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Encapsulated Diffusion of Sulphur into InP

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Abstract

This talk outlines a simple process for the fabrication of n^+-p solar cells in indium phosphide. Large area cells (>0.25 cm^2) have been made by this process, with a photovoltaic conversion efficiency of 15.21% under AM0 conditions of illumination. An ideality factor of 1.1 and a saturation current density of 8×10^{-15} A/cm^2 have been observed for these cells.

The technique for cell fabrication involves the diffusion of sulphur into InP by an open tube process, and gives highly reproducible results from run to run. A vacuum-deposited layer of gallium sulphide (Ga_2S_3) was used as the source for sulphur diffusion, with a chemically vapor deposited SiO_2 cap layer to prevent decomposition of the InP surface during heat treatment. Diffusions were carried out in a flowing nitrogen ambient at 585°C to 708°C, and characterized by their surface carrier concentration and the diffusion constant. The diffusion profile for sulphur in InP is estimated to be of the complementary error function type. The activation energy of the diffusion was estimated to be 1.94 eV.

The technique described here is ideally suited for the fabrication of shallow n^+-p junctions in InP, and has been used for space-borne solar cells.

Introduction

At the present time, there is considerable interest in indium phosphide as an active material for solar cells. InP is a direct bandgap semiconductor with an energy gap of 1.34 eV, which is close to that required for maximum conversion efficiency at AM 1.5 [ref. 1]. An important property of this material is its ability to be surface passivated. Typically, the surface recombination velocity of n-type InP is about 10^3 cm/sec as compared to 1×10^7 cm/sec for GaAs [ref. 2]. It has been reported that InP solar cells have a higher resistance to gamma ray radiation degradation than Si or GaAs solar cells of comparable junction depths [ref. 3]. Thus, these solar cells are of particular interest for space applications.

Conventionally, diffusion of n-type impurities in III-V compounds has been carried out [refs. 4-6] in sealed tubes, in order to prevent evaporation of the more volatile group V element, which leads to massive deterioration of the surface. These diffusions require both high temperature as well as long duration, due to the low diffusion coefficient of donor impurities, with some vapor phase etching of the substrate.

There are two other problems associated with the sealed tube diffusion technique. First, the diffusion constants of impurities in III-V compounds are critically dependent upon the vacancy concentrations, and thus on the partial pressures of the host lattice elements. The inability to

maintain identical partial pressure conditions from run to run makes results hard to reproduce, so that there is a large disagreement between different workers because of the different diffusion conditions involved. The second problem is the necessity of handling the highly toxic substances such as arsenic, or hygroscopic materials such as phosphorus, which have to be carefully weighed and sealed in tubes.

The possibility of an open tube technique [ref. 7], where the diffusion can take place in a flowing inert ambient gas, is thus very attractive. Ease of implementation, adaptability to large scale batch processing, and potential low cost are its main advantages.

This paper describes the technical details and the results obtained with the open tube diffusion of sulphur into InP.

We have used a vacuum evaporated layer of gallium sulphide as the source for sulphur doping, capped by a chemical vapor deposited film of SiO_2 to prevent the loss of phosphorus from the surface of InP. This results in excellent morphology even after high temperature processing. The equilibrium vapor pressure of phosphorus during diffusion does not depend upon extrinsic parameters as in the case of sealed tube diffusion, where the phosphorus vapor pressure is set by the amount of phosphorus in the tube. As a result, this technique is simple to implement, and is highly reproducible from run to run. Solar cells made by this method have demonstrated equal (or slightly superior) performance than those made by the sealed tube process [refs. 8, 9].

Experimental

The p-type substrates used for the fabrication of n^+-p InP solar cells were pre-polished LEC grown 50 mm diameter slices, obtained from Crystacom, Inc., Mountain View, CA 94043. These were (100) misoriented 2° towards (110), and doped with Zn to a concentration of 5×10^{16}/cc. The as-received material was cut into suitable pieces and degreased in successive hot baths of trichloroethylene, acetone and methanol. Next, they were etched in a 1% Br-methanol solution for 5 minutes to remove the residual polishing damage. This was followed by etching in $HF:HCl:H_2O_2:H_2O$ in a ratio of 2:2:1:8 by volume, and by a rinse in 10% H_3PO_4 solution to remove the oxide present on top. Finally gallium sulphide (99.99% purity) was evaporated onto the frontside of the wafer using an alumina coated tantalum boat.

