

EFFECTS OF SOLAR CELL ENVIRONMENT ON CONTACT INTEGRITY

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The III-V semiconductors react extremely rapidly with most commonly used contact metallizations. This precludes the use of elevated temperatures in the contact formation process for solar cells and other shallow junction devices. These devices must rely upon contact metallizations that are sufficiently conductive in their "as-fabricated" state. However, while there are a number of non-sintered metallizations that have acceptable characteristics, the lack of a sintering step makes them vulnerable to a variety of environmentally induced degradation processes. This paper describes the degrading effects resulting from the exposure of unsintered devices to a humid environment and to a vacuum (space) environment. It is shown, further, that these effects are magnified by the presence of mechanical damage in the contact metallization. The means to avoid or prevent these degrading interactions are presented.

INTRODUCTION

It is generally accepted that in forming contacts on shallow junction III-V devices, processing at elevated temperatures should be avoided if at all possible. The benefits attendant to unsintered contacts are an undegraded emitter and a smooth and well defined contact topology. The main drawback to the use of as-fabricated contacts is a higher-than-optimum value of the specific contact resistivity ρ_c . A second disadvantage that is incurred if sintering is avoided is that the unsintered contacts are susceptible to several environmentally induced degradation processes.

Before discussing these, however, let us consider the range of as-fabricated contact resistivities that have been achieved for contacts to n-type InP. Fig. 1 shows the values we have found for various metal combinations on (100) oriented n-type InP, Si doped to $1.7 \times 10^{18} \text{ cm}^{-3}$. The resistivity measurements were made on unsintered devices using the transmission line method (TLM).

As can be seen, the lowest Rc values (in the high 10^{-6} ohm cm^2 range) were found for Au contacts in which a thin (20 Å) layer of Au_2P_3 had been introduced at the InP-Au interface (ref.1). Unfortunately these and other unsintered Au-based contacts are subject to several environmentally induced degradation mechanisms. The first involves a significant increase in the metal-semiconductor interaction rate when the contacts are exposed to a vacuum (space) environment. This phenomenon is common to all Au-contacted III-V semiconductors in which the metal-semiconductor reaction rate is controlled by the vacancy generation rate at the free surface of the contact metallization. Both InP and GaAs are included in this group.

The second degradation process that we will discuss concerns the reaction of ambient humidity with the contact metallization and, ultimately, with the semiconductor substrate. Although both InP and GaAs are affected by this process, there is a fundamental difference between the reactions in these two systems. Let us first discuss the effects of a vacuum environment and then consider the effects of ambient humidity.

VACUUM INDUCED DEGRADATION

A vacuum environment greatly increases the sensitivity of Au-based contacts on both InP and GaAs to thermal excursions. Fig. 2, for example, shows the difference in the degree of pitting in the GaAs surface for two Au-contacted GaAs samples after being heated to 300°C for 8 minutes, one in vacuum and one in a nitrogen ambient. While there is only a hint of activity on the sample annealed in nitrogen, the vacuum-annealed sample is severely pitted. It is estimated that the metal-semiconductor reaction rate was increased between three and four orders of magnitude by performing the heat treatment in a vacuum environment rather than in a gaseous ambient.

The mechanism believed to be responsible for the enhanced reaction rate is based on the fact that, in the early stages of these metal-semiconductor interactions, the group III element (i.e., Ga or In) leaves the semiconductor and enters the Au contact metallization interstitially (ref. 2,3). These interstitial metal atoms then diffuse through the metal until encountering vacant lattice sites on the metal lattice, at which point they enter the vacant sites and take substitutional sites on the metal lattice. The vacancies needed for this reaction are generated at the free surface of the metallization, and it has been shown that both the Au-GaAs and the Au-InP interaction rates are controlled by the rate at which these vacancies are generated (ref. 2,3).

It should be recalled, furthermore, that the generation of a vacancy at the surface of the metallization requires the removal of a near-surface atom from the metallization (thus creating a vacancy) and the placement of that atom on the metal surface. It has been postulated that the continuous kinetic impact of ambient gas molecules on the Au surface inhibits the rate of thermal ejection of these near-surface Au atoms out of the lattice to high energy sites on the surface (vacancy generation) (ref. 2). In this way the vacancy generation rate is enhanced when the impinging ambient gas atoms are removed by placing the sample in a vacuum. The greater the vacancy generation rate, the greater the rate of In (and P) entry into the metallization, and the greater the rate of emitter dissolution/ degradation.

