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A Very Low Resistance, Non-Sintered Contact System for Use on Indium Phosphide Concentrator/Shallow Junction Solar Cells

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ABSTRACT

An investigation is made into the possibility of providing low resistance contacts to shallow junction InP solar cells which do not require sintering and which do not cause device degradation even when subjected to extended annealing at elevated temperatures. We show that the addition of In to Au contacts in amounts that exceed the solid solubility limit lowers the as-fabricated (unsintered) contact resistivity R_C to the 10^{-5} ohm cm^2 range. If the In content is made to correspond exactly to that required to form the intermediate compound Au_9In_4, then the contacts so formed are stable, both electrically and metallurgically, even after extended annealing (12 hours) at 400 C. We next consider the contact system Au/Au_2P_3 which has been shown to exhibit as-fabricated R_C values in the 10^{-6} ohm cm^2 range, but which fails quickly when heated. We show that the substitution of a refractory metal (W, Ta) for Au preserves the low R_C values while preventing the destructive reactions that would normally take place in this system at high temperatures. We show, finally, that R_C values in the 10^{-7} ohm cm^2 range can be achieved without sintering by combining the effects of In or Ga additions to Au contacts with the effects of introducing a thin Au_2P_3 layer at the metal-InP interface.

INTRODUCTION

The achievement of low resistance electrical contact to InP has, in the past, inevitably been accompanied by mechanical degradation of the InP itself. One method of achieving low contact resistance, for instance, is to create lattice disorder in the semiconductor via ion etching and/or sputter deposition of the contact metallization.[1-4] Depending on the severity of the damage to the InP lattice, the contacts so formed exhibit low resistance either as-fabricated or after mild heat treatment.

If lattice damage is not introduced prior to metal deposition, a sintering treatment at higher temperatures is necessary after deposition. Although a number of metal-semiconductor combinations have been tried, they all require heat treatments that result in the dissolution of substantial amounts of InP into the metallization in order to achieve low resistance values.[4-10]

For some applications the dissolution of the semiconductor due to the sintering process and/or the damage resulting from ion etching can be tolerated. Devices such as the solar cell, however, where shallow junctions are the rule can be severely degraded if the damage to the semiconductor substrate is not precicely controlled.

While there are several remedial approaches to control the sinter-induced metallurgical interactions in shallow junction devices, such as the use of rapid thermal annealing (RTA) techniques[4,9-11] or the imposition of diffusion barriers between the semiconductor and the current carrying metallization[12,13], their use adds complexity and an element of trial and error to the contacting process.

A better solution would be to eliminate the need to sinter the contacts and thus avoid the device destroying metallurgical interactions that accompany the high temperature processing. The ideal solution would be to devise a contact system that exhibits low contact resistance as-fabricated, and which, in addition, would be able to withstand thermal stress, either intentional or unintentional, without destroying or degrading the device upon which it has been deposited.

In a previous publication we have described two methods of reducing the specific contact resistivity R_C of as-fabricated Au based contacts to n-InP.[14] We have shown that the addition of small amounts (1 a%) of Ga to Au contacts results in as-fabricated R_C values in the high 10^{-5} ohm cm^2 range. We have also shown that the insertion of a thin layer of Au_2P_3 at the interface between Au and InP produces R_C values in the high 10^{-6} to the low 10^{-5} ohm cm^2 range. In both cases the R_C reductions are observed in the as-fabricated state, without the need for sintering. Because the devices are not subjected to elevated temperatures there is negligible dissolution of InP into the metallization and thus no degradation of the electrical characteristics of the shallow 2000 A n/p junction under the contacts.

While the achievement of these low as-fabricated Rc values is a useful accomplishment, we find that both of the above approaches quickly fail when subjected to temperatures in the 300 to 400 C range. Vigorous emitter destroying metal-InP reactions are observed when devices with Au/Au_2P_3 contacts are heated above 350 C for a few minutes. With regard to the Au-Ga contact system, we find that while there is essentially no metallurgical interaction between InP and the Au-Ga metallization even at elevated temperatures[14], a few minutes at 400 C is sufficient to cause a rise in Rc to values in the 10^{-3} ohm cm^2 range.