After the deposition of the Ga_2S_3 film, the slices were transferred to a cold wall resistance heated chemical vapor deposition system operated at atmospheric pressure. The transfer time was kept short (under 10 min.) to avoid any possible contamination from the atmosphere. The samples were first encapsulated on the frontside with 0.5 μm of SiO_2, which was grown by the oxidation of SiH_4 in an argon ambient. The partial pressures of oxygen and silane used for this purpose were 6.46×10^{-3} and 7.5×10^{-4} atm. respectively. The growth temperature was 325°C with an approximate growth rate of 100Å/min. Next, the samples were turned over and the backside was also capped with 0.5 μm of SiO_2. This is necessary to prevent phosphorus evaporation from the back of the slices during the diffusion step. Moreover, it provides a balancing of stress in the InP during heat treatment, and thus avoids dislocation formation, as well as damage to the cap layers.

Diffusions were carried out at temperatures ranging between 585°C and 708°C in an open tube diffusion system with a flowing nitrogen ambient, for times varying from 5 minutes to 24 hours. After diffusion, the SiO_2 cap was removed in dilute HF. The Ga_2S_3 layer was then removed in the

etch formulation described earlier ($HF:HCl:H_2O_2:H_2O$=2:2:1:8 by vol.). No visual damage of the InP surface was observed after the entire diffusion process.

In order to make solar cells on these diffused structures, back contacts to the p-substrates were made by evaporating Au/5% Zn and alloying at 420°C in forming gas (80% H_2, 20% N_2) for 20 seconds. Next, the front contact grids were defined photolithographically. Electroplated gold was used to make contacts to the top n^+-layer. These top contacts were well adhering, and ohmic (as plated) without any heat treatment. This is because the top n^+-layer is very heavily doped. A total cell area of 0.31 cm^2 was delineated by photolithography and mesa etching in an iodic acid (10% by wt.) bath, with the aid of a second photomask.

Diffused junctions were characterized using the van der Pauw technique. A clover leaf pattern was delineated on the InP slices for this purpose by etching in 1% Br-methanol. Ohmic contacts to the n^+ layers were formed by alloying tin dots at 260°C for 1 minute in a flowing forming gas ambient. The sheet conductance and the effective Hall mobilities on these samples were measured at room temperature and at 77K. Following this, samples were etched in a 3% iodic acid etch with an approximate etch rate of 200Å/min for short durations of time. After each successive etch (i.e., the removal of a thin n^+ layer), Hall measurements were made until the sheet conductance of the remaining layer was less than 1% of the initial value. The etch rate of the individual samples was determined by simultaneously etching part of an identically diffused sample and then measuring its etched depth by a multiple beam interferometer. An etch rate of approximately 200Å/min was measured in this manner.

Results and Discussion

Figure 1 shows the sheet conductance of the diffused layers, plotted as a function of the square root of the diffusion time for three different thicknesses of the Ga_2S_3 layer. All the diffusions were carried out at a fixed temperature of 625°C. The straight line nature of the graphs shows that, for the diffusion durations considered here, the Ga_2S_3 layer always served as an infinite source of sulphur [ref. 10]. The effective mobilities of the diffused layers were found to be independent of the Ga_2S_3 thickness. If we assume that the general nature of the sulphur diffusion profile into InP is the same for all these diffusion cases, and that the mobility of these diffused layers is limited by impurity scattering, and hence doping dependent, it follows that the surface concentration is independent of the Ga_2S_3 source layer thickness. For a given doping profile (e.g., a complementary error function type) with a fixed surface concentration, the sheet conductance changes in proportion to the change in $(Dt)^{1/2}$. The parallel nature of the three sheet conductance vs. $(time)^{1/2}$ graphs leads to the conclusion that the diffusion constant of sulphur into InP is the same for all three cases, and hence is independent of the Ga_2S_3 thickness.