While the metal-semiconductor interaction rate increases significantly when heat treatment takes place in a vacuum environment, the situation is made even worse if, in addition, the free surface of the Au metallization is mechanically disordered. Fig. 3, for instance, shows the drastic increase in GaAs surface pitting that occurred beneath several small scratches that had been made in the Au surface prior to heat treatment (in vacuum) at 300°C for several minutes. Since regions of lattice disorder would be expected to be regions of enhanced vacancy generation, the increased reaction rate is without doubt due to an increase in the vacancy supply in the scratched regions.

It is estimated that if the Au surface contains mechanical damage, thermal excursions (in vacuum) of a few seconds at 300°C or a few tens of minutes at 200°C would seriously degrade devices with junction depths of 0.2 μm or less. Both GaAs and InP would be equally affected.

HUMIDITY INDUCED DEGRADATION

A humid ambient atmosphere also has a detrimental effect on unsintered Au-based contacts on both InP and GaAs (ref. 4,5). After aging for a matter of months in a humid environment, islands have been observed to grow on the metal surfaces of Au contacted InP and GaAs. Figures 4 and 5 are micrographs of the growths observed on Au contacted InP and GaAs, respectively, after prolonged room temperature aging. In both cases the volume of the growths has been shown to be a direct function of the aging time and the humidity level of the ambient atmosphere.

In both cases the islands have a liquid-like consistency as the result of water accumulation by deliquescent compounds that form on the metal surface. It has been determined that the compound that forms on the Au/InP

surface is an indium (group III) based compound, $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (ref. 5). In the case of the Au-GaAs system, on the other hand, the growths have been identified as the group V related compound As_2O_3 (ref. 4). This difference is very important when one considers the potential harm that these phenomena might cause. Let us first discuss the Au-InP system.

The Au-InP System.

As mentioned, the islands on Au/InP have an as-grown liquid-like consistency (Fig. 4). When put in a vacuum, however, as is done for observation in the scanning electron microscope, they become desiccated and revert to the solid $\text{In}(\text{NO}_3)_3$ (Fig. 6). The process by which this compound forms can be understood by considering the details of the Au-InP interaction.

As has been mentioned, the room temperature reaction of Au with InP consists of the entry of both In and P into the contacting metallization. The In atoms enter the Au lattice as interstitials and diffuse rapidly until encountering vacant sites in the Au lattice, at which point they enter the vacant sites and take substitutional positions in the Au lattice. Since the vacant lattice sites are generated only at the free surface of the metallization, the probability of the vacancy-interstitial encounter is greatest there. The resulting In concentration profile therefore reaches a maximum at the free surface of the contact metallization (ref. 3).

Because of this profile, a large number of In atoms are in a position to react with atmospheric oxygen and nitrogen to form the nitrate at the metal-ambient interface. Once formed, the nitrate, because of its deliquescent nature, attracts and adsorbs large quantities of atmospheric water. The water then removes the nitrate from the metal surface by taking it into solution. The action of the water is thus to clear the metal surface so that the process can be repeated over and over again. The entire process is envisioned to continue as long as O_2 , N_2 , and water vapor are available to the Au surface, leading to extensive decomposition of the semiconductor substrate. Fig. 7 illustrates the pitting observed in the surface of an InP sample (Au removed) after eight months at room temperature under normal humidity conditions.

If the above considerations are correct, the rate at which the islands grow should depend on the rate at which In is transported from the InP substrate to the metal-ambient interface, which, in turn, should be dependent on the vacancy generation rate at that interface. We should thus expect to see an enhancement in the rate of nitrate formation if the vacancy generation rate at the Au surface is increased. Evidence that the island growth rate is sensitive to the vacancy generation rate is given in Fig. 8. The free surface of the Au contact metal on the sample shown in the figure had been mechanically damaged (scratched) prior to room temperature aging (increasing the vacancy generation rate in those regions). As can be seen, after several months at room temperature, island growth on the scratched Au surface is substantially greater than on the undamaged portion of the Au surface. Thus both the vacuum induced degradation process and the humidity induced degradation process are affected by the condition of the free surface of the contact metallization.