Our purpose here is to describe the results of our efforts to preserve the low as-fabricated values of R_c during extended heat treatment at elevated temperatures. We will also show that an additional order-of-magnitude decrease in the as-fabricated value of R_c to the 10^{-7} ohm cm^2 range can be achieved by combining the effect of Ga (or In) additions to Au contacts with that of inserting an Au_2P_3 layer at the metal-InP interface.

EXPERIMENT

The devices studied here were all n/p diodes with epitaxially deposited emitters, 2000 A thick, Si doped to 1.7 X 10^{18} cm^{-3}. Substrate doping (Zn) was 8 X 10^{16} cm^{-3}. Specific contact resistivity measurements were made using the transmission line method (TLM). We used electron beam evaporation to deposit the contact metallization. The samples were not actively cooled during evaporation. A metal thickness of 2000 A was used throughout, unless otherwise stated. The Au/In alloy deposition technique is described elsewhere.[15] Ga was introduced into the metallization by sandwiching a 200 A Ga layer between two 900 A Au layers.

The Au_2P_3 interlayer was formed by depositing a 40 A Au layer on the InP and annealing it for a few minutes at 395 C.[14] The result is an array of Au_2P_3 islands (approximately 0.5 micrometers in diameter, several micrometers apart) under a thin layer of Au_3In. The contacts are subsequently built up by metal deposition after carefully redefining the TLM pattern photolithographically.

Sintering was performed in a rapid thermal annealing (RTA) apparatus that provides rise times of 10 seconds or less with negligible overshoot (forming gas ambient). To monitor the degree of emitter dissolution/perforation caused by the sintering process we observed the quality of the diode I-V characteristic. As a measure of the I-V quality we arbitrarily defined a diode conduction voltage V_1 as the voltage at which the forward current through the TLM patterned diode (area 5.6 X 10^{-3} cm^2) is 1 mA.[14] A good pn junction should exhibit a V_1 of about 900 mV. Lower values of V_1 indicate a degraded emitter.

Compositional analysis was performed via x-ray photoelectron spectroscopy (XPS). The XPS system was specifically calibrated for use with both the Au-In and the Au-Ga binary systems.[16]

THE EFFECT OF Ga AND In ADDITIONS

As illustrated in figure 1, the addition of small amounts of Ga to Au contacts results in a tenfold reduction in the specific contact resistance.[14] As seen in figure 2, however, the resistance gains are quickly lost if the temperature is raised briefly to the 300 to 400 C range.[14] As well as reducing R_c, Ga additions have also been shown to drastically reduce the dissolution of InP into the metallization by inhibiting the interstitial entry of In into the Au lattice.[14] The suggested connection between these two effects (i.e., between the electrical effects and the metallurgical effects) is that Ga, in slowing the In entry rate, permits the dissipation of the P atoms that are released at the Au-InP interface when In interstitially enters the metallization. The result is a decrease in the amount of accumulated P at the interface and thus a reduction in R_c.[14]

If this mechanism is correct, then other methods of reducing the In entry rate should also be effective in lowering R_c. One method of inhibiting In entry would be to purposely saturate the Au contact metallization with In. Since low temperature In entry (stage I) stops once the In concentration reaches the solid