The reason for the initial delay could be due to strain enhanced diffusion, as has been observed [ref. 11] during Zn diffusion into GaAs. However, this explanation does not seem to hold here. Note the absence of a slow diffusion regime in the beginning; rather, the sheet conductance rises abruptly after a finite time delay. Moreover, mobility values measured on these samples are sufficiently high so as to rule out the possibility of significant stress in the diffused layer. This has been reaffirmed by the fact than n^+-p diodes formed by this diffusion technique have ideality factors close to unity, as seen in Fig. 2.

Figure 2 shows the delay as a function of the (Ga_2S_3 thickness)^2. The character of this curve is indicative of the fact that S diffusion into InP is taking place through a barrier. We propose that atomic sulphur required for the sulphur diffusion is primarily generated at the Ga_2S_3/SiO_2 interface, and then diffuses through the Ga_2S_3 layer to reach the InP. This would introduce a specific time delay before any substantial diffusion is observed. In addition, this delay should be proportional to the square of the Ga_2S_3 thickness, as seen in Fig. 3.

Figure 4 shows the sheet conductance and room temperature Hall mobility, measured after successive etching and removal of thin layers of the n^+ region. The sample shown here had 200Å of Ga_2S_3 as the dopant source and was diffused for 4 hours at 625°C. The mobility values shown here are the effective values for the remaining n^+ layer. Local mobility values were determined from these by a technique described elsewhere [ref. 12]. Here, we assumed that the drift mobility of electrons in these n^+ layers is the same as the measured Hall mobility, since the layers were degenerately doped [ref. 13].

The carrier concentration can be determined by differentiating the sheet conductance curve; however, unless the data is smoothed out, the error introduced by this process will be very large. Because of this, we preferred to assume a profile and specific values of the surface concentration and $(Dt)^{1/2}$, and have iteratively fit the sheet conductance data points using the mobility values obtained by the technique outlined above. The best fit (as denoted by the dark continuous line in Fig. 4) was obtained for a complementary error function (erfc) type of profile, with a surface concentration of $3.4 \times 10^{18}/cm^3$ and a $(Dt)^{1/2}$ of 633Å. Similar graphs were obtained for samples diffused at different temperatures and different times. In all cases, erfc doping profiles were obtained, independent of the time and temperature of the diffusion. Similar results have been obtained for sulphur diffusion profiles in GaAs [ref. 14], which are also of the complementary error function type.

Figure 5 shows the sheet conductance versus (diffusion time)$^{1/2}$ for diffusions carried out at 585°C, 625°C, and 708°C. The thickness of the Ga_2S_3 layer was kept constant at 200Å for all these diffusions. The conventional practice here is to plot junction depth vs. (diffusion time)$^{1/2}$, which necessitates diffusion into a substrate of opposite polarity, in this case, p-type. However, diffusion into p-type InP introduces the problem that heat treatment of Zn doped InP alters the carrier concentration in the substrate [ref. 15], thus seriously affecting the interpretation of junction depth data. Consequently, we have made our diffusions into semi-insulating InP. Here if we assume (as shown above) that the doping profile is of the erfc type irrespective of the diffusion time and temperature, and that the surface carrier concentration is a function only of the diffusion temperature, then the rate of change of sheet conductance should be directly proportional to the change in $(Dt)^{1/2}$. This is indeed the case, as seen in this figure.

Doping profiles were measured on several samples diffused at these temperatures, for different durations of time. The surface concentration and diffusion constants were determined by the method outlined before. Table 1 presents the data on sulphur diffusion into InP at these temperatures. These include the surface concentration, D and the effective Hall mobility of the diffused layer as a function of the diffusion temperature. Finally, Fig. 6 shows the log of the diffusion constant as a function of 1/T. The activation energy of sulphur diffusion into InP was calculated to be 1.94 eV. The pre-exponential term was calculated to be 3.6×10^{-4} cm^2/sec.

Conclusion

Open tube diffusion of sulphur into InP was studied in the temperature range of 585°C to 708°C. The diffusion profile was found to be of the complementary error function nature. Diffusion was dependent on the thickness of the Ga_2S_3 layer, which was used as the source sulphur diffusion. It was proposed that diffusion occurs through a barrier, which in this case is the Ga_2S_3 layer itself.

A capped diffusion, of the nature described here, results in a constant overpressure of phosphorus and sulphur at any given temperature. This is a distinct advantage over conventional diffusion methods, from the point of obtaining reproducible diffusions as required in device applications.

