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Au/Zn CONTACTS TO *p*-InP: ELECTRICAL AND METALLURGICAL CHARACTERISTICS AND THE RELATIONSHIP BETWEEN THEM

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ABSTRACT

The metallurgical and electrical behavior of Au/Zn contacting metallization on *p*-type InP was investigated as a function of the Zn content in the metallization. It was found that ohmic behavior can be achieved with Zn concentrations as small as 0.05 atomic percent Zn. For Zn concentrations between 0.1 and 36 at.%, the contact resistivity ρ_c was found to be independent of the Zn content. For low Zn concentrations the realization of ohmic behavior was found to require the growth of the compound Au_2P_3 at the metal-InP interface. The magnitude of ρ_c is shown to be very sensitive to the growth rate of the interfacial Au_2P_3 layer. The possibility of exploiting this sensitivity to provide low resistance contacts while avoiding the semiconductor structural damage that is normally attendant to contact formation is discussed.

INTRODUCTION

The difficulty in making low resistance electrical contact to *p*-type InP is well known. In spite of years of effort, there is still a three order of magnitude disparity between minimum values of ρ_c that have been achieved for *n*- and *p*-type InP. While ρ_c values in the low E-8 $\Omega\text{-cm}^2$ range have been achieved with *n*-InP[1], the best reported values for *p*-InP are in the low E-5 $\Omega\text{-cm}^2$ range.[2-6]

Another difficulty encountered with *p*-InP is that all known contacting systems require sintering at elevated temperatures to achieve ohmic characteristics. There are no reports of any as-deposited low resistance contacts. It is difficult, therefore, to avoid structural damage to the semiconductor during the contacting process. These troubles are compounded by a lack of understanding of the mechanisms underlying the metallurgical and electrical behavior of these contact systems. Until these mechanisms are known, there are no obvious ways to eliminate or circumvent the device-degrading metal-InP metallurgical interactions that take place during sintering.

A search of the literature indicates that the only successful contacts to *p*-InP are Au-based systems. The most widely used contact system, and the system that has provided the lowest values of ρ_c, is the Au-Zn/InP system.[2-8] The purpose of this work is to determine the mechanisms responsible for the low ρ_c values observed in the Au-Zn/InP contact system, with the ultimate goal of using this knowledge to lower ρ_c, and to do so without damaging the semiconductor device under the contacts. While the precise role of Zn still eludes us, we have been able to show that, to achieve low contact resistance, 1) only minute amounts of Zn are necessary, 2) the interfacial compound Au_2P_3 must also be present, and 3) the formation rate of the interfacial Au_2P_3 is critical in determining ρ_c.

EXPERIMENT

The transmission line method (TLM), unless otherwise stated, was used throughout this work to measure ρ_c. The details of the technique are described elsewhere.[1] To provide verification of the validity of the TLM measurements, selected samples were remeasured using the Cox &

Strack measurement technique. No differences were observed. The structures used for the TLM measurements were epitaxially deposited p^+ or n^+ layers on semi-insulating substrates. The p^+ layers were 6000Å thick, Zn doped to 2E18 cm^{-3}. The n^+ layers were 3000Å thick, Si doped to 2E18 cm^{-3}. Bulk p^+ samples, Zn doped to 3E18 cm^{-3}, and bulk n-type samples, Cd doped to 5E17 cm^{-3} were also used as noted in the text.

Deposition of the contact metallization was done by electron beam evaporation. The evaporation sequence used throughout was InP/200Å Au/XÅ Zn/1800Å Au, where the thickness X of the Zn layer was varied to provide the desired Zn concentration. Post deposition sintering was performed in a rapid thermal processing (RTP) apparatus that provided rise times of about 10 seconds with negligible overshoot. The ambient during sintering was N_2.

Compositional analysis was performed via energy dispersive spectroscopy (EDS). EDS analysis was facilitated by the use of a thiourea-based chemical etchant[9,10] that permitted direct access to subsurface detail.