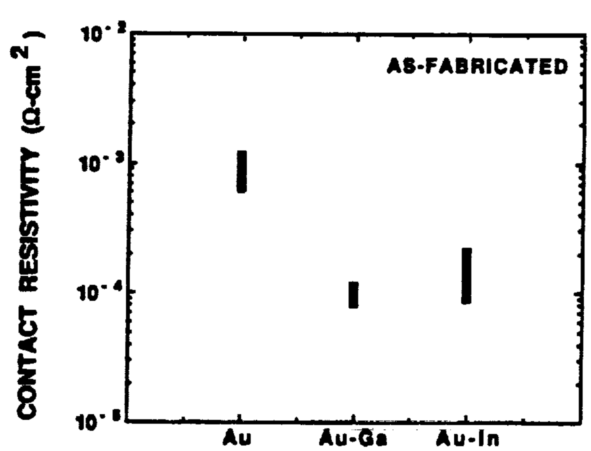

Figure 1. Measured as-fabricated contact resistivities for Au-only (8), Au-Ga (6), and Au-In (16) contacts on InP. Parentheses indicate number of samples.

solubility limit[15], a saturated Au(In) solid solution contact system would preclude In entry, at least at low temperatures. With this in mind we fabricated a number of samples contacted with various Au-In mixtures. The In content in the contacts ranged from 12 to 35 a%. When we measured the as-fabricated contact resistivities of these samples (figure 1) we found, as suspected, an order of magnitude drop in R_c. This finding not only provides support for the suggested mechanism, but it also presents us with the opportunity to deposit a thermodynamically stable Au-In alloy which will not react with the InP substrate when the temperature is raised.

Au_9In_4 is thermodynamically stable with respect to InP. It has been shown to be the terminal compound that is formed in the series of solid state reactions that take place between Au and InP.[17] Figures 3 and 4 show the behavior of contacts composed of Au_9In_4 and other Au-In mixtures during heat treatment at 400 C. As can be seen, the conduction voltage of the Au_9In_4 contacted diode remains invariant even after 12 hours at temperature. The contacts with In content either greater than or less than the 30 % or so needed to form Au_9In_4, on the other hand, can be seen to react with the InP, effectively destroying the underlying n/p diodes.

In the case of the 23 % In contacts, the In required to convert the metallization to Au_9In_4 was obviously supplied by the dissolving InP emitter. If the In content is greater than that of Au_9In_4 (i.e. the 35 a% In sample), then higher In content alloys, such as $AuIn_2$, apparently nucleate and grow, again requiring InP dissolution. Evidence for this is the fact that the metallization exhibits large pink areas after heat treatment, indicating that In is being leached from the silver colored Au_9In_4 (leaving behind the pink colored Au_3In) to form $AuIn_2$ or other high In content alloys. Since some of the In to form these alloys comes from the InP substrate, the integrity of the underlying emitter is degraded, as evidenced by the drop in V_1. It should be noted, however, that the 35 a% In sample is stable for several hours at 400 C while the higher In content phase is being nucleated. For this sample a nucleation time of two hours at 400 C is indicated by the initial invariance of V_1.

Thus, as-fabricated contact resistivities in the high 10^{-5}/low 10^{-4} ohm cm^2 range that are not affected by extended heat treatment at 400 C can be readily achieved through the use of the thermodynamically stable alloy Au_9In_4.

THE EFFECT OF AN Au_2P_3 INTERLAYER

As mentioned in the introduction, we have shown that as-fabricated R_c values in the high 10^{-6} to the low 10^{-5} ohm cm^2 range can be achieved with Au contacts by introducing a thin Au_2P_3 layer at the Au-InP interface (figure 5).[14] These contacts, however, cannot withstand exposure to elevated temperatures. The metallurgical interactions that take place in a few minutes at 350 C are sufficient to destroy an underlying 2000 A thick emitter. In an attempt to avoid these device destroying reactions we sought to replace the reactive Au metallization with a more metallurgically inert refractory