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TABLE 1

Temperature °C	N_{SURF} ($/cm^3$)	EFFECTIVE MOBILITY (cm^2/V-sec)	$D_{S,InP}$ (cm^2/sec)
485	1.9×10^{18}	2050	1.6×10^{-15}
625	3.4×10^{18}	1800	5.0×10^{-15}
670	5.6×10^{18}	1600	1.1×10^{-14}
708	7.7×10^{18}	1350	5.2×10^{-14}

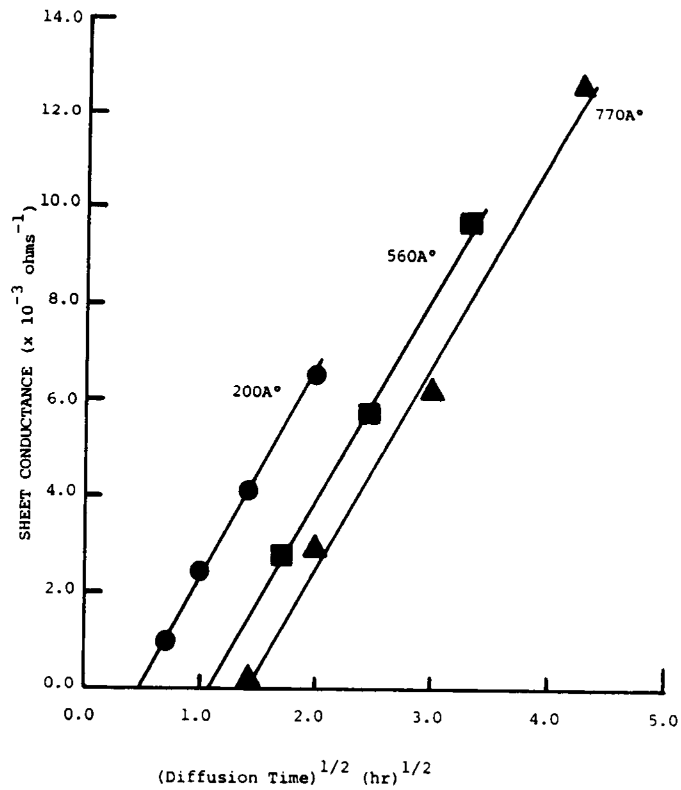

Fig. 1. Sheet conductance of the diffused n^+ layer as a function of (diffusion time)$^{1/2}$. Different curves are for different Ga_2S_3 layer thicknesses.

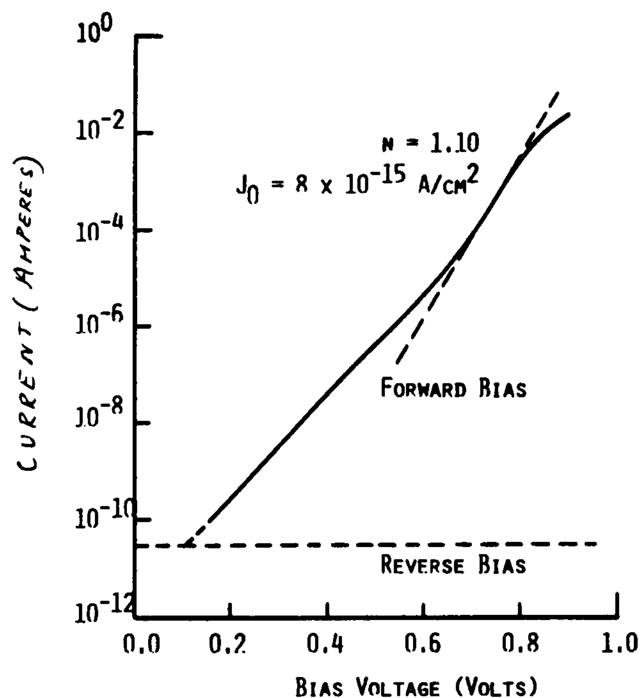

Fig. 2. Forward and reverse log I vs. V characteristics of an n^+-p cell made by this technique. (Taken without illumination.)