RESULTS

The Au-Zn Contact System

The most thoroughly investigated contact system to *p*-InP is the Au-Zn system. According to the literature, the lowest values of ρ_c (in the E-5 Ω-cm^2 range) have been achieved with Au-Zn mixtures containing from 20 to 50 atomic percent Zn.[2-6] Higher, but equally impressive values (when one takes into account the N_d^{-1} variation of ρ_c with substrate doping N_d), are the E-3 Ω-cm^2 values obtained with Au-10 at.% Zn contacts on 3E16 cm^{-3} doped substrates.[7,8] Several investigators have reported using lower amounts of Zn, but the results have been inferior to those obtained with higher Zn content.[6,11]

In an attempt to determine the percentage of Zn required to optimize the electrical characteristics of this contact system, we contacted a large number of samples with Au containing various amounts of Zn. These samples were then sintered at various temperatures to determine their minimum ρ_c values. The Zn contents in these samples ranged from 36 at.% to 0.05 at.%.

The results of this study are shown in Fig. 1 where it can be seen that ohmic behavior can be achieved with the addition of as little as 0.05 at.% Zn. It should be noted that this is accomplished by incorporating a layer of Zn only 1Å thick in a 2000Å thick layer of Au.

Above about 0.1 at.% Zn, the minimum ρ_c values appear to be independent of Zn content. The optimum sintering conditions for all but the 36 at.% Zn samples were 1 min. at 400°C. We found that the 36% samples required RTP at 490°C for about 15 sec. to achieve minimum ρ_c values.

Since the achievement of low resistance ohmic behavior with such small Zn additions has not been observed before, we will, in what follows, describe the results of our investigation into the electrical and metallurgical characteristics of low Zn content contacts, concentrating on the Au-1 at.% Zn contact system.

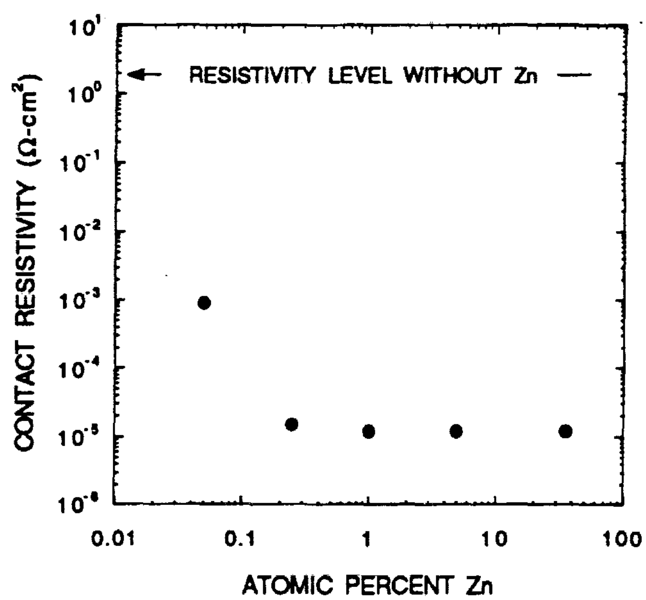

Fig. 1 Minimum ρ_c values for Au-Zn contacts containing various amounts of Zn.

Au-1 at.% Zn Contacts

When high Zn content Au-Zn contacts are sintered, numerous Zn, In, Au, and P containing compounds are formed.[2] When we performed an EDS analysis on sintered Au-1 at.% Zn contacts, however, we found a behavior that is quite similar to that of Au-only contacts. As in the Au-InP system[9], we have found that heat treatment of Au-1 at.% Zn contacts in the 300-to-400°C range results in the formation of Au_2P_3 at the metal-InP interface and Au_3In at the free surface of the metallization.

Fig. 2 shows the growth of the Au_3In layer with time at the sintering temperature of 350°C. Also shown in the figure is the progress of the same phase transition for Au-only/InP system. As can be seen, the addition of Zn slows the Au-to-Au_3In phase transition. The two samples also differ in their curve shapes. In contrast to the linear nature of the Au-only data, the Zn-containing sample exhibits a distinctly sigmoid character.

Fig. 3 shows the variation in ρ_c during the Au-to-Au_3In transition for both the Au-only and the Au-Zn contacts. As can be seen, the addition of only 1 at.% Zn results in a four order of magnitude drop in ρ_c. Once the Au-to-Au_3In transition is complete, ρ_c does not respond to further heat treatment. It thus appears that the changes induced by this transition are critical to the achievement of low contact resistance.

