JOURNAL OF MATERIALS SCIENCE 10 (1975) 1929–1937

Interfacial properties governing ohmic contacts between gold alloys and oriented gallium arsenide crystals

LEO Y. ZEE, Z. A. MUNIR*
Department of Materials Science and Engineering, California State University, San Jose, San Jose, California, USA

Contact angles between Au–Ge and Au–Sn alloys and {1 1 1} oriented gallium arsenide crystals were determined over the temperature ranges 360 to 450° C and 280 to 400° C, respectively. Three characteristic regions of the temperature dependence of these angles were observed. At the lower temperatures, contact angles, θ, decreased sharply with increasing temperature. This region was followed by another in which the values of θ were essentially independent of T and finally, at the higher temperatures, θ decreased again as T increased up to the highest limit indicated above. Based on microstructural and electron microprobe analyses these observations are explained in terms of diffusional processes at the interfacial regions between the gold alloys and GaAs crystals. Furthermore, from observations of the temperature dependence of contact angles between GaAs and pure tin, it is suggested that gold plays an important role in the observed interfacial phenomena.

1. Introduction

Efficient use of high current density GaAs devices depends largely on the successful fulfilment of the requirement of low contact resistance. The formation of an intimate metal-semiconductor contact, characterized by low resistance, is highly dependent on the wetting characteristics between the substrate and the metal. Various metals and alloys have been utilized as contact materials on both n- and p-type gallium arsenide [1–10]. Of these, alloys of gold–germanium and gold–tin have demonstrated exceptionally reliable behaviour [5, 9] and have had the added advantage of low melting temperatures [11]. These and other advantages have been the reason behind the widespread use of the eutectic compositions of Au–Ge and Au–Sn as contact alloys.

The dependence of the performance of ohmic contacts on the wettability of the substrate has been demonstrated [12–14]. In the case of gallium arsenide, wettability by liquid Ga has been shown to be a function of crystalline anisotropy and various additional substrate characteristics [15, 16]. Within the limits of experimental observations, the contact angles between liquid gallium and {1 1 1} oriented gallium arsenide were found to be insensitive to variations in the composition of the ambient gas. While these observations were limited to nitrogen, argon, and residual vacuum gas, they do suggest that the roles played by the liquid–gas and solid–gas interfaces are secondary. Much more difficult to establish and by far least understood is the role of compositional variations at the liquid–solid interface resulting from the interdiffusion of one or more species. In this paper we report the results of an investigation of the contact angles between gold alloys (Au–Sn and Au–Ge) and gallium arsenide and the concommitant changes in the semiconductor/metal interface.

* Present address: Department of Mechanical Engineering and the Materials and Devices Research Group, University of California, Davis, California 95616, USA.

2. Experimental methods

Alloys of gold–germanium and gold–tin were made from 99.99% pure gold and tin and from 99.999+% pure semiconductor grade germanium. Typical impurities in the gold samples are at the following levels: 1 ppm (Cu, Al, Fe, Si), 2 ppm (Pb), and 15 ppm (Ag). In ppm, the following represent the concentrations of impurities in the tin samples: 10 (Cu), 1 (Ag, Fe, Si, Mg), and 3 (Al). Appropriately weighed mixtures of these elements were placed in an alumina crucible then heated at temperatures exceeding by at least 70° C the corresponding liquidus temperature of the anticipated alloy. All alloying processes were made in a reducing atmosphere of cracked ammonia for at least 2 h. Approximately 2 mm diameter beads were made from gold–tin alloys having the compositions 78, 80 and 82 wt% Au. The compositions of beads made from the gold–germanium alloys were 86, 88 and 90 wt% Au. The alloys 88% Au–12% Ge and 80% Au–20% Sn represent eutectic compositions in these two binaries.

N-type gallium arsenide crystals with a $1.1 \times 10^{16} cm^{-3}$ carrier concentration and having a resistivity of 0.14 Ω cm were cut along the {1 1 1} planes into approximately 2 mm thick wafers. Laue back-scattering patterns showed that the desired orientation was achieved within a maximum deviation of 2 degrees. Each wafer was rough-polished with 600 grit SiC paper, then fine-polished through a series of 15, 9, 3, 1 and $\frac{1}{4}$ μm diamond paste polish. Prior to the last stage of polishing, each wafer was etched with a 1 : 1 :2 solution (by volume) of H_2SO_4, H_2O_2 and H_2O, respectively. A final etch, using the same solution was made just before commencing with the contact angle measurements. The identification of the polarity of the {1 1 1} planes was accomplished by chemical etch techniques [17]. Well defined triangular etch pits were the characteristic features on the (1 1 1), Ga face. The $(\bar{1}\,\bar{1}\,\bar{1})$ As face gave irregular etch patterns.