The Au-GaAs System.

Similar appearing islands have been observed to grow on aged Au-contacted GaAs (Fig. 5). Although the growths appear to be quite similar to those observed in the Au-InP system, even to the extent that they are deliquescent, they are fundamentally different. Compositional analysis indicates that, rather than containing the group III element (Ga), the islands are composed of the group V compound As_2O_3 (ref. 4). The major difference between this system and the Au-InP system, therefore, is that the present reaction does not result in the removal of the group III element from the metallization. Because of this, island growth in the Au-GaAs system should be self limiting. This follows from the fact that in both the Au-InP system and in the Au-GaAs system, the entry of the group III element into the Au contact metallization always precedes the entry of the group V element (ref. 2,3). When

group III atoms stop entering the metallization, the entire reaction stops. In both the Au-InP system and the Au-GaAs system the group III elements diffuse into the metallization until solid solubility limits are reached. At this point the Au lattice can hold no more group III atoms and the reaction stops. In both cases the group V atoms entering with the group III atoms slowly leave the system without reacting (ref. 2,3).

During the humidity induced island growth in the Au-InP system, In atoms are removed from the Au lattice, permitting the entry of additional In atoms from the InP substrate. During island growth in the Au-GaAs system, on the other hand, group V, not group III, atoms are removed from the Au. Since the Au lattice remains saturated with group III atoms, no further dissolution of the GaAs substrate takes place. The only group V atoms that are available to take part in island formation are those liberated before the Au becomes saturated with group III atoms. Thus, in contrast with the Au-InP system, island growth in the Au-GaAs system stops when the Ga content in the Au lattice reaches its solid solubility limit.

ENVIRONMENTALLY STABLE CONTACTS

Vacuum Induced Degradation.

According to the preceding analysis the vacuum induced degradation process operates by enhancing the vacancy generation rate at the free surface of the contact metallization. The metal-semiconductor systems that are susceptible to this type of degradation are those in which the metal-semiconductor interdiffusion rate is controlled by the vacancy generation rate at that surface. If it were possible to alter these systems in such away as to eliminate their vacancy generation rate dependency, the degradation problem would vanish. It appears that this should be possible without too much trouble in both the Au-InP and the Au-GaAs systems.

Studies of both of these systems have shown that the metal-semiconductor interaction rates are vacancy generation rate dependent only if the group III concentrations in the Au contact metallization are less than the solid solubility limits (ref. 2,3). It follows, therefore, that by adding sufficient Ga or In to the Au contact metallization in the Au-GaAs and the Au-InP systems, respectively, to raise the concentrations to their respective limits, the systems will no longer be vacancy generation rate dependent and vacuum degradation will no longer be a problem.

Humidity Induced Degradation.

As we have shown, the humidity problem fortunately only has severe effects on the Au-InP system. It causes a continual flow of In atoms from the InP, through the metallization, to the surface of the metallization where they chemically combine with species in the ambient. The obvious preventative approach would be to stop In entry into the metallization. The use of a saturated solid solution of In in Au (as we did to prevent vacuum degradation) would be effective in preventing more In from entering the Au if it were not for the fact that the In level would continually be lowered below the saturation level as In is leached out by the growing nitrate islands.

Another approach that does hold promise involves the addition of Ga to the Au metallization in amounts that exceed the solubility limit for Ga in Au (~1 at% at 20°C). It has been shown that when Ga is added, a portion of the Ga enters and saturates the interstices of the Au lattice so that no other interstitial species can enter (ref. 1). The addition of Ga, therefore, would prevent In entry into the Au lattice and thus prevent the destructive growth of indium nitrate islands on the surface of the contact metallization. Fig.9 shows a comparison of Auger electron spectroscopy (AES) depth profiles of Au-only and Au-1%Ga on InP heat treated for 40 minutes at 355°C. As shown, even at elevated temperatures, the presence of 1 at% Ga in Au completely suppresses the In out-diffusion from the InP substrate to the Au surface.

Resistivity Improvements.