The presence of Zn, of course, is also necessary. As illustrated in the figure, Au-only contacts remain non-ohmic (on p-type InP) throughout the entire Au-to-Au_3In transition.

As mentioned above, we have found that the growth of Au_3In is accompanied by the growth of Au_2P_3 at the metal-InP interface. To investigate the relationship between the growth of Au_3In and the growth of Au_2P_3 underlayer, we used a thiourea-based chemical etchant[9,10] to remove the Au_3In layers from a group of samples that had been sintered to various stages of completion in the Au-to-Au_3In transition. Because this etchant does not remove the Au_2P_3 underlayer, we were able to observe its growth relative to that of the Au_3In surface layer.

The results indicate that there is a close correlation between the growth of the two layers. Thus the observed reduction in ρ_c is correlated not only with the growth of the Au_3In surface layer, but also with the growth of the interfacial Au_2P_3 layer. The importance of the Au_2P_3-InP interface is illustrated by the fact that when the resistance measuring probes are placed directly on the Au_2P_3 layer (after the Au_3In layer has been etched off), the resulting ρ_c values (Cox & Strack technique used here) are very close to those measured before etching.[12]

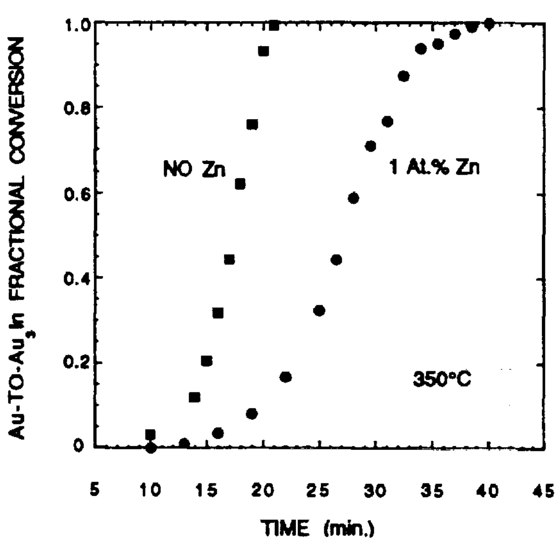

Fig. 2 The progress of Au-to-Au_3In transition as a function of time at 350°C.

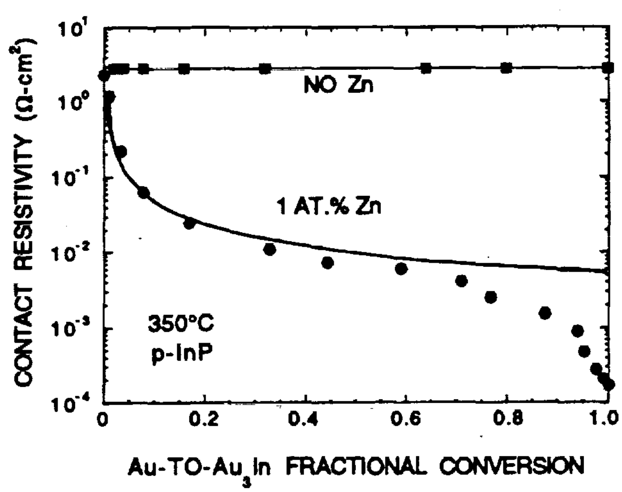

Fig. 3 The variation of ρ_c with Au-to-Au_3In fractional conversion: *p*-InP at 350°C.

Au-1 at.% Zn on n-InP

For comparison purposes we also deposited Au-1 at.% Zn contacts on several n-type InP substrates. The variation of ρ_c during sintering at 350°C is shown in Fig. 4. As can be seen, the contacts are ohmic as-fabricated, but become non-ohmic as the Au-to-Au_3In transition proceeds. Heat treatment beyond the completion of the Au-to-Au_3In transition does not cause a significant change in ρ_c. Thus, in this case also, changes in ρ_c are correlated with the formation of Au_3In/Au_2P_3 in the contact metallization.

