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Non-Destructive, Ultra-Low Resistance, Thermally Stable Contacts for Use on Shallow Junction InP Solar Cells

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(NASA-TM-106228) NON-DESTRUCTIVE,
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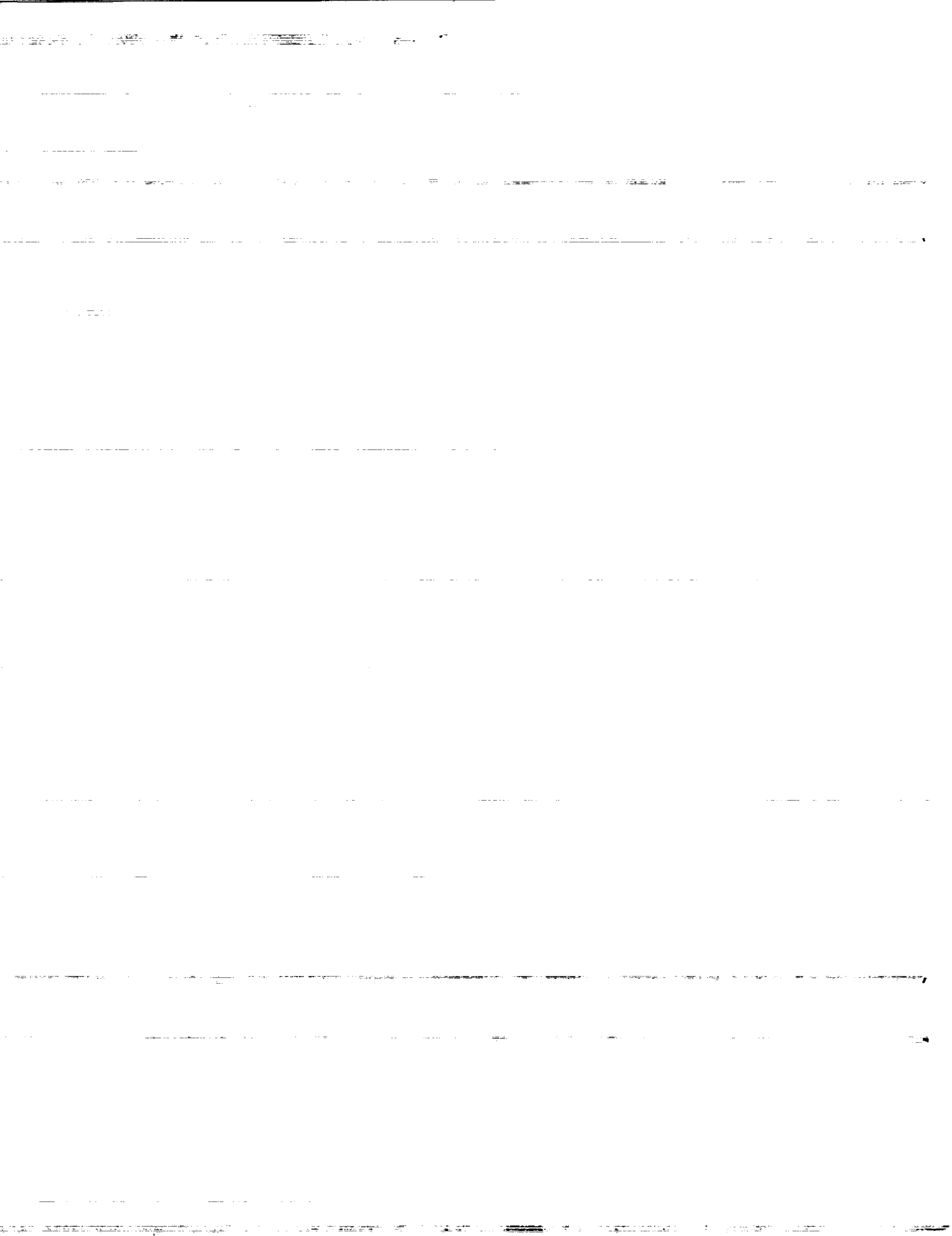
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NON-DESTRUCTIVE, ULTRA-LOW RESISTANCE, THERMALLY STABLE CONTACTS
FOR USE ON SHALLOW JUNCTION InP SOLAR CELLS