Contact angle measurements were made in an apparatus which has been described in considerable detail in earlier publications [15, 16]. It consists basically of a bell-jar vacuum system equipped with a horizontally positioned, cylindrical tantalum heating element. A graphite block in the form of a "D" served as a platform for the GaAs substrates. A chromel–alumel thermocouple was inserted through the graphite block so as to be in intimate contact with the gallium arsenide wafer. Methods for measuring the contact angles and procedures for establishing confidence in the measurements have been adequately described previously [15].

Typically, a spherical alloy bead was placed on a GaAs wafer which was in turn positioned on the graphite block in the centre of the heating element. The chamber was then evacuated down to at least 5×10^{-6} Torr and power was introduced so as to attain a temperature of about 100° C. These conditions were maintained for about 15 to 30 min to allow for the outgassing of the system. This step was then followed by a rapid increase in temperature to about 20° C below the liquidus of the investigated alloy. At this point the rate of temperature increase was lowered to a slow rise of $2° C min^{-1}$ up to the first experimental determination. At any temperature setting, contact angle readings were taken at 5 min intervals to establish the existence of a steady state condition between the liquid drop and the gallium arsenide substrate. Measurements were made between 360 and 450° C for the Au–Ge alloys and between 280 and 400° C for the Au–Sn alloys. Contact angles were also measured under a 10^{-3} Torr background pressure Ar of N_2, Ar and He gases.

At the end of each experiment the metallic sphere was removed and the area of contact on the GaAs crystal was carefully examined. This was done by first mounting, polishing, and then etching the sample for $\frac{1}{2}$ min with aqua regia. The interfacial region was then examined under the microscope and photographed. Further examination of this region was done through an electron microprobe analysis. A simultaneous scan of three of the five elements (Au, Ge, Sn, As, and Ga) was done in 2 μm steps across the metal/GaAs interface and well into the two adjacent regions. In each case background intensities were measured for each element.

3. Results

Contact angles between gold–tin and gold–germanium alloys, and {1 1 1} oriented gallium arsenide crystals are shown as a function of temperature in Figs. 1 to 4. The curves depicted in these figures show three relatively characteristic regions. In the first, the low temperature region, the contact angle is a decreasing function of temperature. The second region is that characterized by relatively temperature-independent con-

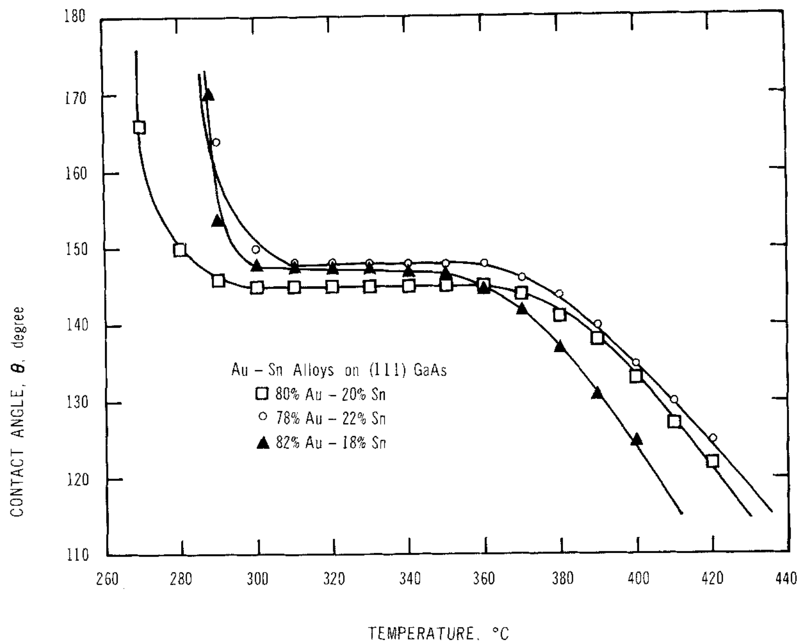

Figure 1 Temperature dependence of the contact angles between Au–Sn alloys and (1 1 1) oriented GaAs.

