The Achievement of Low Contact Resistance to Indium Phosphide: The Roles of Ni, Au, Ge, and Combinations Thereof

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THE ACHIEVEMENT OF LOW CONTACT RESISTANCE TO INDIUM PHOSPHIDE:  
THE ROLES OF Ni, Au, Ge, AND COMBINATIONS THEREOF  

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ABSTRACT

We have investigated the electrical and metallurgical behavior of Ni, Au-Ni, and Au-Ge-Ni contacts on n-InP. We have found that very low values of contact resistivity ($\rho_c$) in the E-7 $\Omega$-cm$^2$ range are obtained with Ni-only contacts. We show that the addition of Au to Ni contact metallization effects an additional order of magnitude reduction in $\rho_c$. Ultra-low contact resistivities in the E-8 $\Omega$-cm$^2$ range are obtained with both the Au-Ni and the Au-Ge-Ni systems, effectively eliminating the need for the presence of Ge in the Au-Ge-Ni system. The formation of various nickel phosphides at the metal-InP interface is shown to be responsible for the observed $\rho_c$ values in the Ni and the Au-Ni systems. We show, finally, that the order in which the constituents of Au-Ni and Au-Ge-Ni contacts are deposited has a significant bearing on the composition of the reaction products formed at the metal-InP interface and therefore on the contact resistivity at that interface.

INTRODUCTION

Historically, the most widely used and researched contact system on n-type III-V semiconductors has been the Au-Ge-Ni system. This is mainly due to the very low values of specific contact resistivity ($\rho_c$) achieved with this system. Au-Ge-Ni contacts on InP have been shown to exhibit $\rho_c$ values in the low E-7 $\Omega$-cm$^2$ range [1, 2]. However, few investigations have been concerned with the roles played by the individual constituents or combinations thereof.

Although it has been firmly established that Ge in the Au-Ge-Ni system plays a crucial role in lowering $\rho_c$ to very low values on GaAs [3, 4], we have found that its presence is not necessary to achieve very low $\rho_c$ values on InP. Our investigations of Ni, Au, Au-Ni, and Au-Ge-Ni contact systems on InP have resulted in several findings. First, while heat treated Ni-only and Au-only contacts exhibit $\rho_c$ values in the low E-7 $\Omega$-cm$^2$ range and in the low E-6 $\Omega$-cm$^2$ range, respectively, combining the two in the Au-Ni system produces $\rho_c$ values in the E-8 $\Omega$-cm$^2$ range. Second, these ultra-low $\rho_c$ values observed with the Au-Ni system are also obtained with the Au-Ge-Ni system, indicating that Ge is not an essential component. Finally, for both Au-Ni and Au-Ge-Ni contacts the order in which individual metal layers are deposited determines the resulting $\rho_c$ value.

Different deposition orders result in contact resistivities that vary by several orders of magnitude. Our previous studies of Au and Ag contacts on InP have shown that the formation of Au$_2$P$_3$ and AgP$_2$, respectively, at the metal-InP interface is responsible for the low values of $\rho_c$ achieved in these systems [5, 6]. In this paper we consider both the Ni-InP and the Au-Ni-InP systems and show that the formation of various nickel phosphides at the metal-InP interface is responsible for the low values of $\rho_c$ observed in these systems. We have found that up to three orders of magnitude variation in contact resistivity are observed depending on what nickel phosphide is formed at the metal-InP interface.

In what follows, we will present the results of our investigations into the electrical and metallurgical behavior of the above mentioned contact systems on InP. We will also discuss the relationship between the formation of a given nickel phosphide at the metal-InP interface and the resulting contact resistivity.
EXPERIMENT

Epitaxially grown n/p InP diodes were used in both metallurgical and electrical studies. The n-type emitters were 0.2 μm thick with a doping density of 1.7E18 cm⁻³ (Si). The p-type (100) oriented substrates were Zn doped to 8E16 cm⁻³. The transmission line method (TLM) was used to measure ρ_c values for all contact systems [7].

Contact deposition was by e-beam evaporation at a pressure in the 10⁻⁶ Torr range. Elemental, binary, and ternary contact systems were deposited to a total thickness of 2000Å in consecutive layers as follows, with the layer in contact with the semiconductor substrate listed first: Ni (2000Å), Au (2000Å), Au-Ni (400-1600Å), Ni-Au (400-1600Å), Ge-Au-Ni (200-400-1400Å), and Au-Ge-Ni (400-200-1400Å). The Au to Ge thickness ratio corresponds to the eutectic composition of about 12% wt. Ge in Au.

All heat treatments were performed in a rapid thermal annealing (RTA) furnace in a forming gas ambient. A temperature of 400°C was chosen for all heat treatments. Auger electron spectroscopy (AES) and energy dispersive spectroscopy (EDS) were used for metallurgical investigations. EDS spectrum were calibrated to identify various nickel phosphides using the commercially available Ni₂P standard.