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ABSTRACT

Contact formation to InP is plagued by violent metal-semiconductor intermixing that takes place during the contact sintering process. Because of this the InP solar cell cannot be sintered after contact deposition. This results in cell contact resistances that are orders of magnitude higher than those that could be achieved if sintering could be performed in a non-destructive manner. We report here on a truly unique contact system, involving Au and Ge, which is easily fabricated, which exhibits extremely low values of contact resistivity, and in which there is virtually no metal-semiconductor interdiffusion, even after extended sintering. We present a description of this contact system and suggest possible mechanisms to explain the observed behavior.

INTRODUCTION

The most common contact metallization systems in use on n-InP devices consist of various combinations of Au, Ge, and Ni.⁽¹⁻¹³⁾ In order to secure optimum values of the contact resistivity R_C , these systems must be sintered at elevated temperatures after metal deposition. The sintering step, while reducing R_C , has the undesirable effect of inducing substantial metallurgical interdiffusion between the metallization and the InP substrate. This interdiffusion, unless carefully controlled by the imposition of diffusion barriers⁽¹⁴⁾ or by the use of techniques such as rapid thermal annealing^(14,15), can quickly degrade or destroy the device being contacted. The solar cell and other shallow junction devices are most sensitive to these effects. For these devices especially, a trade-off must be made between contact performance and device integrity.

The degrading effects of contact sintering can be easily seen in the simple case of elemental Au contacts on n-InP. In this system, R_C reduction during sintering is due to the formation of the compound Au_2P_3 at the metal-InP interface.⁽¹⁶⁾ Au_2P_3 formation, however, does not take place immediately, rather it forms during the second of three stages that occur during the Au-InP sintering

process. During the first stage of the reaction, prior to the formation of Au_2P_3 , sufficient InP dissolves into the contacting Au metallization to raise the In content in the Au lattice to the solid solubility limit (about 10 at%). The phosphorus atoms released during this stage dissipate without reacting. Thus, before the resistivity begins to drop, there is a significant amount of metal-semiconductor intermixing.

Similar interdiffusion problems have been shown to occur in the Ni-InP⁽¹⁻³⁾, the AuNi-InP^(11,12), and the AuGeNi-InP⁽¹⁻⁵⁾ systems. In these systems the formation of Ni-based compounds at the metal-InP interface are responsible for the sinter-induced resistivity drops.^(11,13) As in the case of Au-only contacts, extreme care must be taken to avoid cell degradation during contact formation.

In the course of an investigation into the mechanisms involved in the reactions of Au, Ge, Ni, and various combinations of these with InP, we have discovered a contact system that provides extremely low contact resistivity, which is easily fabricated, and in which there is virtually no metal-semiconductor interdiffusion, even after extended sintering. The purpose of this paper is to describe this unique contact system, involving Au and Ge, and to suggest possible mechanisms that explain the observed behavior.

EXPERIMENT

The structures used in this investigation were all n/p diodes with epitaxially deposited emitters, 2000 Å thick, Si doped to $1.7 \times 10^{18} \text{ cm}^{-3}$. The (100) oriented substrates were Zn doped to $8 \times 10^{16} \text{ cm}^{-3}$. Specific contact resistivity measurements were made using the transmission line method (TLM). Deposition of the contact metallization was done by electron beam evaporation. The samples were not actively cooled during deposition. Unless otherwise stated, the contact metals, Au and Ge, were deposited in a layered structure in the sequence: InP/400 Å Au/200 Å Ge/1600 Å Au. While these contacts contain about 7 at% Ge, we have found essentially the same results for InP/200 Å Au/700 Å Ge/1200 Å Au (28 at% Ge) contacts.