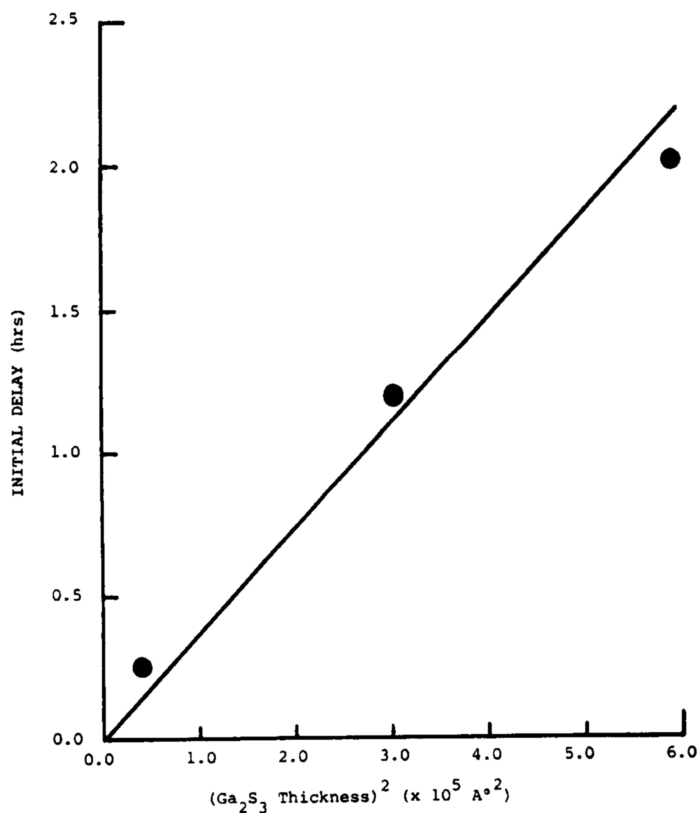

Fig. 3. Initial delay vs. square of the Ga_2S_3 layer thickness. Diffusions at 625°.

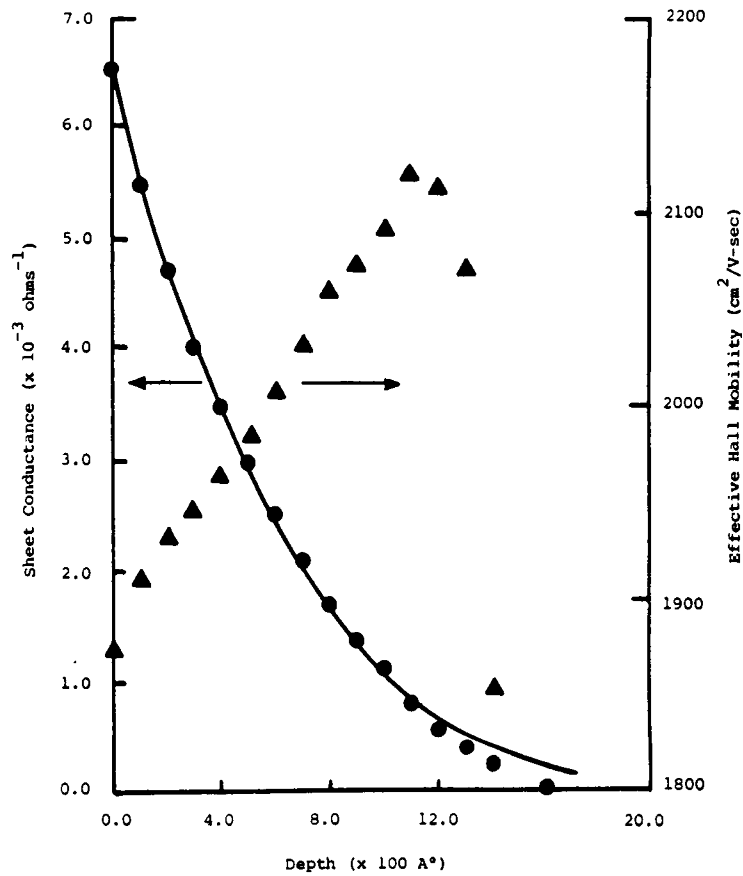

Fig. 4. Sheet conductance and effective mobility of the diffused layer after successive etching.