In the preceding we have suggested ways of eliminating both the vacuum- and the humidity-induced degradation phenomena by adding various amounts of In or Ga to the Au contact metallization. In addition to preventing device degradation, we have found that these additions actually lower the unsintered contact resistivity values. Figures 10 and 11, for example, show the reductions in Au-only and Au-on-Au₂P₃ contact resistivities that are obtained with the addition of various amounts of In or Ga to the Au metallization. As can be seen, order of magnitude reductions are effected.

It is suggested that the cause of the observed resistivity reductions is a change in the In-to-P ratio at the metal-semiconductor interface. When In and P leave the InP and enter the Au metallization, the In atoms rapidly diffuse (interstitially) away from the InP-metal interface. The P atoms, on the other hand, dissipate much more slowly. The result is an interface that is relatively phosphorus rich. There is ample evidence in the literature correlating a P-rich interface with elevated contact resistivity. When In or Ga are added, their main effect is to slow down the rate of In entry, giving the newly entering P atoms time to dissipate. The result is an increase in the In-to-P ratio and thus a reduction in the contact resistivity.

SUMMARY

The major conclusions that can be drawn from the preceding analysis can be summarized as follows:

1. As-fabricated contacts to III-V semiconductors are susceptible to several environmentally induced degradation processes. The degradation is caused by an increase in the metal-semiconductor reaction rate when the cells are placed in a vacuum (space) or humid environment.
2. The increased rate of metal-semiconductor interactions in a humid ambient is self-limiting for contacts to GaAs. In contrast, this reaction rate is not self-limiting, and therefore catastrophic, for contacts to InP.
3. This metal-semiconductor reaction rate is further increased if the surface of the metallization is mechanically damaged.
4. The introduction of small amounts of Ga or In (1-10 at%) into the Au metallization stops the metal-semiconductor interactions, even if the cell is placed in a vacuum or a humid environment or the surface of the metallization is mechanically damaged.
5. Furthermore, The addition of Ga or In to Au effects an order of magnitude reduction in the metal-InP contact resistance.

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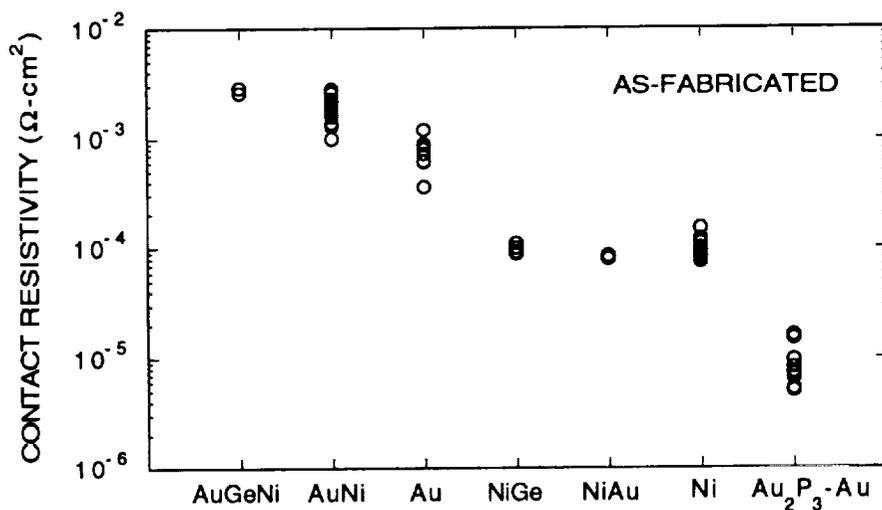


Fig. 1 As-fabricated contact resistivities for various contact systems.