THE Ni-ONLY CONTACT SYSTEM

In a previous work, we have investigated the reaction of InP with Ni [6]. The variation of contact resistivity during isothermal heat treatment at 400°C is illustrated in Fig. 1. Within a few minutes at that temperature, ρ_c drops from its as-fabricated value in the low E-4 Ω-cm² range to a minimum value in the mid E-7 Ω-cm² range. Further heat treatment, however, results in a rise in contact resistivity back to the E-4 Ω-cm² range.

We have determined that the contact structure after only a few minutes at 400°C is made up of three layers. As shown in Fig. 2a, the layer in direct contact with InP is composed of the alloy Ni₃P. The second layer immediately above this layer is composed of the 33 at.% phosphorus compound Ni₂P. The third or outermost layer of this structure consists of In containing about 15 at.% P.

Our analysis of the samples heat treated for tens of minutes at 400°C and whose contact resistivities had risen back up to the E-4 Ω-cm² range shows that the contact structure in these samples consists of only two layers. As shown in Fig. 2b, this structure consists of a Ni₂P layer in contact with InP and a surface layer of In containing about 15 at.% P. Thus, heat treatment at 400°C for a few minutes causes an Ni₃P layer to form at the metal-semiconductor interface. This is accompanied by a two order of magnitude drop in contact resistivity. As the heat treatment continues at the same temperature, the Ni₃P layer at the metal-InP interface is converted to Ni₂P, resulting in a two order of magnitude drop in contact resistivity.
Fig. 2  Contact-InP structure after heat treatment at 400°C. a) Ni, 4 min., b) Ni, 30 min., and c) AuNi, 1 min.

increase in contact resistivity.

THE Au-Ni CONTACT SYSTEM

A study of the metallurgical interactions of the Ni-Au system by Ivey, et al. [8] has shown that the compound Au3In forms at the metal-InP interface upon heat treatment at 400°C. These investigators, however, did not study the electrical characteristics of this system. The results of our measurements of the contact resistivity of this system during heat treatment at 400°C are shown in Fig. 3. As can be seen in the figure, \( \rho_c \) values remained rather invariant in the E-5 Ω-cm\(^2\) range even after extended sintering. This value of \( \rho_c \) is consistent with the results of our previous investigation of the Au-In-InP system [9].

However, when we reversed the order of the Au and Ni depositions we found, to our surprise, an entirely different situation. As shown in Fig. 3, \( \rho_c \) values near the theoretical limit in the E-8 Ω-cm\(^2\) range are achieved when Au rather than Ni is deposited first on the InP. In order to determine why the electrical behavior of the Au-Ni system is so different (and better) than the Ni-Au system, we attempted to identify the reaction products at the metal-InP interface. To enable an analysis by EDS we removed, via a thiourea-based etchant, the top metallization layer to access the reaction products that are in direct contact with the InP. Fig. 4 is a light micrograph of the resulting interfacial structure. As shown in the micrograph, elongated dark-colored features are co-planar with a light-colored smoother matrix. Our EDS results indicate that the structure of the light-colored matrix is identical to the double layer structure (Ni\(_3\)P/Ni\(_2\)P) found when Ni-only contacts are heat treated under similar conditions. The dark-colored phase, however, was found to have a composition of about 20% P in Ni. This corresponds to the compound Ni\(_4\)P. Careful study of this phase with a scanning electron microscope (SEM) and EDS has shown that it is in direct contact with InP. The resulting interfacial structure is schematically described in Fig. 2c. It appears, then, that reversing the order of Au and Ni deposition on InP results in the formation of entirely different compounds at the metal-InP interface. It is interesting to note that both in the case of Au-Ni and Ni-Au, the metal deposited first on InP does not react with the substrate to form compounds at the metal-InP interface. Rather the reaction products at that interface are the result of the interactions between InP and the second (more remotely) deposited metal.

A comparison between the Ni (Fig. 2a) and the Au-Ni (Fig. 2c) contact structures indicates
that the reaction products for both systems at the metal-InP interface are identical except for the presence of Ni₄P in the Au-Ni system. This strongly suggests that the formation of Ni₄P is responsible for the order of magnitude lower minimum $\rho_c$ values observed with Au-Ni as compared to Ni-only contacts.

THE Au-Ge-Ni CONTACT SYSTEM

The results of isothermal heat treatment of Ge-Au-Ni on InP at 400°C are shown in Fig. 5. As shown, minimum $\rho_c$ values in the E-7 $\Omega$-cm² range are obtained after a few minutes at 400°C. These $\rho_c$ values are consistent with contact resistivity values reported in the literature [1, 10]. It is also apparent that the electrical behavior of Ge-Au-Ni is very similar to Ni-only contacts (Fig. 1). This similarity has also been observed by other workers [11, 12].