Post-deposition sintering was performed in a rapid thermal annealing (RTA) apparatus that provides rise times of about 10 seconds with negligible overshoot. The ambient during sintering was nitrogen.

To monitor the degree of emitter dissolution/perforation caused by the sintering process, we observed the quality of the diode current-voltage (I-V) characteristic. As a measure of the I-V quality we arbitrarily defined a conduction voltage V_1 as the voltage at which the forward current through the TLM patterned diode (area $5.6 \times 10^{-3} \text{ cm}^2$) is 1 mA.⁽⁹⁾ A good pn junction should exhibit a V_1 of about 900 mV. Lower values indicate a degraded emitter.

Compositional analysis was performed via energy dispersive spectroscopy (EDS). To reveal subsurface detail for EDS analysis we used a thiourea-based^(16,17) chemical etch.

LOW RESISTANCE, NON DESTRUCTIVE CONTACTS

We have found that the addition of small amounts of Ge to Au contact metallization has a significant effect on both the metallurgical and the electrical characteristics of those contacts. Figure 1 shows the variation of the specific contact resistivity during sintering at 350 C for Au-only contacts and for Au contacts containing 7 at% Ge. The difference between the two samples is striking. Whereas the resistivity of the Au-only sample remains in the 10^{-3} ohm cm^2 range for tens of minutes at 350 C, only 1 minute at that temperature is necessary to bring the resistivity of the Au-7 at% Ge sample down four orders of magnitude to the low 10^{-7} ohm cm^2 range. These resistivities match the best reported values for any contact system on InP and are ten times lower than those that can be

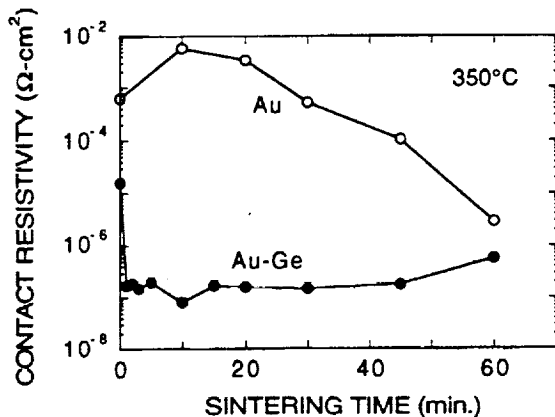


Figure 1. The variation of the specific contact resistivity with time during sintering at 350 C.

achieved with Au-only contacts⁽⁹⁾.

Another, even more striking difference between the two types of contacts is illustrated in figure 2. The figure compares the sinter-induced variations in the conduction voltages for the Au-only and the Au-7 at% Ge contacted samples. While the value of V_1 for the Au-only contacted sample has dropped significantly after 30 minutes at 350 C, V_1 for the Au-7 at% Ge sample remains unchanged under identical sintering conditions. Thus, even though the resistivity of the Au-7 at% Ge contacted sample has been drastically reduced by the sintering process, there is no evidence of any metal-semiconductor interdiffusion. Optimization of the contact resistivity has thus been achieved without compromising the integrity of the underlying device. This has never been seen before.

Further evidence that Ge additions retard Au-InP intermixing during sintering can be seen in the metallurgical data shown in figure 3. We have shown in previous work that during the second stage of the Au-InP sintering process, concurrent with the formation of the R_C -reducing compound Au_2P_3 at the metal-InP interface, the pink colored compound Au_3In forms at the free surface of the metallization.⁽¹⁶⁾ Figure 3 shows the percentage of the contact metal surface that has been converted to Au_3In as a function of time at 350 C for both the Au-only- and the Au-7 at% Ge contacts. As can be seen the Au-only contacts begin to react almost immediately, whereas Ge-containing contacts show no sign of reaction even after 45 minutes at that temperature.