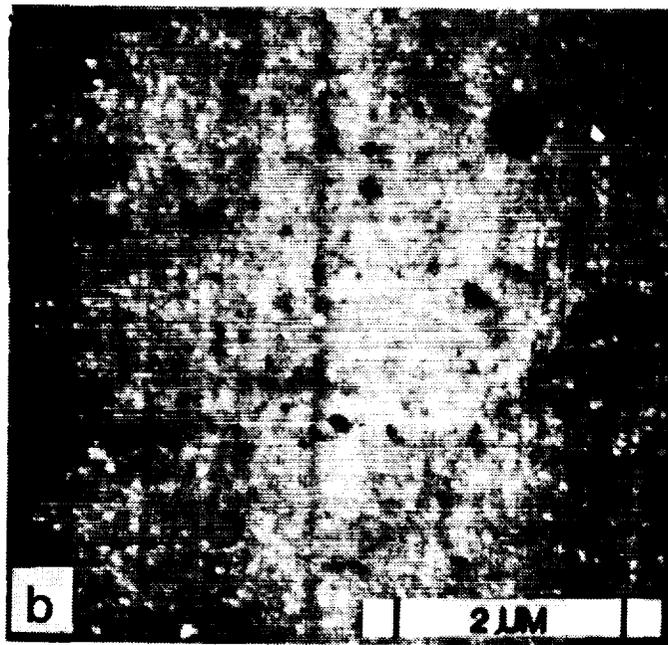
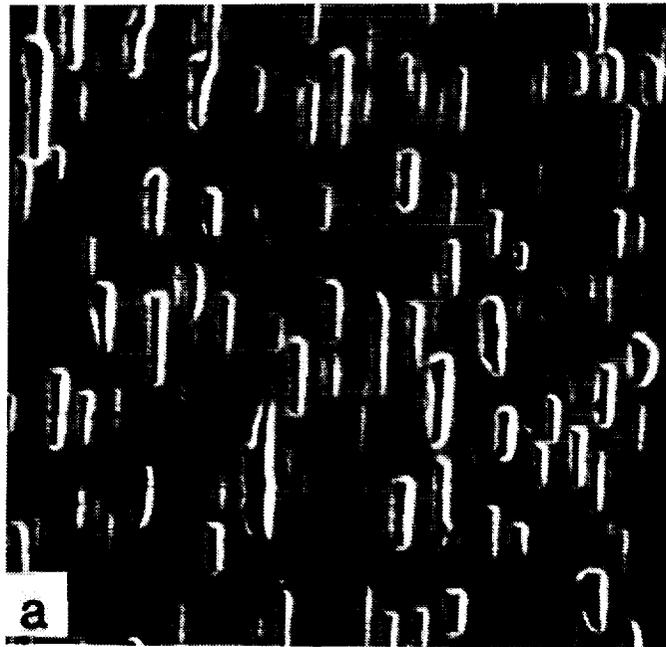


Fig. 2 GaAs surface pitting (Au metallization removed) after 8 min., 300°C heat treatment: (a) in vacuum, (b) in nitrogen.

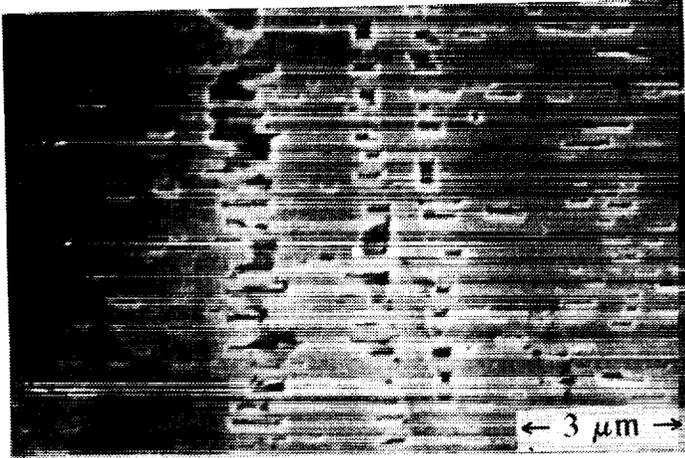


Fig. 3 GaAs surface pitting under three scratches made on Au surface prior to heat treatment at 300°C (8 min.) in vacuum.

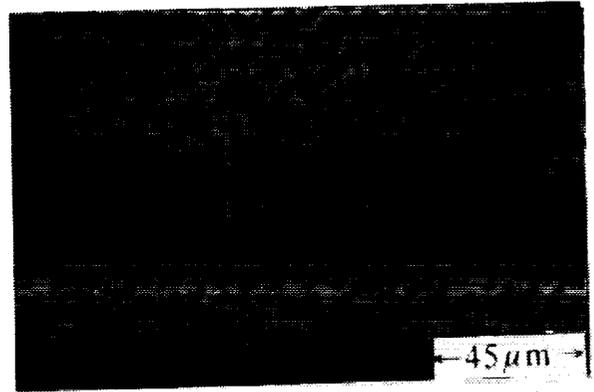


Fig. 4 Light micrograph of growths on Au surface on InP aged at room temperature for 12 mo.