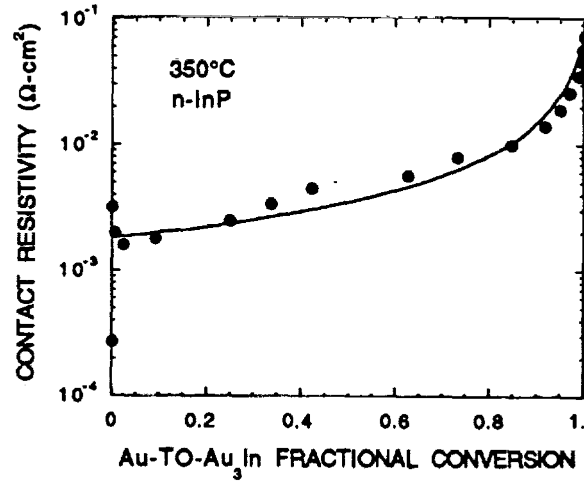

Fig. 4 The variation of ρ_c with Au-to-Au_3In fractional conversion: n-InP at 350°C.

DISCUSSION

Areal Dependence

The progress of the Au-to-Au_3In phase transition (Fig. 2) can be monitored during the contact sintering process by following the nucleation and growth of pink-colored Au_3In islands in the gold-colored Au matrix.[13] As the sintering process proceeds, the Au_3In islands can be seen to nucleate, grow, and finally merge together as the transition nears completion.

It should be noted that the data in Fig. 3 were generated with the implied assumption that the total area of the electrical contact remains constant through the phase transition. However, if the actual (ohmic) contact area is that between the Au_2P_3 islands and the InP, then the contact area is continuously changing during the transition and the ρ_c values in Fig. 3 are only apparent values.

If one assumes that ρ_c in fact remains constant but the effective area changes as the Au_2P_3 islands grow during transition, then one would expect an apparent change in ρ_c (solid curve in Fig.3) that is inversely proportional to the Au_2P_3 areal coverage. As can be seen, the data in Fig. 3 can be quantitatively accounted for by the increase in the size of the Au_2P_3 islands, at least until about 70% conversion.

The data in Fig. 4 for Au-Zn contacts on n-InP can be accounted for in a similar manner. In this case, however, a relatively low resistance interface is being slowly replaced with a higher resistance interface. The equivalent circuit for this situation is comprised of two parallel resistances with apparent resistivities dependent on their relative fractional areas. The apparent resistivity R of this pair is thus:

$$R = R_1\,[(R_1 A/R_2)+1-A]^{-1}$$

where R_1 is the initial (low) resistivity, R_2 is the final (high) resistivity, and A is the fractional high resistivity area. As shown in Fig. 4 (solid curve), this simple areal dependence closely describes the data over the entire transition. The apparent value of ρ_c is seen to increase in direct response to the amount of Au_3In/Au_2P_3 present.

Reaction Rate Dependence

As seen in Fig. 3, when the Au-to-Au_3In transition reaches about 70% completion, the contact resistivity begins to decline much more rapidly than would be expected from areal considerations. An insight into what is happening may be gained by considering the time dependence of the transition (Fig. 2). As can be seen, the transition starts out slowly. The