The addition of a small amount of Ge to Au-only contacts has thus enabled the achievement of R_C values that are among the lowest reported, while at the same

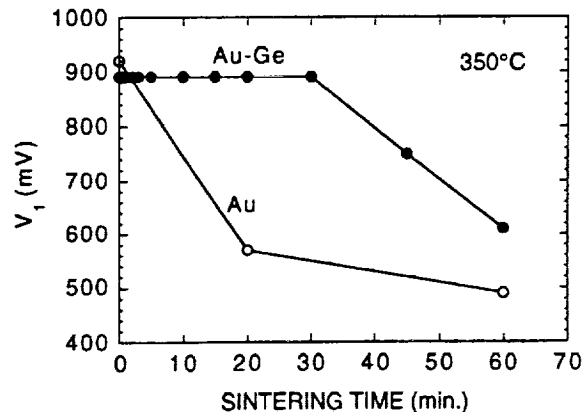


Figure 2. The variation of the conduction voltage with time during sintering at 350 C.

time preventing the device-destroying metallurgical interactions that would normally occur during the sintering process.

DISCUSSION

As discussed above, the presence of Ge in Au contact metallization retards metal-InP intermixing during sintering. Similar reaction retarding (but not R_C reducing) effects have been observed when small (several atomic percent) amounts of gallium are added to Au contacts on InP.⁽⁹⁾ We know from previous work that the dissolution of InP into contacting Au metal takes place via a dissociative diffusion process.⁽¹⁶⁾ In this process In atoms from the InP substrate enter the Au lattice interstitially and diffuse until encountering vacant sites in the Au lattice, at which point they enter the vacancies and take substitutional sites on the Au lattice.

It has been suggested that gallium, when added to the Au metallization, enters and saturates the interstices of the Au lattice, thereby preventing entry of interstitial In.⁽⁹⁾ When In is prevented from entering the metallization, the Au-InP interdiffusion process comes to a halt. In the present case, with regard to the reaction retarding effects that accompany the addition of Ge, we propose that a similar mechanism is involved. We propose that a portion of the added Ge atoms enter and saturate the interstices of the Au lattice, thereby suppressing metal-semiconductor interdiffusion.

Given that Ge interstitial saturation retards metal-InP interdiffusion, the cause of the drastic drop in R_C after only 1 minute at 350 C remains to be explained. In an attempt to identify the mechanisms responsible for the low values of R_C , we subjected a number of Au-7 at% Ge contacted samples to a thiourea-based chemical etch which has

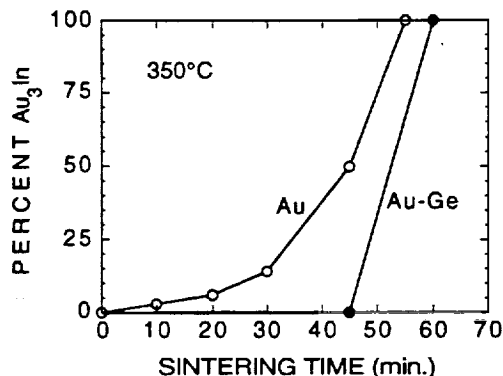


Figure 3. Percent Au-to-Au₃In conversion as a function of time during sintering at 350 C.

been shown to dissolve Au and Au-In alloys while doing negligible harm to the InP substrate.^(16,17) The samples that were etched had been sintered for 1 minute at either 350 or 400 C, and they showed R_C values in the low 10^{-7} ohm cm^2 range and V_1 values near 900 mV.

As shown in figure 4, the etching process exposed a tenacious fine grained layer at the metal-InP interface. An energy dispersive spectrographic (EDS) analysis of the residual layer, using Au₂P₃ and eutectic Au/Ge as standards, indicated that the layer contained Au, Ge, and P in the proportion 2:3:4. A similar analysis on a sample sintered for 60 minutes at 350 C gave identical results, indicating that the layer is a stable end product.

Questioning whether the layer is a Au₂Ge₃P₄ ternary or a combination of binaries such as Au₂P₃ and GeP, we subjected a previously etched sample to a second heat treatment which is known to decompose any Au₂P₃ that is present.⁽¹⁶⁾ We thus re-sintered an etched sample at 480 C for 10 minutes, and followed this with a second chemical etch to remove any Au₂P₃ decomposition products. When an EDS analysis was performed on the double-etched sample we found no change in the composition of the residual layer. We thus conclude that the layer is indeed a ternary compound.

