

Gold Alloying to Germanium, Silicon and Aluminum-Silicon Eutectic Surfaces[†]

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Part I

The results of separate studies of large and small area bonds to germanium and silicon surfaces are discussed. Metallurgy and choice of backing material to avoid cracking are described. Compositions of gold-tin offer the most versatile bonds in a variety of atmospheres. Electrode attachments to the aluminum-silicon eutectic regions in semiconductor devices, by means of gold or gold alloys, often produce a condition referred to as the "purple plague" (the AuAl₃ phase formation) with subsequent mechanical failure. Conditions which promote its formation in addition to the more desirable Au₂Al phase are discussed. Wetting and surface tension problems associated with attachments to the Al-Si surface via Au-Sn, Au-Ge and Au-Si alloys are described in connection with the gold-aluminum compound formation. Typical photomicrographs and thermal expansion curves for the systems involved are presented herein.

OF ALL THE COMMON TECHNIQUES for making electrode attachments in fabricating semiconductor devices (pressure, evaporated films, electroplating, thermocompression bonding, and alloying) the alloy fusion technique, where feasible, is the most satisfactory method for obtaining an intimate and permanent contact.

In device processing, corrosive acids are often used to etch p-n junctions to improve electrical properties. Alloying materials with good corrosion resistance therefore are not only desirable, but at times necessary. Gold meets this requirement quite well. The melting points of gold eutectics with germanium and silicon (356° and 370°C, respectively) are high enough to provide adequate device stability, yet low enough to provide ease of fabrication. In addition, they contain sufficient quantities of gold (88 and 94 wt %, respectively) to provide good etch resistance.

A common practice in producing p-n junctions in silicon is to alloy aluminum onto an n-type silicon surface. Upon cooling, the end product is the aluminum-silicon eutectic. General experience at the Hughes Semiconductor Division has been that devices made by attaching a gold or gold-alloy electrode to the eutectic, have occasionally shown mechanical failures concurrent with the appearance of a brittle, porous, and purple phase. It is the purpose of this study to record the results of some investigations into alloys which may prove useful in electrode attachments, and also to determine the nature of this

purple phase. The study deals with the problems in alloying gold to germanium and silicon surfaces with emphasis on cracking due to thermal mismatch and the problem of initiation of wetting.

Alloying to Silicon and Germanium Surfaces

Although there has been much published data on the less noble metal contacts to silicon and germanium, a literature search produced very little on gold alloying. Taylor^{1,2,3}, concerned himself primarily with conditions under which semiconductor surfaces are cracked during fabrications. Sullivan⁴ and Eigler discuss the hydriding technique for alloying onto silicon. Henkels⁵ presents a generalized usage of germanium and silicon contact solders. Peterson⁶ and co-workers, and Jenny,⁷ studied lead alloying onto germanium. Indium alloying onto germanium surfaces was investigated by Thomas and Dacey,⁸ Goldstein,⁹ Mueller,¹⁰ Pankove,¹¹ and Rose.¹² Lead-tin and aluminum-indium alloying for "thyristor" fabrication was discussed by Mueller and Hilibrand.¹³ Gudmundsen¹⁴ and co-workers studied tin-alloying to silicon using a flux. In addition, they discussed the problems associated with gold alloyed to silicon surfaces. Aluminum contacts to silicon were investigated by Prince,¹⁵ Gudmundsen and Maserjian,¹⁶ and Wannlund and Waters.¹⁷

Electrode attachments were divided into two groups—those in which contacts were relatively small in area compared to the Si or Ge surface, and those in which the semiconductor was fused to a clad substrate larger in area than its surface. The former are referred to as small area contacts, the latter as large area contacts. The silicon or germanium dice used in this study were .100 x .100 x .020 before etching or cleaning.