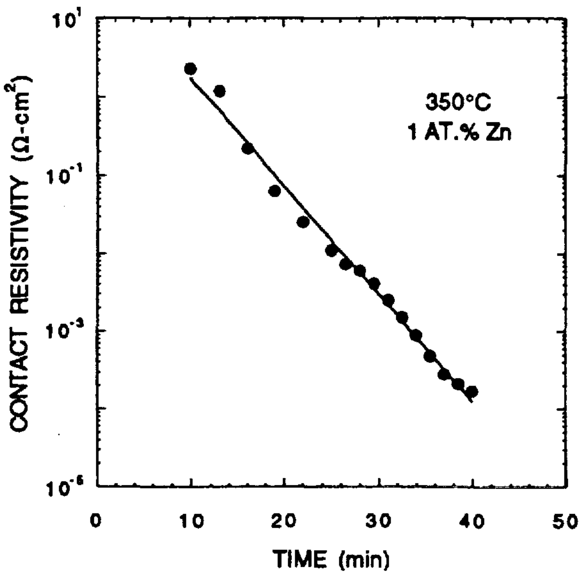

Fig. 5 The variation of ρ_c with time

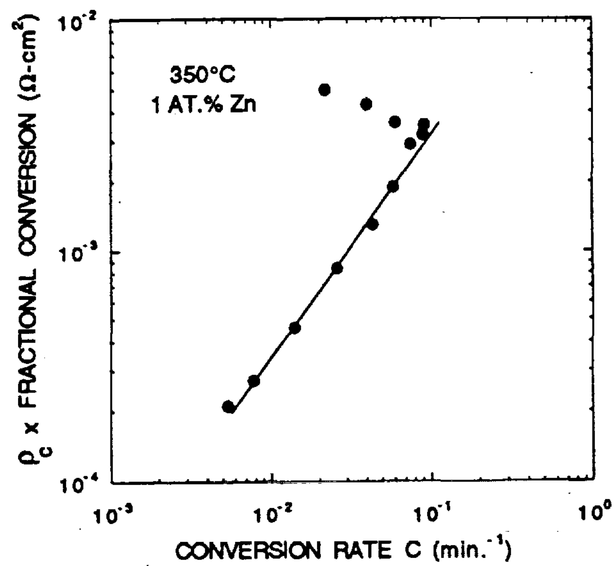

Fig. 6 Variation of ρ_c (area-corrected) as a function of the Au-to-Au_3In phase transition rate.

conversion rate then increases until the Au_3In islands begin to merge, after which the rate decreases significantly, especially for the final 20% of the transition.

The large decrease in ρ_c during the final stages of the transition takes place concurrently with this decrease in the transition rate. As the conversion rate drops, the contact resistivity decreases accordingly. The correlation between the two processes can be illustrated by plotting the logarithm of ρ_c versus time. The resulting curve, shown in Fig. 5, can be seen to be linear over four orders of magnitude. The decrease in the conversion rate exactly compensates for the rate of decrease of ρ_c so as to yield the same slope seen in the early (well-behaved) stages of conversion.

The relationship between the conversion rate and the resistivity can be extracted from the data in figures 2 and 3. As shown in Fig. 6, a log-log plot of the Au-to-Au_3In conversion rate (from Fig. 2) versus the resistivity (from Fig. 3 after correcting for actual area) indicates that the resistivity is independent of the conversion rate until the transition has reached about 60% completion. During the final 40% of the phase transition, however, the resistivity is directly proportional to the conversion rate. The contact resistance is thus very sensitive to the rate at which the Au-to-Au_3In phase transition takes place.

The Role of Zn

Since the contact resistivity is apparently controlled by conditions at the Au_2P_3-InP interface, and since Zn is obviously involved, we examined the Au_2P_3 layer and the Au_2P_3-InP interface for evidence of the presence of Zn. Using EDS, we looked for Zn in both the Au_3In surface layer and, after removing the Au_3In chemically, in the Au_2P_3 underlayer. In the latter case the EDS penetration depth was such that it sampled both the Au_2P_3 layer and the near-surface InP substrate below it. In no case did we observe a Zn signal.

Suspecting that the Zn concentration in the Au-1 at.% Zn metallization may be below the EDS detection limit, we performed a similar analysis on samples where the metallization contained 5 at.% Zn. In this case we found substantial amounts of Zn in the Au_3In surface layer, but only a trace in (or under) the Au_2P_3 interfacial layer. At the time of this writing we have not yet calibrated the EDS measurements with a Zn-bearing standard, so that it is not clear how much Zn is actually present. Also since the Au_2P_3 layer has a lacy or porous structure, it is uncertain whether the trace Zn signal we observed was due to the residual $Au_3In(Zn)$ embedded in the Au_2P_3 structure.

At this time, therefore, we are not sure of the location or the chemical state of the Zn, nor do we know how such small amounts could bring about such large changes in the electrical characteristics.

However, even though the role of Zn is uncertain, the above analysis indicates that it may be possible to reduce or eliminate the structural damage to the semiconductor that is attendant to contact formation. The observation (Fig. 6) that the interfacial resistance between Au_2P_3 and InP is an order of magnitude lower when the Au-to-Au_3In conversion rate is reduced from 10%/min. to 1%/min., suggests that if a similar reduction in the conversion rate could be effected early in the phase transition, a low contact resistance could be achieved without requiring the phase transition to go to completion. This would eliminate much of the destructive interdiffusion that accompanies it. We are currently looking into this possibility.

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13. ABSTRACT *(Maximum 200 words)*

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