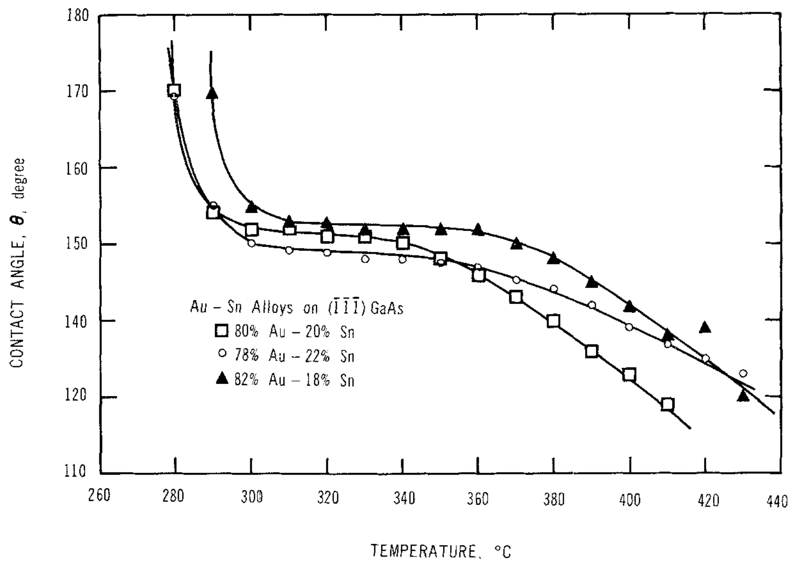

Figure 2 Temperature dependence of the contact angles between Au–Sn alloys and ($\bar{1}\ \bar{1}\ \bar{1}$) oriented GaAs.

tact angles. At higher temperatures, the measured contact angles decrease sharply with increasing temperature. Table I lists the temperature values corresponding to the end of the second region and the contact angles associated with them for the investigated alloys.

Attempts aimed at measuring the contact angles between the pure elements (Ge, Sn and Au) and GaAs were partially successful. At the melting points of gold and germanium the thermal dissociation of gallium arsenide is so significant as to make contact angle measurements difficult to interpret. Furthermore, in the case of gold, visual evidence of extensive reaction with the substrate was apparent at temperatures well below the melting point of this metal. Successful measurements, however, were made on the Sn/GaAs system. Fig. 5 depicts the temperature dependence of the contact angles between tin and gallium arsenide.

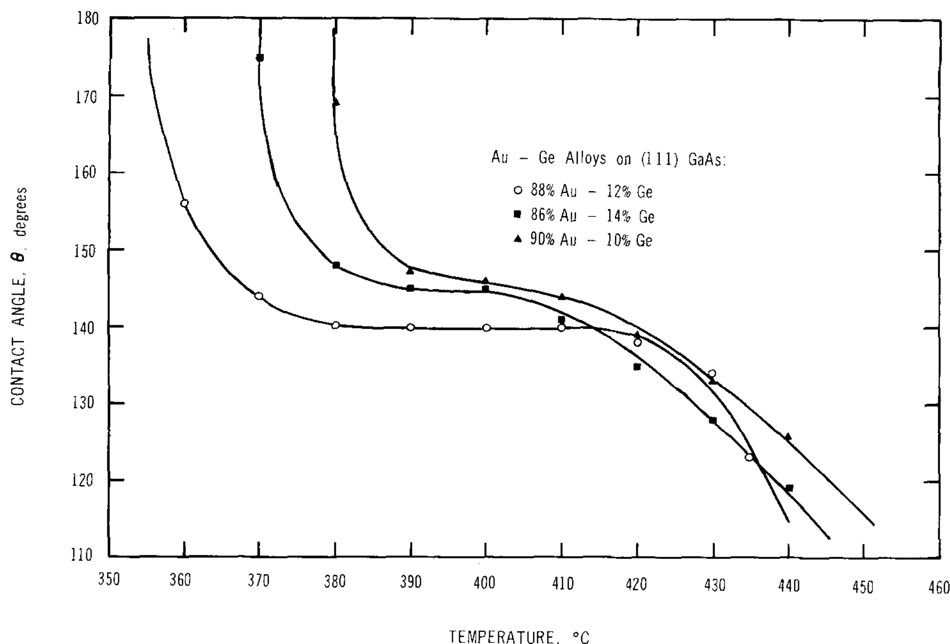

Figure 3 Temperature dependence of the contact angles between Au–Ge alloys and (1 1 1) oriented GaAs.