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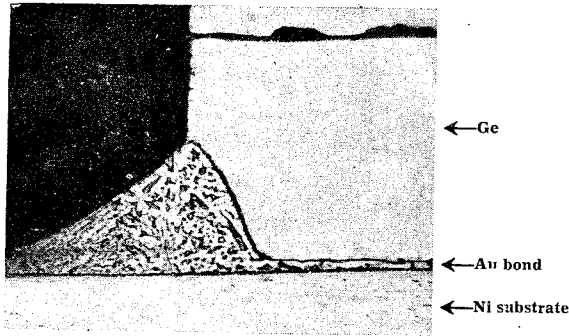


Fig. 1—Ge on Au clad Ni. (From a 250X photomicrograph)

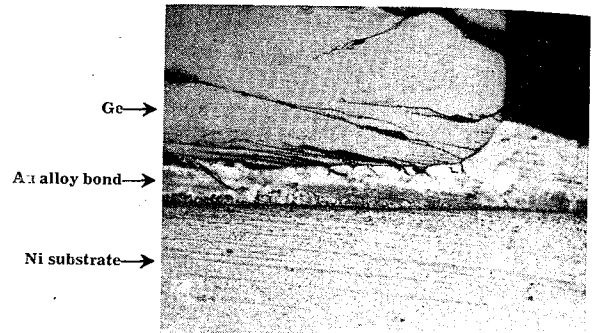


Fig. 2—Ge on Sn plated Au clad Ni, No excess Au. (From a 250X photomicrograph)

Large area contacts were studied using nickel, nickel-iron and molybdenum backing materials which were either gold or gold-alloy clad or plated. In some cases there was an additional tin or antimony plate before alloying. Fabrication temperatures ranged from 300-500°C. All fusions were made under dry hydrogen atmospheres. Vacuum bonding produced similar results, but the technique was not generally used in this study because of the greater ease of alloying under protective gas ambient. In all experimental runs the size of the fusion alloy and geometry of contact were kept constant. The cooling rate was controlled according to the technique described by Peterson and co-workers⁶.

Large area electrode attachments where dice were attached to tabs of gold or gold-alloy clad nickel resulted in cracked silicon or germanium unless high ratios of gold to nickel were employed. Results are shown in Fig. 1 (Ge on Au clad Ni). This is typical of silicon, as well. Note the horizontal cracking which is typical of thermal expansion mismatch between die and tab.

The iron-nickel alloys are better thermal expansion matches for silicon and germanium, but their thermal and electrical conductivities are poorer. Generally speaking, no cracking problem was observed in making bonds to this type of clad substrate.

Where "scrubbing" action to break through oxide films cannot be employed, and the furnace atmosphere is relatively wet, some other systems must be

resorted to. One such example is to plate tin on gold to the proper thickness ratios so that after the tin melts the stoichiometric 80 Au/20 Sn wt % composition is formed. This produces a surface to which Ge and Si can be readily bonded with atmospheric conditions being relatively non-critical. However, if no excess gold remains, the die will crack. Fig. 2 shows this type of attachment to germanium although typical of silicon as well. Note the cracks emanating from the corners as compared with the horizontal cracks described earlier. This type of crack seems more likely to be due to a thermal expansion mismatch between die and solder than between die and substrate. With excess gold on the same backing material, no cracking is observed.

Figure 3 shows a typical attachment using this approach when alloying to silicon (germanium attachment is similar).

This suggests the possible solution to be simply "flashing" the tin on the gold layer before alloy attachment is made.

Gold-boron and gold-arsenic have been successfully used to make p or n-type attachments, respectively, to most resistivity ranges of material. In some cases, primarily those where low resistivity Ge or Si were used or where the total gold and tin thicknesses were greater than .001", it was found necessary to introduce the doping impurity in the Sn layer.

A second method developed for bonding under a non-critical atmosphere for making n⁺ attachments

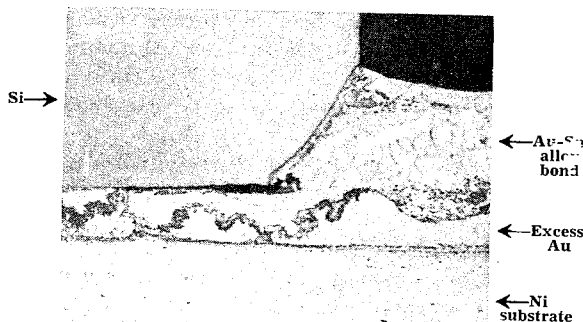


Fig. 3—Si on Sn plated Au clad Ni, excess Au. (From a 250X photomicrograph)