Because the presence of the Au₂Ge₃P₄ ternary coincides with the measurement of low contact resistance, we suggest that it is the cause of the observed resistivity drop. It should be noted that an interfacial Au-Ge-P ternary phase has also been reported to form in sintered AuGeNi contacts containing very small amounts of Ni.⁽¹⁸⁾

The addition of Ge thus does two things. First, it suppresses the Au-InP metallurgical interaction. Second, it causes the phosphorus atoms that are released during stage I of the Au-InP

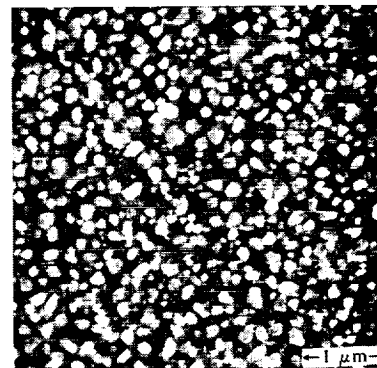


Figure 4. Residual layer remaining on InP surface after chemical etch to remove Au and Au alloys.

reaction to chemically react rather than to dissipate, as is observed with Au-only contacts.⁽¹⁹⁾ These two effects combine to produce an extraordinary contact system. The rate suppressing effect slows down emitter dissolution so that sintering can be performed without sacrificing emitter integrity. In addition, the presence of Ge induces the P atoms released during stage I (which would dissipate in the absence of Ge) to react rapidly with Au and Ge to form a stable, resistance-lowering ternary at the metal-semiconductor interface. These attributes make this system a truly unique and highly useful contact system.

AS-FABRICATED Au/Ge CONTACTS

Some final comments are in order concerning the low as-fabricated value of R_C observed in the Au-7 at% Ge system compared to that observed with Au-only contacts (figure 1). It has previously been shown that when Au metallization contains small amounts of additives that retard the metal-InP interaction rate (such as Au-Ga⁽⁹⁾ and Au-In⁽¹⁰⁾), the as-fabricated R_C values are significantly lower than those measured for Au-only contacts. The suggested mechanism is that when In entry into the contacting Au is retarded, the In-to-P ratio at the metal-InP interface is increased, and the contact resistance is lowered as a result.⁽⁹⁾ It is suggested that the same mechanism is involved here also where Ge additions are effective in retarding the Au-InP reaction rate.

There are a number of ways in which the addition of Ge (or Ga or In) could retard the metal-InP reaction rate. As mentioned above, we have postulated that the metal-InP reaction rate is suppressed because Ge saturates the interstices of the Au lattice, preventing the entry therein of In from the InP substrate. There is evidence, however, that certain active metals, such as Ni, when placed at the metal-InP interface, directly influence the relative outdiffusion rates of In and P, and thus control the In-to-P atomic ratio at the interface.⁽²⁰⁾ This can be seen by comparing the as-fabricated R_C values of the Ni/InP system⁽¹³⁾ (Ni being an active metal⁽²⁰⁾) with those of the Au/InP system⁽¹³⁾ (Au being an inactive metal⁽²⁰⁾). The former values are about an order of magnitude lower than the latter.

To determine which of these mechanisms is operating when Ge is introduced into the contact system, we fabricated a number of samples where Ge was deposited first, in direct contact with the InP substrate, followed by Au deposition. We found the as-fabricated resistivities of these InP/Ge/Au samples to be no better than those measured for Au-only contacted samples, even though Ge

is in direct contact with the InP substrate. The direct involvement of Ge at the metal-InP interface can thus be discounted. The evidence thus supports interstitial saturation as the mechanism that controls the (as-fabricated) In-to-P ratio (and thus the as-fabricated value of R_C) at the Au(Ge)/InP interface.

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