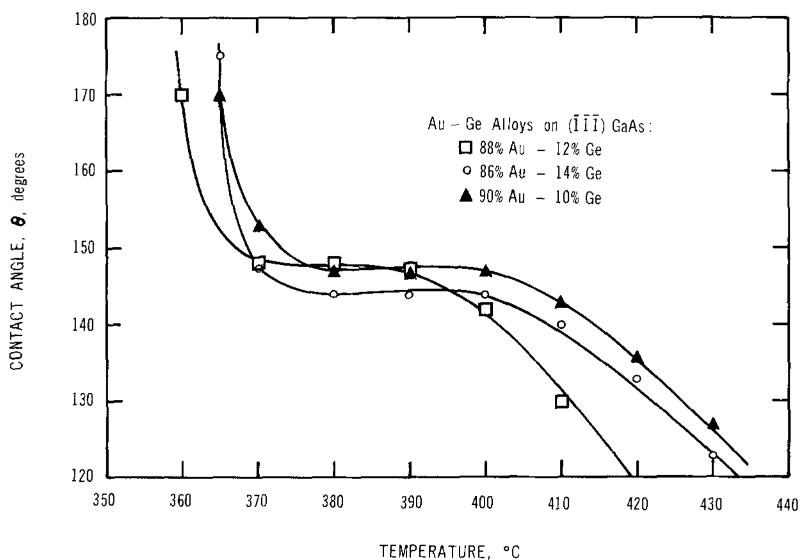

Figure 4 Temperature dependence of the contact angles between Au–Ge alloys and ($\bar{1}\,\bar{1}\,\bar{1}$) oriented GaAs.

The time dependence of contact angles in the second region of the curves of Figs. 1 to 4 was also investigated. Measurements were made at 390° C for the 88% Au–12% Ge alloy and at 295° C for the 80% Au–20% Sn alloy for up to 2 h. The results of these constant temperature measurements are shown in Figs. 6 and 7.

Photomicrographs of the interface resulting from heating liquid eutectic gold–germanium alloys on gallium arsenide are shown in Figs. 8 and 9. As indicated in these figures, the highest temperatures to which they were heated (in the process of contact angle measurements) correspond to the third region of the typical θ versus T curve. Substantial changes in the interface between Au–Ge and GaAs are readily recognizable. In contrast, photomicrographs of the resulting interface between Au–Sn alloys and GaAs, Figs. 10 and 11, show a relatively limited interfacial region even after heating to temperatures beyond the steady-

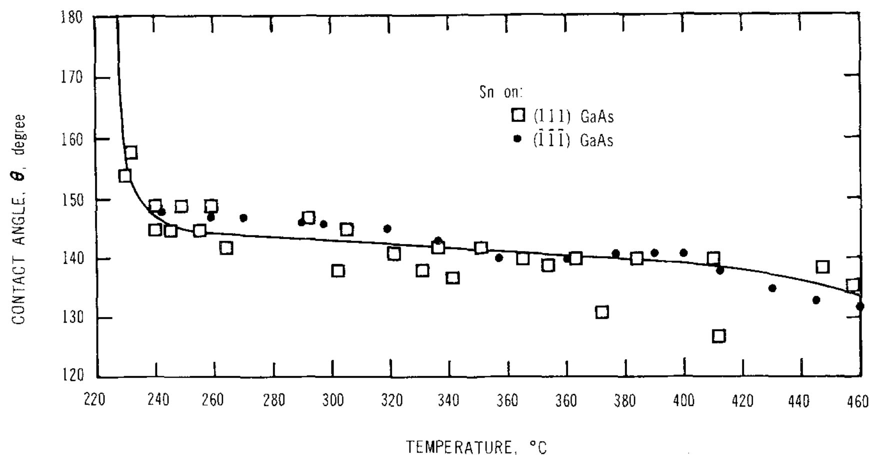

Figure 5 The contact angles between liquid Sn and $\{1\,1\,1\}$ planes of GaAs.