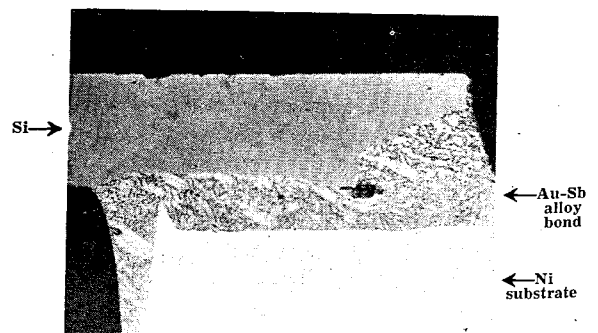


Fig. 4—Si on Sb plated Au clad Ni. (From a 250X photomicrograph)

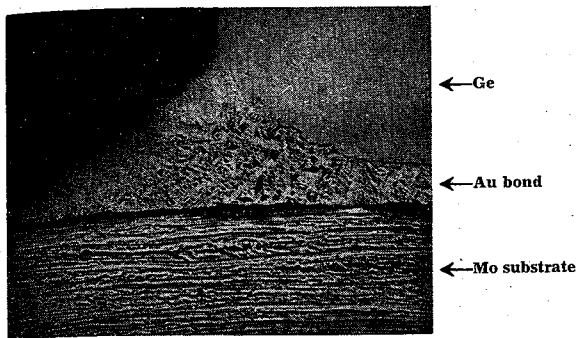


Fig. 5—Ge on Au clad Mo. (From a 250X photomicrograph)

is to antimony flash the gold clad material. The Sb seems to "flux" the reaction. Fig. 4 demonstrates this effect in the case of Si on Sb plated Au clad Ni, where the ratio of gold to nickel thicknesses (one to ten) is high enough to overcome cracking. The mechanism is probably due to the fact that this is a reaction which results in a ductile layer of excess Au remaining and negates the effect of high Ni expansion.

Where one wishes to achieve a good expansion match with high thermal and electrical conductivity, and magnetic properties are unimportant, molybdenum is the obvious choice for the tab material. Fig. 5 shows an attachment of Ge on gold clad molybdenum. A similar condition exists for silicon and/or gold plated Mo instead of cladding.

It will be shown that indium additions to gold alloys improved wetting properties in making small area contacts, therefore a similar approach was attempted in large area contacts. A 95 Au - 5 In alloy was clad on Fe-Ni and used to make attachments to germanium and silicon dice. General working experience with these materials indicated improved wetting properties.

Small area contacts were studied using eight different gold bearing binary alloys containing Pb, Bi, In, Ga, Ge, Sn, Sb, and Si as the other element.

Generally speaking atmosphere and mechanical forces appear to be the primary factors in determining the kind of bond achieved. With a "poor" atmosphere agitation is required to rupture surface films and permit contact. However, only surface wetting with little or no penetration, without subsequent cracking, occurs. On the other hand, in bonding with an "excellent" atmosphere, only pressure sufficient to hold the parts in good contact is required to initiate wetting which is followed by penetration which sometimes is sufficient to produce cracking upon cooling. In the case where the bond is a thin film either between two large pieces or on top of one of its surfaces, penetration is too shallow to play a role.

Of all the binary alloys studied, Au-Sn was most consistent in its behavior in direct alloying to silicon and germanium under a multitude of conditions. A major limitation of its use is the cracking between the alloy and base semiconductor upon cooling, shown in Fig. 6, after alloying to silicon.

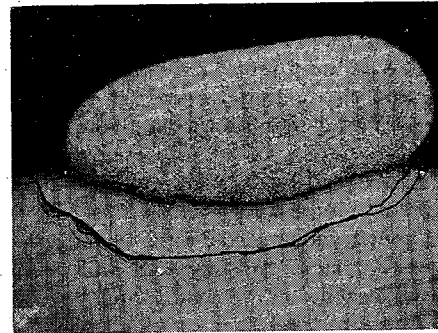


Fig. 6—Au-Sn on Si. (From a 250X photomicrograph)

Taylor¹ discusses some remedial measures for making crack-free alloyed junctions. While stress relieving heat treatments were generally used in this study where applicable, the major effort was directed towards alloy modification. Taylor points out six results of alloy modifications which may account for elimination of cracking. A goal of this investigation was to produce an alloy which changed less on freezing or one which was a better thermal expansion match with the semiconductor material. Hence, an evaluation on the basis of thermal expansion data was collected.