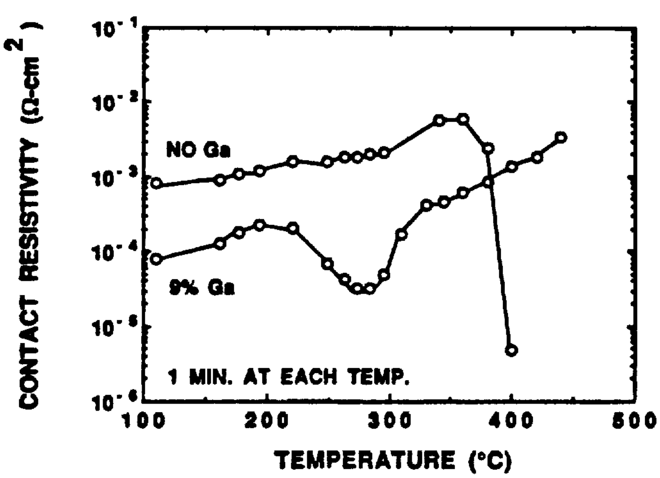

Figure 2. The effect of sintering on the specific contact resistivity of Au-only and Au-9 a% Ga contacts on InP.

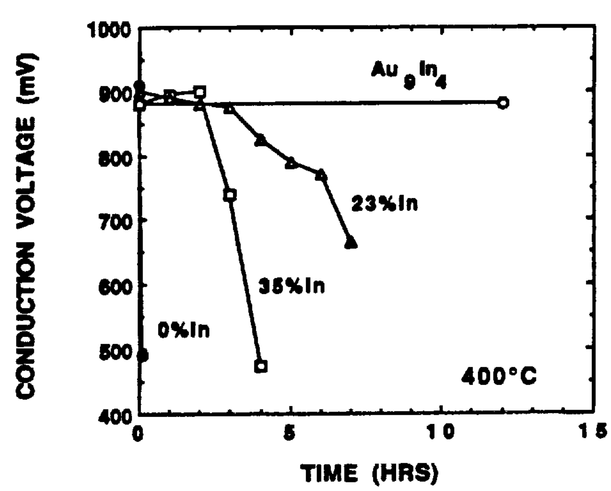

Figure 3. The variation of conduction voltage with time at 400 C for Au contacts containing various amounts of In.

metal. Thus, after depositing and annealing a 40 A Au layer to form an Au_2P_3/Au_3In interlayer, we built up the TLM contact pattern with a 2000 A layer of either W, Ta, or Mo.

As seen in figure 5, the use of a refractory metal instead of Au does not significantly affect the value of the as-fabricated contact resistivity. Values in the low 10^{-5} ohm cm^2 range are easily achieved.

The next question was whether these contacts would react destructively with InP at elevated temperatures. The results of annealing Ta/Au_2P_3- and W/Au_2P_3-contacted InP at 400 C for a number of hours are shown in figures 6 and 7, respectively. In both cases the contact resistance remained low and there was effectively no metallurgical reaction with the InP substrate. Thus the substitution of Ta or W for Au in the Au/Au_2P_3 system preserves the low as-fabricated R_c values achieved with Au/Au_2P_3, while at the same time preventing the high temperature InP-metal interactions that would otherwise destroy shallow junction devices such as these.

THE Au_2P_3 INTERLAYER WITH Ga-Au AND In-Au BUILDUP

The R_c reductions obtained by adding Ga or In to Au contacts and the reductions effected by adding an Au_2P_3 interlayer are apparently additive. Figure 8 shows the as-fabricated R_c values achieved by depositing either Au-9 a% Ga or a Au-In mixture over a thin Au_2P_3 interlayer. As can be seen, R_c values in the 10^{-7} ohm cm^2 range have been achieved, again as-fabricated, without the need for sintering. The additive nature of these two effects is not easily understood. Some sort of synergistic mechanism must come into play to produce R_c values significantly lower than either effect can produce by itself.