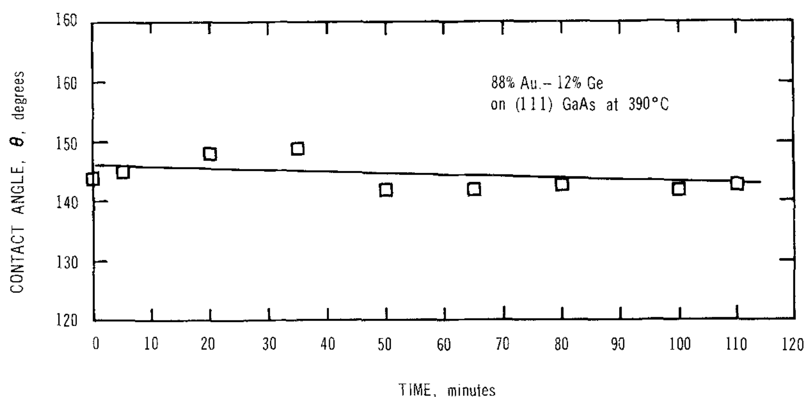

Figure 6 Time dependence of the contact angle between an 88% Au–12% Ge alloy and (1 1 1) oriented GaAs at 390° C.

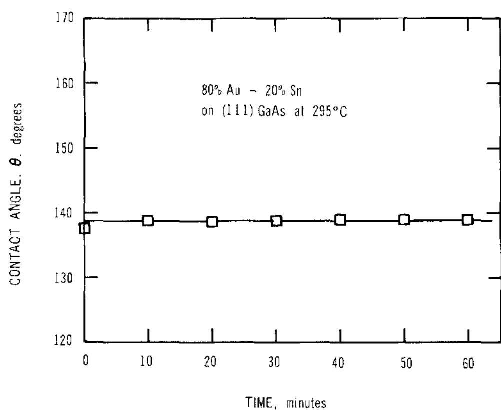

Figure 7 Time dependence of the contact angle between an 80% Au–20% Sn alloy and (1 1 1) oriented GaAs at 295° C.

TABLE I Contact angles and upper temperature limits for the second region of the θ versus T curves for $\{1\,1\,1\}$ faces of GaAs

Alloy	(1 1 1) face		($\bar{1}\,\bar{1}\,\bar{1}$) face	
	θ, deg	T, °C (approx)	θ, deg	T, °C (approx)
90 Au–10 Ge	146	410	147	410
88 Au–12 Ge	140	420	148	400
86 Au–14 Ge	145	400	144	410
82 Au–18 Sn	148	360	152	360
80 Au–20 Sn	145	370	152	340
78 Au–22 Sn	148	360	148	360

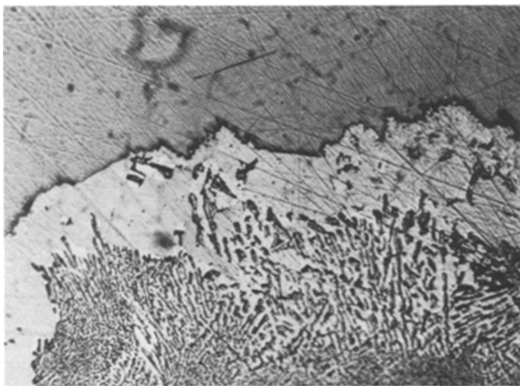

Figure 8 Photomicrograph of the interfacial region between an 88% Au–12% Ge alloy and GaAs after heating to ~ 430° C.

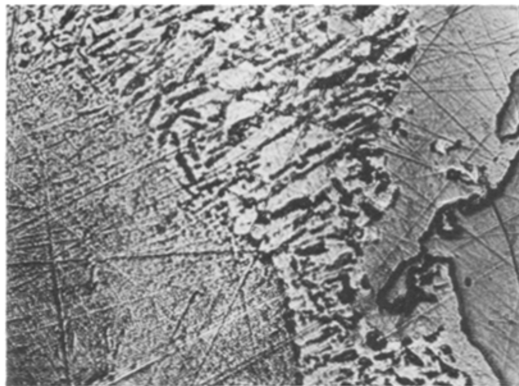

Figure 9 The interfacial region between an alloy of 86% Au–14% Ge and GaAs after heating to ~ 440° C.

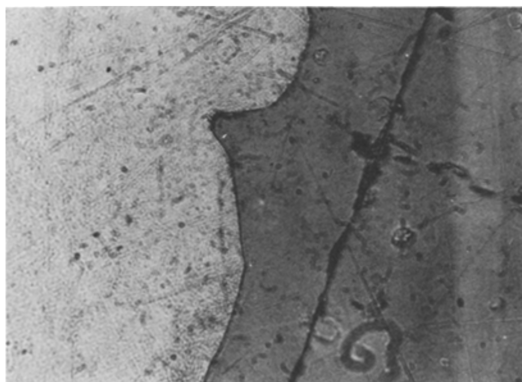

Figure 10 The interface resulting from heating the eutectic 80% Au–20% Sn on GaAs at 440° C.

