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Sinterless Contacts to Shallow Junction InP Solar Cells

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SINTERLESS CONTACTS TO SHALLOW JUNCTION INP SOLAR CELLS

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In the past, the achievement of good electrical contact to InP has inevitably been accompanied by mechanical degradation of the InP itself. Most contact systems require heat treatment after metal deposition that results in the dissolution of substantial amounts of InP into the metallization. Devices such as the solar cell, 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 such as the use of rapid thermal annealing (RTA) techniques or the imposition of diffusion barriers between the InP and the current carrying metallization, 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 high temperature processing. In this paper we describe two contact systems that provide low contact resistance to InP solar cells that do not require subjecting the current carrying metallization to a post deposition sintering process. We show that these two systems, one nickel-based and the other silver-based, provide contact resistivity (R_C) values in the low 10^{-6} ohm cm^2 range, as fabricated, without the need for sintering.

Before discussing our results, however, let us consider the metal-semiconductor reactions that take place between InP and Ni and between InP and Ag.

The InP-Ni Interaction

Figure 1 shows the variation of R_C (TLM measurements) for Ni contacts (2000 A thick) on (100) n-InP (Si: 1.7 x 10¹⁸ cm³) during heat treatment at 400 C. Within a matter of minutes R_C is seen to drop several orders of magnitude to the mid 10⁻⁷ ohm cm² range. As the sintering proceeds, however, R_C eventually rises back up to the 10⁻⁴ ohm cm² range.

To determine the causes of the R_c variations we attempted to profile the sintered contacts using both AES and EDS. We performed these measurements on



Fig. 1 The variation of R for Ni-contacted InP during sintering at 400°C.

samples that had been sintered for several minutes (low R_C) and for extended periods (high R_C). Prior to EDS examination we chemically etched the samples using HNO₃- and Thiourea-based etches so as to expose the subsurface structure.

Both the EDS and the AES analyses indicated that the contacts sintered for only a minute or so (low R_C) consist of three distinct layers. The outermost layer consists almost entirely of In metal containing a small amount (15%) of P. Beneath the In layer in these low R_{c} samples we found two Ni-P layers. The analysis indicates that the layer which is in contact with InP is the compound Ni₃P with a phosphorus content of 25 at%. The analysis further indicates that the more remote layer consists of the 33 at% phosphorus compound Ni₂P. A schematic diagram of the suggested structure is given in figure 2a. The relative positions of the two phosphide layers is somewhat surprising in light of the C. fact that the phosphorus source is the InP. One would have expected the more P rich compound to form adjacent to the InP, and not vice-versa.

A similar analysis was performed on samples subjected to extended sintering (high R_c). The only major difference between these

and the previous samples was that, in this case, only one phosphide layer is observed between the InP and the In-rich layer. The data indicates that this layer is composed of Ni₂P. The resulting structure is described schematically in figure 2b.

Since the presence of the Ni₃P interlayer is correlated with the achievement of low R_c values, we suggest that the formation of this layer in the early stages of the sintering process is the cause of the dramatic drop in R_c , and that its disappearance (via conversion to Ni₂P) upon extended heating results in the observed rise in R_c . Similar R_c -lowering characteristics have been reported for Au₂P₃ in the Au-InP system. (1)

The Ag-InP Interaction

In a manner similar to the Ni-InP system, the specific contact resistivity of Ag-contacted InP drops quickly upon sintering at 400 C. Figure 3 shows the variation of R_C with time at 400 C for 2000 A thick Ag contacts on the same InP substrate material described previously. R_C values in the low 10^{-6} ohm cm² range are readily









achieved after a minute or so at 400 C. This system differs from the Ni-InP system, however, in that minutes at 400 C) results in the extended sintering does not cause a dissolution of large amounts of rise in R_c.

As we did in the previous case, we attempted to profile the reacted metallization by combining various chemical etches with EDS and XPS analyses. Employing KIand Thiourea-based etches to reveal subsurface details, we have found that there are two major layers in the sintered metallization. Our analysis indicates that at the free surface of the contact metal there is a layer of Ag containing some Between this layer and the InP In. surface we have found a second layer consisting of regions of an Ag-P compound coplanar with regions means. While it is no doubt This structure (figure of Ag(In). 2c) is present after sintering for 1 minute at 400 C and remains qualitatively unchanged during extended sintering at that The Ag-P compound temperature. which we have shown to be in intimate contact with the InP and to account for about 50 % of the metal-semiconductor contact area, has been observed by others and positively identified as AgP2.⁽²⁾

The correlation between the drop in R_c and appearance of AgP₂ at the metal-InP interface leads one to suspect that there is a cause-and-effect relationship between the two events. It is suggested, therefore, that in the Ag-InP system, as in the Au-InP and the Ni-InP systems, significant reductions in the specific contact resistivity can be achieved by introducing an appropriate metal-phosphide layer between the InP and the current carrying metallization.

Non Destructive Contacts

In the foregoing we have shown that low contact resistivities can be achieved with either Ni or Ag contacts. In both of these systems, however, a

sintering schedule sufficient to produce low R_c values (several InP into the contact metallization. The result is emitter perforation and a shunting of the electrical characteristics of the device. The diodes used in figures 1 and 3, for example, were seriously shunted after a minute at 400 C.

Since the reason for the sintering step is thought to be to generate certain metal phosphides at the metal-InP interface, it follows that one should be able to eliminate the need for sintering by introducing the appropriate phosphide layer by some other possible to introduce a phosphide layer via vapor or chemical deposition, there is a simpler, albeit slightly more destructive, way to deposit the layer.

Since the electrical characteristics of the contact system are controlled by the nature of the interface between the InP and the metal phosphide, it seems reasonable to conclude that a very thin phosphide layer would suffice. Thus, if a very thin (Angstroms thick) metal layer were deposited on the InP and sintered, the required phosphide would form, but it would be accompanied by only a very small amount of emitter dissolution. The contacts could then be built up with a conductive metal. In this way gross damage to the semiconductor device could be avoided while still achieving the low R_c values attendant to interfacial phosphide formation. It should be noted that the use of a thin interfacial phosphide layer has proven successful in the Au-InP system.⁽³⁾

To test this idea in the present systems we fabricated a number of TLM patterns by first evaporating 40 A of either Ag or The thin layers were sintered Ni.

at 400 C for two minutes to generate the respective phosphide layers. The samples were then carefully remasked and the patterns built up with a conducting metal (Au used here).

Figure 4 shows electron micrographs of the thin sintered layers prior to remasking and buildup. The Ag structure consists of unconnected islands that cover about one third of the surface area. Ni, on the other hand, forms an open dendritic lattice with about a 50 % surface coverage. The resulting as-fabricated R_c values (after Au buildup) are shown in figure 5 where they are compared with





previous results employing a thin gold phosphide interlayer⁽³⁾ and with R_c values typical of Au contacts prior to sintering. When the current-voltage characteristics of the diodes upon which these contacts were deposited (2000 A junction depth) were inspected, there was no sign of device shunting. The conduction voltages (see ref 1) for all of the Ni- and Ag-contacted samples in figure 5 were in the 900-to-950 mV range, indicating negligible diode degradation.

We can conclude, therefore, that it is indeed possible to achieve specific contact resistivities in the low 10^{-6} ohm cm² range without compromising emitter integrity through the introduction of any of a number of metal-phosphide interlayers including Ni₃P, AgP₂, and Au₂P₃.



Fig. 5 As-fabricated contact resistivities for contacts with Au_2P_3 , Ni_3P_1 , & AgP₂ interlayers.

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