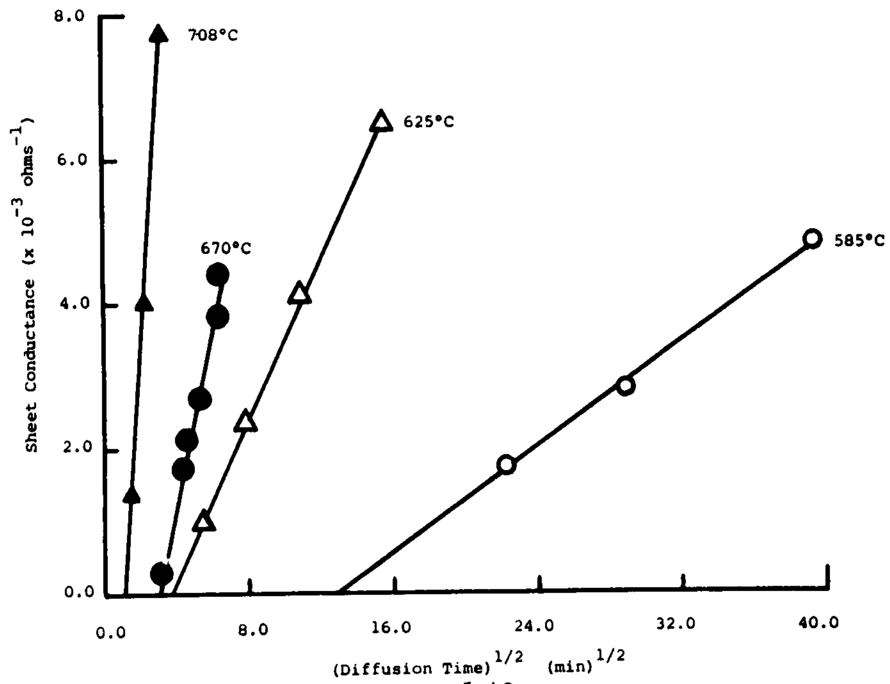

Fig. 5. Sheet conductance vs. (time)$^{1/2}$ for samples diffused at different temperatures.

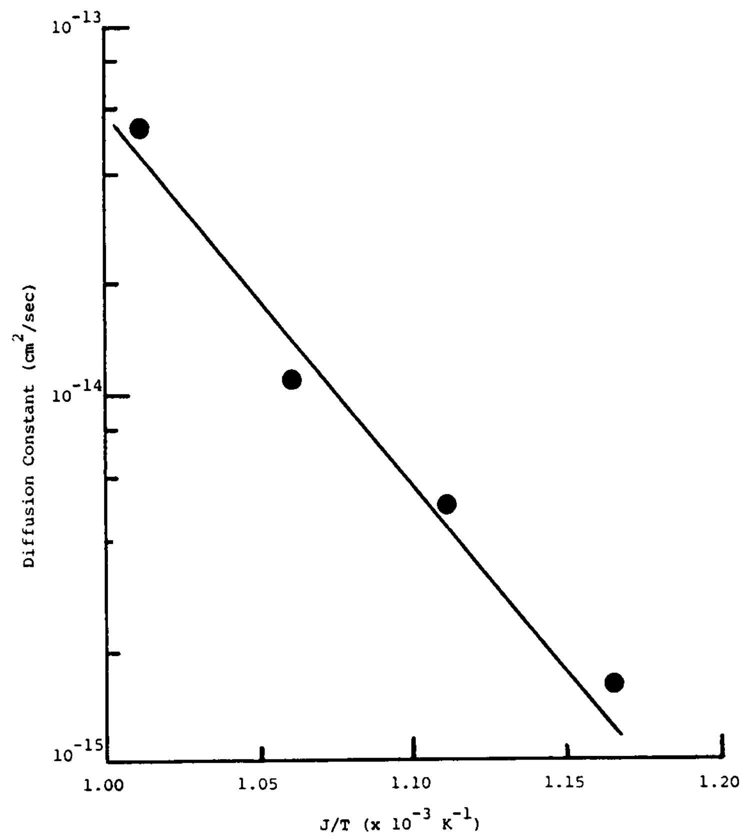

Fig. 6. Diffusion constant of sulphur in InP vs. 1/T .