When instead of Ge we deposited Au first on InP, we observed an additional order of magnitude reduction in the minimum $\rho_c$ to the E-8 $\Omega$-cm² range (Fig. 5). This reversal in the order of deposition has made this system electrically similar to the Au-Ni system rather than to the Ni-only system. Indeed, a comparison of the electrical behavior of the Au-Ni system (Fig. 3) and the Au-Ge-Ni system (Fig. 5) indicates that the electrical characteristics of the two systems are quite similar. Therefore, it appears that the addition of Ge to the Au-Ni system is
not necessary to achieve $\rho_c$ values in the $\text{E-8} \ \Omega\text{-cm}^2$ range.

An EDS investigation of the structure of the heat treated Au-Ge-Ni metallization indicated that a very fine grained layer containing P, In, and an undetermined amount of Ge is in intimate contact with the InP. While the grain size is too small to permit compositional resolution by EDS, we found that the averaged or net phosphorus-to-nickel EDS peak height ratio of the interfacial material is intermediate between that of Ni$_4$P and Ni$_2$P. This means that while it is possible that Ge is an active participant, the low resistivity can be explained as due to the same mechanism as in the Au-Ni system on InP, i.e. to the presence of a mixture of Ni$_4$P and Ni$_2$P/Ni$_3$P. The fact that the Au-Ni and the Au-Ge-Ni systems are nearly identical not only in the minimum $\rho_c$ values achieved, but also in their response to extended heat treatment (Fig's. 3 & 5) supports the suggestion that the same processes are operating in both systems.

In conclusion, we have found that in the Au-Ge-Ni system as in the Au-Ni system the order in which metal components are deposited is of critical importance. In both cases the lowest $\rho_c$ values are obtained when the Au component is deposited first. We have found that heat treated Au-Ni and Au-Ge-Ni show very similar electrical behavior on InP. This effectively eliminates the need for the presence of Ge in the Au-Ge-Ni system. In fact, the addition of Ge to Au-Ni can even be electrically deleterious if deposited before or with the Au component (fig. 5). In addition, since melting occurs at the Au-Ge-Ni-InP interface at temperatures where the contacts are usually heat treated (i.e. >360°C, the eutectic melting point of Au-Ge), the addition of Ge to the Au-Ni system would be detrimental to shallow junction devices that are sensitive to excessive metal-semiconductor interdiffusion. A summary of minimum $\rho_c$ values obtained on InP with the contact systems discussed so far is graphically presented in Fig. 6.

**SUMMARY**

The results of our study of electrical and metallurgical behavior of the Ni, Au-Ni, and Au-Ge-Ni systems on $n$-InP are summarized as follows:

1. Heat treatment of Ni-InP at 400°C for a few minutes results in the formation of the compound Ni$_3$P at the metal-InP interface, causing a drop in contact resistivity to the $\text{E-7} \ \Omega\text{-cm}^2$ range. Further heat treatment for tens of minutes at the same temperature converts the Ni$_3$P layer to the compound Ni$_2$P which results in the $\rho_c$ values to increase to the $\text{E-4} \ \Omega\text{-cm}^2$ range.

2. The Au-Ni system on InP was shown to exhibit $\rho_c$ values in the $\text{E-8} \ \Omega\text{-cm}^2$ range after short periods of heat treatment at 400°C. It was found that this dramatic drop in contact resistance was due to the formation of Ni$_4$P at the metal-InP interface.

3. It was found that the presence of Ge in the Au-Ge-Ni system on InP was not necessary in order to achieve $\rho_c$ values in the $\text{E-8} \ \Omega\text{-cm}^2$ range.
4. The order in which various combinations of metals are deposited on InP was established to be critical in determining the contact resistivities observed with the Au-Ni and the Au-Ge-Ni systems. In both cases the lowest $\rho_c$ values are obtained when the Au component is deposited first.

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We have investigated the electrical and metallurgical behavior of Ni, Au-Ni, and Au-Ge-Ni contacts on InP. We have found that very low values of contact resistivity ($\rho_c$) in the $10^{-7}$ Ohm-cm$^2$ range are obtained with Ni-only contacts. We show that the addition of Au to Ni contact metallization effects an additional order of magnitude reduction in $\rho_c$. Ultra-low contact resistivities in the $10^{-8}$ Ohm-cm$^2$ range are obtained with both the Au-Ni and the Au-Ge-Ni systems, effectively eliminating the need for the presence of Ge in the Au-Ge-Ni system. The formation of various nickel phosphides at the metal-InP interface is shown to be responsible for the observed $\rho_c$ values in the Ni and the Au-Ni systems. We show, finally, that the order in which the constituents of Au-Ni and Au-Ge-Ni contacts are deposited has a significant bearing on the composition of the reaction products formed at the metal-InP interface and therefore on the contact resistivity at that interface.