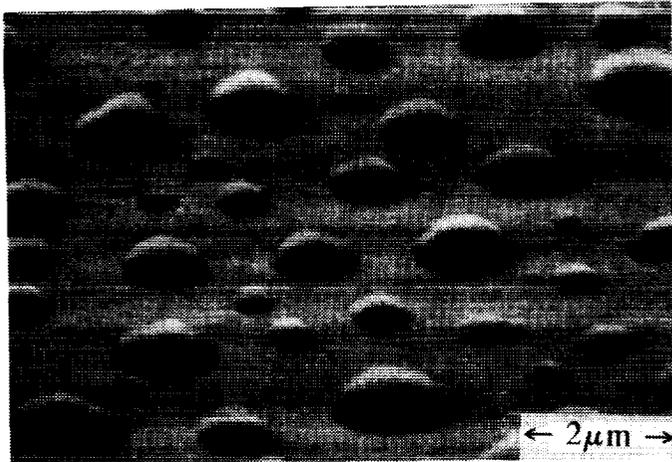


Fig. 5 SEM micrograph of growths on Au surface on GaAs aged at room temperature for 2 yrs.

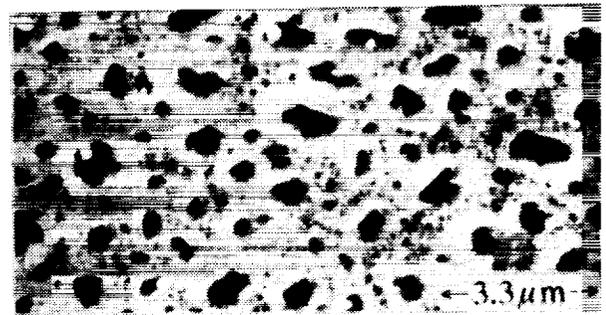
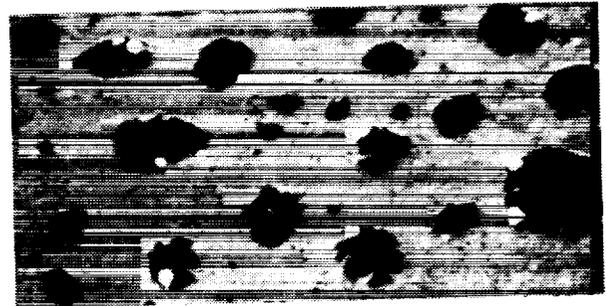


Fig. 6 SEM micrograph of growths on Au surface. Lower: aged for 4 months in ambient humidity. Upper: aged as in lower plus 22 hrs. at 100% humidity.

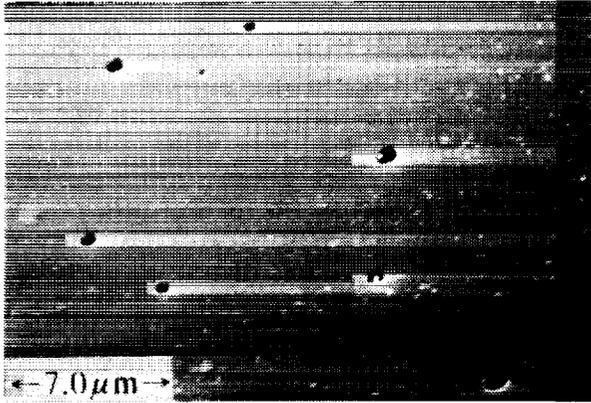


Fig. 7 Pitting in InP surface (Au removed) after aging for 4 months at room temperature in ambient humidity.



Fig. 8 Effect of mechanically damaged (scratched) Au surface on InP on the rate of island growth.