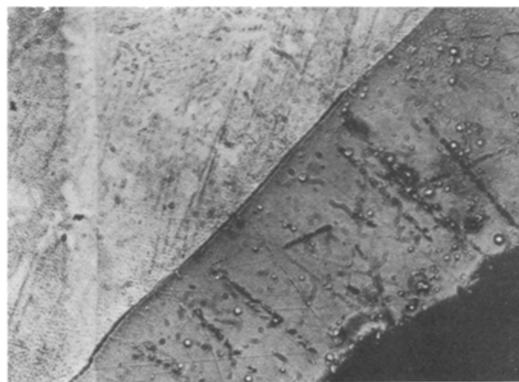

Figure 11 The interface resulting from heating an 82% Au–18% Sn on GaAs at 453° C.

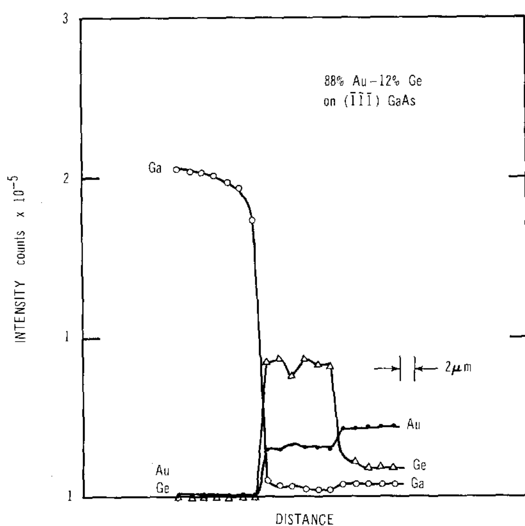

Figure 12 A microprobe scan across the interface between 88% Au–12% Ge and ($\bar{1}\,\bar{1}\,\bar{1}$) GaAs.

state region of the θ versus T curves. Electron microprobe intensity profiles for the alloys mentioned above are shown in Figs. 12 to 15.

Contact angles between the investigated gold alloys and GaAs showed no dependence on the nature of the ambient gases (N_2, Ar and He), and, furthermore, were essentially the same as those determined under vacuum conditions.

4. Discussion

The decrease in contact angle associated with an increase in temperature in the first stage of the θ versus T curves for the Au–Ge and Au–Sn alloys is believed to be caused by an equilibration process with a concommitant change of state. The initial contact angles were those between the solid metallic sphere and gallium arsenide. Thus in general the beginning of the second stage is associated with the melting point (more appropriately,

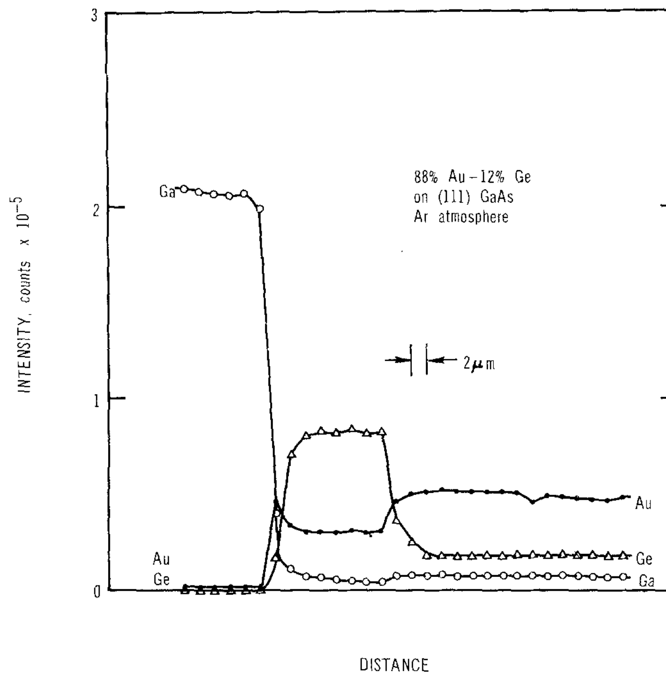

Figure 13 A microprobe scan across the interface between 88% Au–12% Ge and (1 1 1) GaAs.