The task of preserving these low R_c values while preventing semiconductor dissolution as the temperature is increased appears to be made more difficult by the presence of the Au_2P_3 interlayer. Heat treatment of the $Au\text{-}Ga/Au_2P_3$ contact system at temperatures in the 300 to 400 C range, for example, showed that although there was little or no metal-semiconductor intermixing (i.e., no change in V_1), the value of R_c was very sensitive to temperature increases. The value of R_c was observed to rise two orders of magnitude after only 10 minutes at 350 C even though V_1 remained unchanged.

Although one would expect V_1 to remain unchanged because of the reaction suppressing effects of Ga in the metallization[14], the abrupt increase in R_c is somewhat of a surprise. With the suspicion that something had happened at the Au_2P_3-InP interface, we removed the metallization from two samples, one which had been heat treated and one which had not, using a thiourea-based etchant.[18] This etchant readily removes all Au-based metal alloys but does not remove Au_2P_3. Upon microscopic examination of the stripped samples we found Au_2P_3 on the InP surface of the unheated sample (as expected), but not on the heated (high resistance) sample.

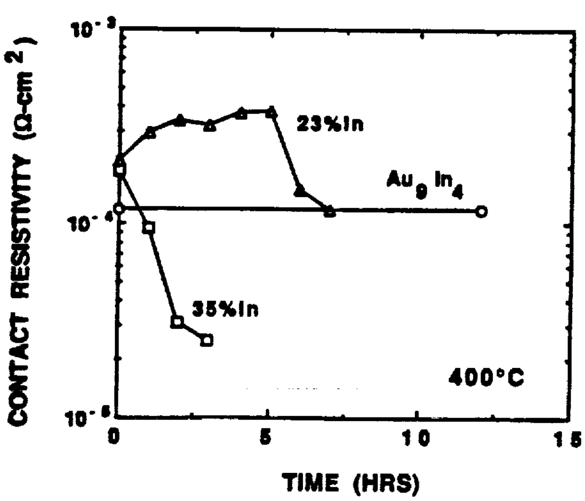

Figure 4. The variation of contact resistivity with time at 400 C for Au contacts containing various amounts of In.

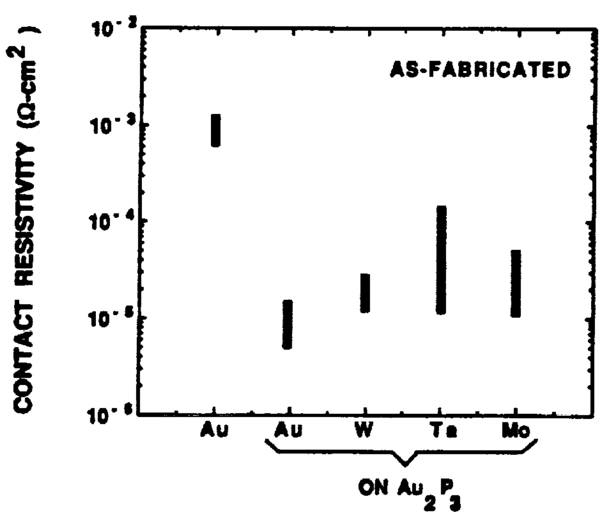

Figure 5. Measured as-fabricated contact resistivities for Au-only and for Au (10), W (6), Ta (7), and Mo (2) on a thin Au_2P_3 interlayer. Parentheses indicate number of samples.

It is felt that the Au_2P_3 in the heated samples may have been physically separated from the InP by the accumulation of vacancies that are generated as In (from InP) enters the metallization interstitially when the sample is heated. If Ga were not present in the metallization, the vacancies generated at the interface would be annihilated by capturing interstitial Au atoms formed during the Au-to-Au_3In phase transition (stage II).[17] The result would be the formation of additional Au_2P_3 at the Au_2P_3-InP interface.[17] However, since the presence of Ga has been shown to prevent Au interstitial formation[14], the vacancies, rather than being annihilated, accumulate at the InP-Au_2P_3 interface where they eventually cause a physical separation. It appears, therefore, that unless vacancy accumulation can be prevented, one must avoid post-fabrication heat treatment of the otherwise thermally stable Au-Ga/Au_2P_3 contact system.