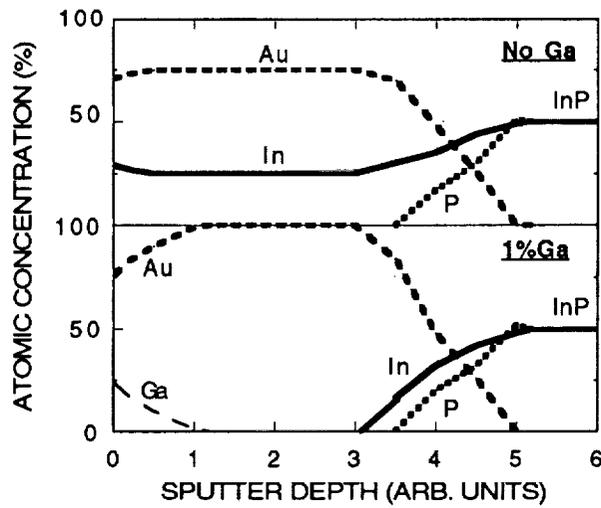


Fig. 9 XPS concentration depth profiles for Au-only (upper) and Au-1 at% Ga (lower) contacts on InP heat treated at 355°C for 40 min.

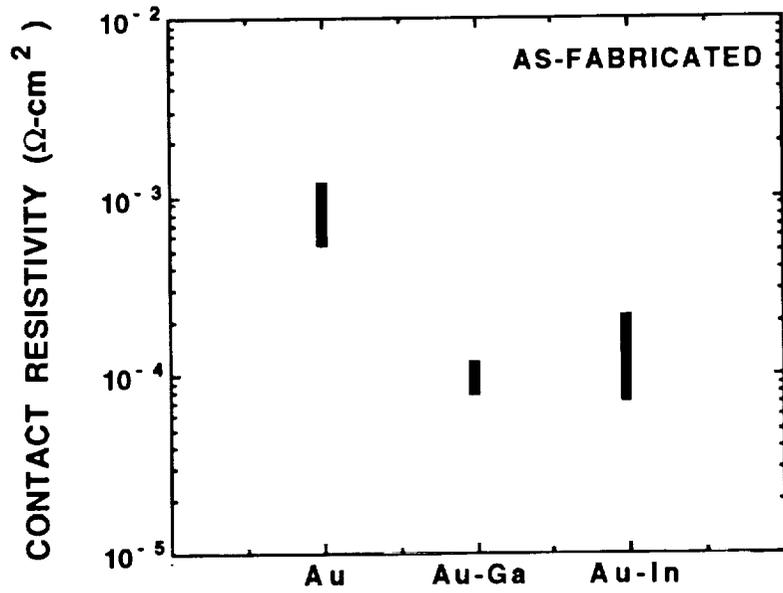


Fig. 10 Measured as-fabricated range of contact resistivities for Au-only, Au-Ga, and Au-In contacts on n-InP.

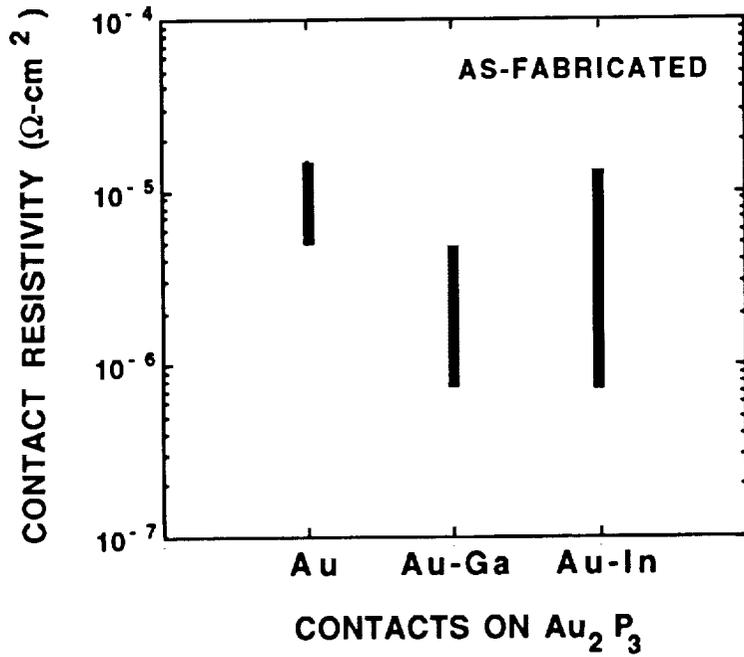


Fig. 11 Measured as-fabricated range of contact resistivities for Au, Au-Ga, and Au-In on Au₂P₃ on n-InP.