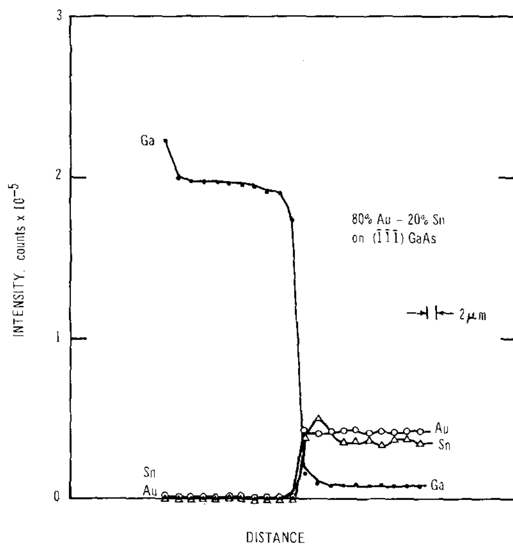

Figure 14 Intensity profiles of Au, Sn and Ga across the interface between 80% Au–20% Sn and ($\bar{1}\ \bar{1}\ \bar{1}$) GaAs.

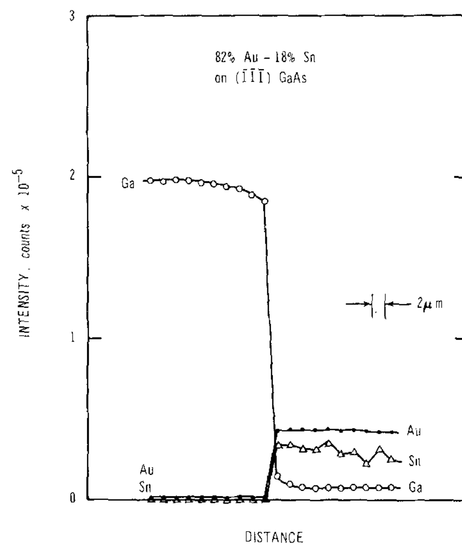

Figure 15 Intensity profiles of Au, Sn and Ga across the interface between 82% Au–18% Sn and ($\bar{1}\ \bar{1}\ \bar{1}$) GaAs.

the liquidus temperature) of the alloy. An examination of Figs. 1 to 4 indicates that as expected, the start of the second stage occurs at a lower temperature for the eutectic compositions. In the second stage, where θ is essentially independent of T, diffusional processes are believed to be at such a low level that significant alteration of the nature of the interface does not occur. In contrast, substantial alterations of the interface are believed to take place at the higher temperatures, i.e. during the third stage. These expectations are verified by both microstructural and electron microprobe observations.

Fig. 16 shows the interfacial region between GaAs and an eutectic Au–Ge alloy which had been heated to ~390° C, i.e. lower than the

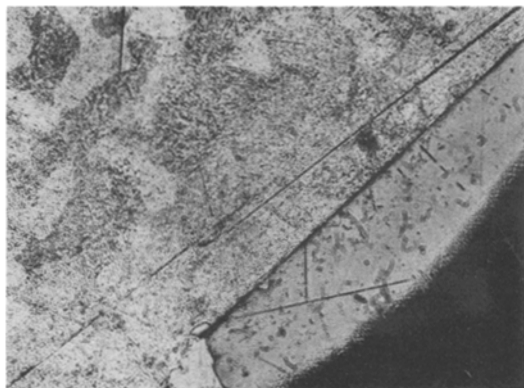

Figure 16 **Photomicrograph of the interfacial region resulting from heating 88% Au–12% Ge on $(\bar{1}\bar{1}\bar{1})$ GaAs at ~ 390° C.**

temperature marking the beginning of the third stage (Table I). The electron microprobe intensities of Ga, Ge and Au across this interfacial region are shown in Fig. 17. These figures show little evidence for a significant change at the interface. In contrast, higher temperatures produce a considerable reaction zone as shown in Fig. 8. Evidence for the interaction between Au–Ge alloys and the gallium arsenide substrate comes from the microprobe analyses. The intensity profiles resulting from these analyses indicate that initially gallium and gold diffuse to and across the original interface, possibly forming one of the Ga–Au intermetallic compounds. The diffusion of Ga into Au–Ge alloys has been observed previously [9]. Similarly, Au has been shown to diffuse with relative ease into gallium arsenide [5]. On the other hand, the diffusion of Ge into GaAs is known to be relatively slow and limited [5].