In our investigation of the thermal stability of the Au-In/Au_2P_3 contact system we concentrated on the 30 a% In alloy Au_9In_4 since it had proved to be non-reactive when deposited alone on InP. When we annealed Au_9In_4/Au_2P_3 contacted diodes in the 300 to 400 C range we found that the R_c values remained essentially unchanged.

In contrast to the Au_9In_4-only contacts, however, the Au_9In_4/Au_2P_3 contacts reacted metallurgically with InP. As seen in figure 9, at 400 C V_1 drops monotonically with time until after 4 hours the underlying pn junction has an I-V characteristic of a Schottky diode. All is apparently not lost for these contacts, however, since we found that if we lower the temperature 50 degrees to the 350 C range, the contacts show no sign of deterioration after 7 hours in the sintering furnace.

While the mechanisms involved are not clear at the present, the presence of the Au_2P_3 interlayer apparently promotes the metallurgical interaction of InP with both of these otherwise stable contact metallizations. Care must therefore be taken to see that post fabrication heat treatments are kept within the allowable limits.

SUMMARY

We have investigated the possibility of providing low as-fabricated resistance contacts to InP which are able to withstand extended thermal stress at elevated temperatures. Our major findings are as follows:

1) We have found that In additions to Au contact metallization result in as-fabricated contact resistivity values in the high 10^{-5} ohm cm^2 range.

2) If the amount of In added corresponds to that required to form Au_9In_4 (30 a%), then the contacts so formed are not affected by extended heat treatment at 400 C.

3) Although the Au/Au_2P_3 contact system provides as- fabricated contact resistivity values in the 10^{-6} ohm cm^2 range, the contacts are not stable when heated. The substitution of a refractory metal (W, Ta, Mo) for Au in this system preserves the low as-fabricated R_c values achieved with Au/Au_2P_3 while at the same time preventing the high temperature InP-metal interaction that would otherwise destroy a shallow junction device.

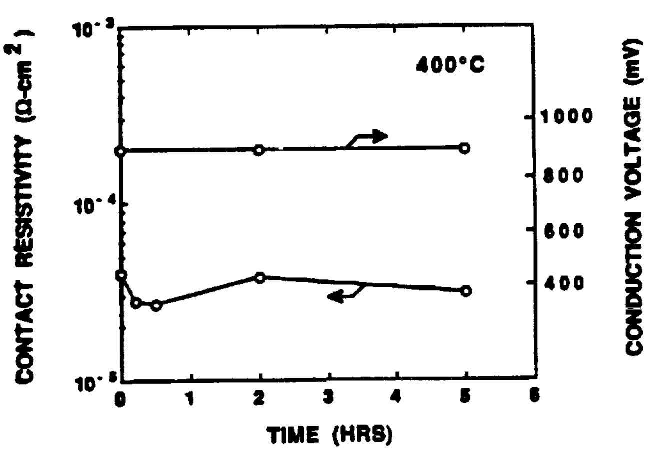

Figure 6. The variation of contact resistivity and conduction voltage with time at 400 C for Ta/Au_2P_3 contacts on InP.

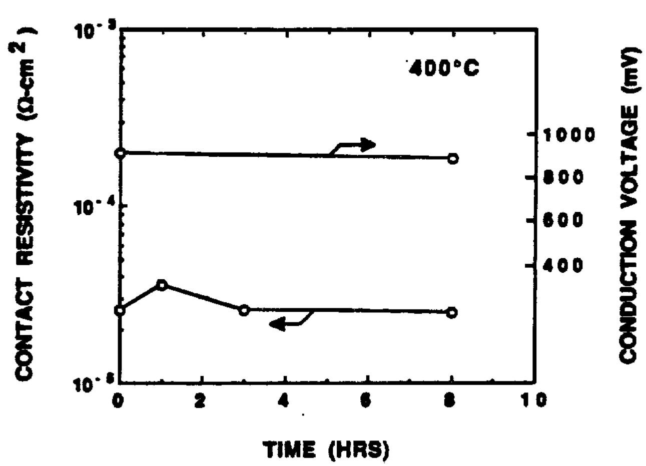

Figure 7. The variation of contact resistivity and conduction voltage with time at 400 C for W/Au_2P_3 contacts on InP.