Thermal expansion curves of the gold-tin and silicon and germanium are shown in Fig. 7, measured through interferometric techniques on specimens submitted to R. J. Beals, Ceramic Staff, University of Illinois. The curve for gold-tin indicates poor compatibility with germanium and silicon and the non-linearity suggests a possible phase transformation or lattice rearrangement. If this non-linear effect is the cause of the cracking, then it was hypothesized that some means of "flattening out" the expansion curve could overcome this problem. In addition, if the solubility of the Au-Sn phase for silicon and germanium

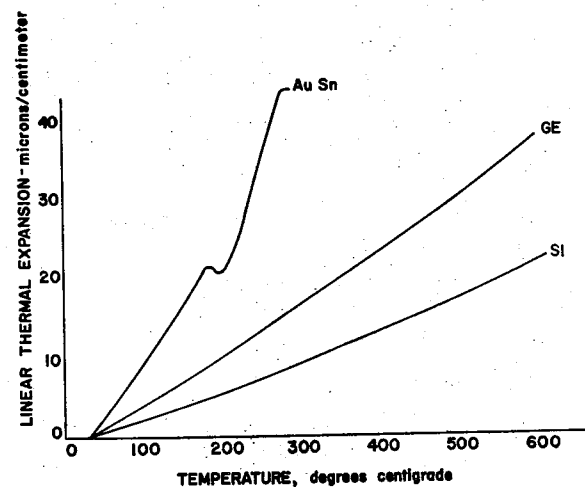


Fig. 7—Thermal expansion curves for Au-Sn, Si and Ge.

were reduced, alloy penetration would be diminished and cracking reduced. Since it is known that small additions to a liquid metal may be considered as impurities, thereby aiding wetting, it was considered that ternary alloys might have the multiple effect noted before. Of course an assumption is made here that if the binary alloy's thermal expansion were more compatible or linear with respect to the semiconductor material, we could extrapolate the data to the ternary system and say that this would probably provide a better thermal match.

Two groups of three ternary alloys were fabricated by adding 2, 3, and 6% silicon and 2, 10, and 15% indium respectively to the Au-Sn eutectic and samples of each were alloyed onto silicon. The addition of silicon diminished but did not entirely eliminate cracking. In all three alloys, penetration was quite limited and no apparent wettability change was noted. Addition of two percent indium appears to improve wetting of the silicon, but the higher indium concentrations impair it. This may be a phenomenon similar to that noted by Bailey,¹⁸ in which successive additions to a liquid metal cause the spreading ability of the solder to go through a maximum. Although none of the additions to the Au-Sn eutectic eliminated the cracking of the silicon surface subsequent to fusion with it, the effect was definitely reduced.

To study the effect of indium additions to the Au-Sn eutectic, thermal expansion curves were run on samples containing 2, 5, and 10% indium (Fig. 8). In-

(To be continued)

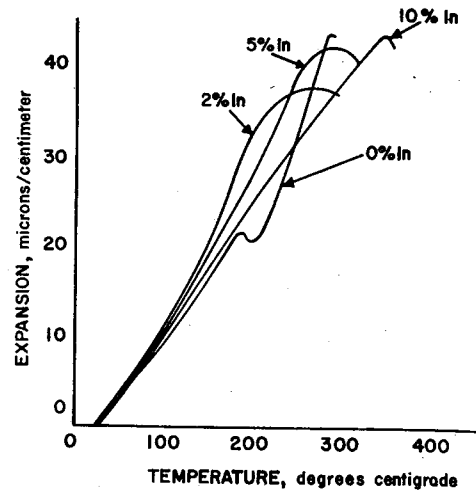


Fig. 8—Linear expansion for Au-Sn alloys.

creasing the indium content reduced the initial softening temperature in addition to narrowing its range. It is believed that by proper selection of additions, the Au-Sn eutectic alloy can be modified to produce alloy junction and/or small ohmic contacts on silicon and germanium without cracking the surface. Of course whether this doping can be done depends on the segregation of impurities in such a system.

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