The depletion of Au in the eutectic Au–Ge alloy at temperatures above the eutectic isotherm, 356° C, causes the nucleation of a solid phase which is essentially pure germanium [18]. Fig. 13 shows a region of approximately 8 μm thick in which the intensity of Ge is significantly higher than that measured at greater distances from the interface. A corresponding decrease in the intensity of gold is also observed. These observations correspond closely with the microstructural evidence. In Fig. 8 the light phase near the interface is believed to be the pro-eutectic Ge which diminishes with increasing distance into the original Au–Ge alloy. The typical eutectic microstructure is clearly evident in regions beyond the interface.

The above observations differ considerably from those in the Au–Sn/GaAs system. The limited interface region is believed to be formed by the diffusion of Ga into the Au–Sn alloy at the lower temperatures, and in addition by the diffusion of Sn into GaAs at the higher temperatures [2]. While not clearly apparent in these results, the diffusion of Au into GaAs is probably contributing to the changes at the interface. With

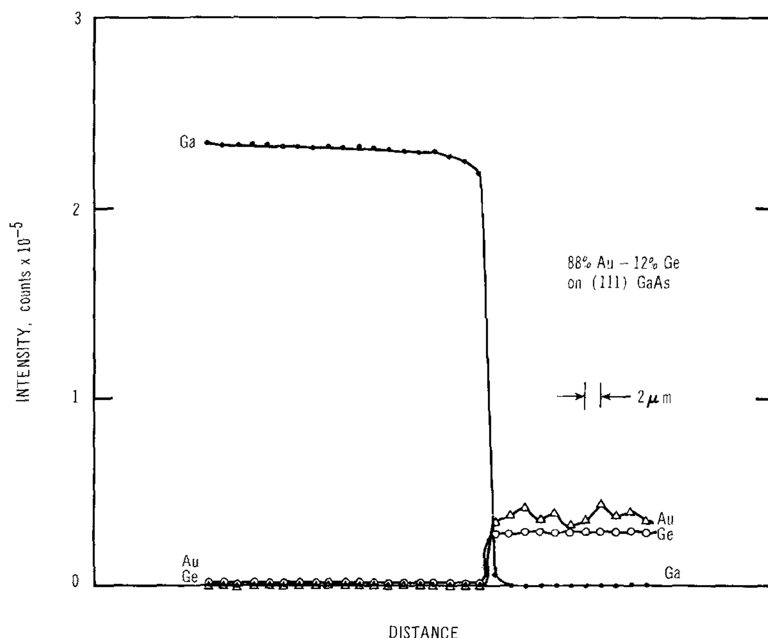

Figure 17 Intensity profiles of Ga, Au and Ge across the interface shown in Fig. 16.

reference to the changes associated with the depletion of Au in the Au–Ge alloys, corresponding changes in the Au–Sn systems cannot occur without extensive depletion of Au from the alloys. For example, for the eutectic composition (80% Au) at 400° C, the existence of a two-phase region is not possible until the depletion of Au has increased the relative concentration of Sn to about 34%. At lower temperatures (~ 300° C), however, relatively small gold depletion can result in a two-phase alloy. In view of the observed concentration profiles resulting from heating up to the second stage (> ~ 350° C), the diffusion of Au must be a relatively slow process. Furthermore, there is experimental evidence that diffusion of Au into GaAs is a complex process, controlled possibly by two mechanisms occurring at two temperature regions [19].

Within experimental uncertainties, no difference in contact angles could be established between the (1 1 1) Ga and $(\bar{1}\,\bar{1}\,\bar{1})$ As faces of gallium arsenide for alloys in both the Au–Ge and Au–Sn systems. Similarly, the contact angles between liquid tin and (1 1 1) oriented GaAs were, within experimental error, the same as those measured on the $(\bar{1}\,\bar{1}\,\bar{1})$ faces. This latter observation contradicts the results of Jadus *et al.* [2] in which the wetting of GaAs by Sn was reported to be dependent on the polarity of the {1 1 1} planes. Contact angles for the Ga and the As faces fall essentially on a straight line when these are plotted against temperature. The curve exhibits a slight negative slope with no indication for the existence of an accelerated decrease in θ associated with the third stage in the gold alloys curves. The absence of the third stage in the θ versus T for tin suggests the apparent initial role of Au in the diffusional processes referred to above.

Acknowledgements

The assistance of Art Cooper and Ray Wittkopp is gratefully acknowledged.

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Received 26 March and accepted 28 April 1975.