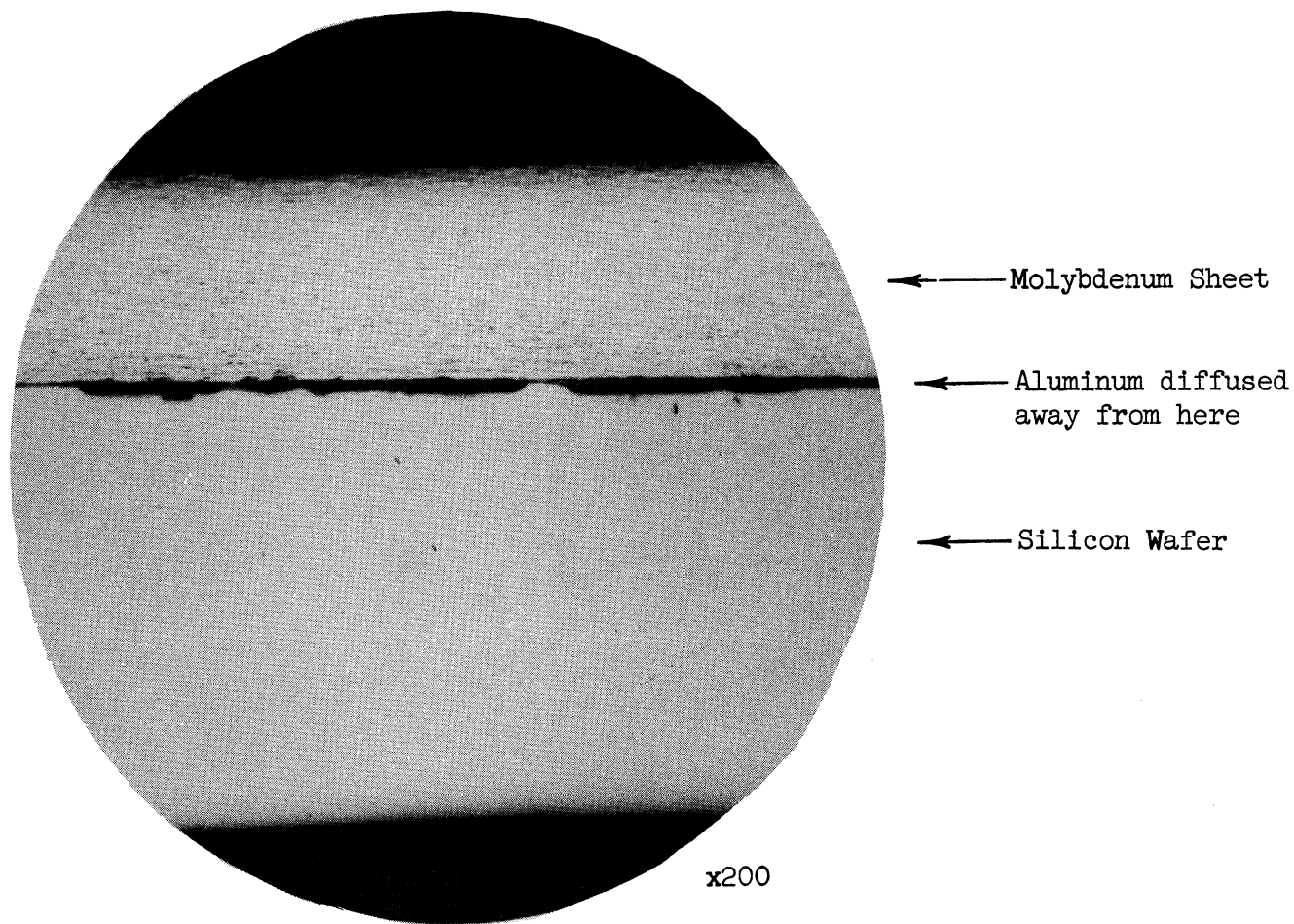


Figure 3. Longitudinal Cross-Section of Attempted Bond to Silicon Using Fluxed and Aluminum-Dipped Molybdenum Strip