4) The R_c reductions achieved by adding Ga or In to Au contacts and the reductions effected by introducing an Au_2P_3 interlayer are apparently additive. As-fabricated R_c values in the 10^{-7} ohm cm^2 range can be achieved by depositing either Au-9 a% Ga or a Au-In mixture over a thin Au_2P_3 interlayer.

5) Au_9In_4/Au_2P_3 contacts with R_c values in the high 10^{-7} to low 10^{-6} ohm cm^2 range, as-fabricated, withstand heat treatment at 350 C for at least 7 hours without degrading. Metallurgical interaction is observed during sintering at 400 C, however, which results in substantial damage to the underlying device.

6) While there is essentially no metallurgical interaction between InP and the Au-9 a% Ga/Au_2P_3 contact system during heat treatment at 400 C, vacancy accumulation at the $InP-Au_2P_3$ interface causes a physical separation of the Au_2P_3 interlayer from the InP with the result that the low as-fabricated values of R_c are quickly lost.

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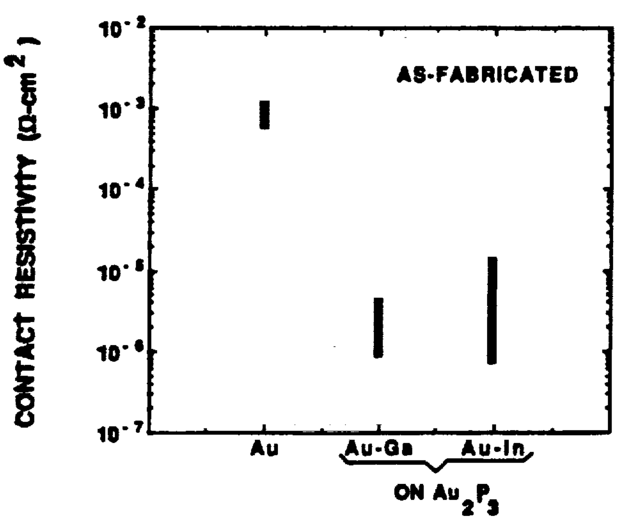

Figure 8. Measured as-fabricated contact resistivities for Au-only and for Au-9 a% Ga (4) and various Au-In mixtures (10) on Au_2P_3 interlayer. Parentheses indicate number of samples.

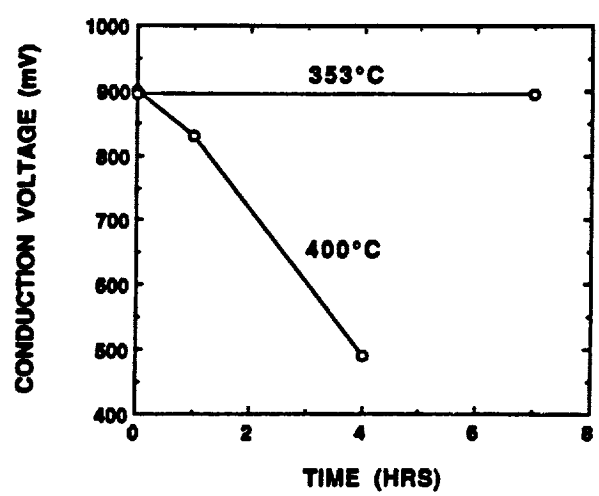

Figure 9. The variation of conduction voltage with time for Au_9In_4/Au_2P_3 contacts on InP.

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