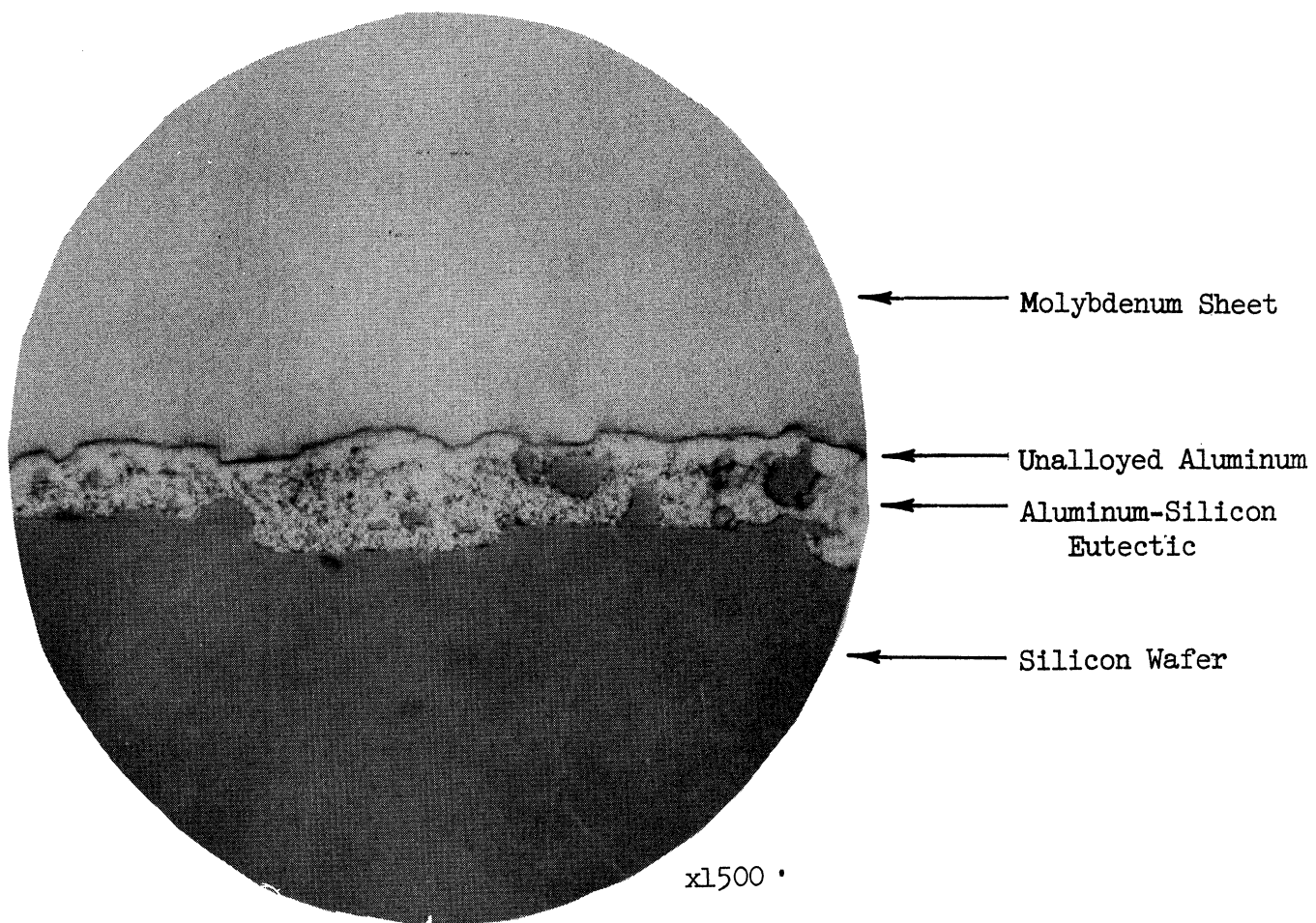


Figure 4. Longitudinal Cross-Section of Bond to Silicon Using Aluminum-Clad Molybdenum

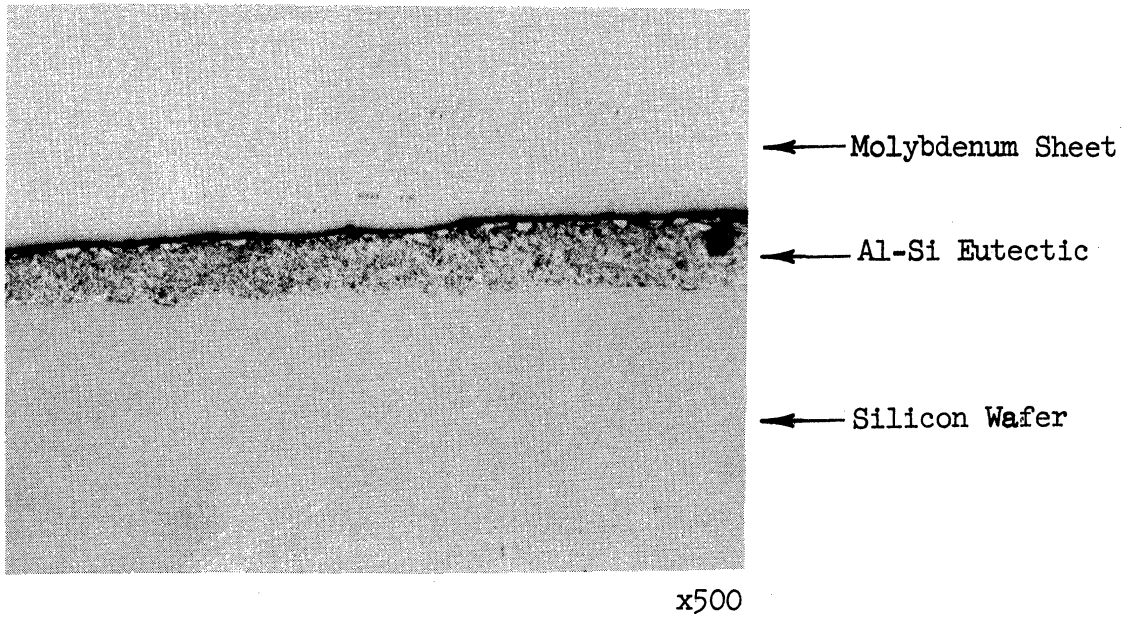


Figure 5. Cross-Section of Bond to Silicon Using Molybdenum Sheet Clad with Aluminum-Silicon Eutectic

