acta physica slovaca vol. 53 No. 3, 231 – 241 June 2003

RELATION BETWEEN PHOTOVOLTAIC CHARACTERISTICS AND ACCEPTOR CONCENTRATION AT THE INTERFACE OF INDIUM OXIDE/INDIUM PHOSHIDE HETEROJUNCTION SOLAR CELL *

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Received 4 December 2002, in final form 8 March 2003, accepted 17 March 2003

Photovoltaic characteristics of a heterojunction solar cell composed of reactively evaporated indium oxide (In_2O_3) film and single crystalline p-type indium phosphide (InP) was found to depend on acceptor concentration at the interface. The value of acceptor concentration was preferable to be high to obtain a high performance cell because larger open-circuit voltage can be obtained due to decrease of diode saturation current of the cell with the increase of the acceptor concentration. The acceptor concentration of the cell was increased by annealing during forming an ohmic contact. The increase of acceptor concentration by annealing thought to be able to explain in terms of outdiffusion of the interstitial zinc atoms in InP bulk. Further, the value of acceptor concentration is modified by substrate heating during deposition of transparent and conductive In_2O_3 film. In order to produce a high performance cell, low substrate temperature (200°C) was preferable during deposition of In_2O_3.

PACS: 81.40.Gh, 84.60.Jt, 78.20.Jq, 66.30.Jt

1 Introduction

Indium phosphide (InP) is one of the most attractive semiconductor materials for many high performance electronic devices such as laser diodes and solar cells. Highly efficient InP homojunction [1] and heterojunction [2] solar cells were reported. We also had reported a 17.7% efficient n-In_2O_3/p-InP heterojunction cell [3] with high short-circuit current of larger than $300\mathrm{A/m^2}$. In our cell, In_2O_3 layer was deposited using reactive evaporation of indium which is thought one of the best process to prepare a transparent conductive surface layer on a semiconductor substrate without any damage caused by high energy particles irradiation.

In order to make a further improvement of the performance of this cell, it is required to improve the value of open-circuit voltage (V_{oc}) because that of this cell was relatively small (V_{oc} :∼ 700 mV) compared with open-cuircuit voltage of the homojunction cell. In the course of investigation, we found that the characteristics of the In_2O_3/InP heterojunction cell is strongly depended on acceptor concentration at the interface. Several authors mentioned that the acceptor concentration of InP wafer is modified by heat treatment [4–6]. However, relation between the

*Presented at Workshop on Solid State Surfaces and Interfaces III, Smolenice, Slovakia, November 19 – 21, 2002.
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photovoltaic characteristics of the cell and acceptor concentration at the surface of InP has not been well known yet.

In this paper, a relation between photovoltaic characteristics and acceptor concentration at the interface of $\mathrm{In_2O_3/InP}$ cells have been shown. An effects of heat treatment on the acceptor concentration of InP bulk was tried to explain in terms of outdiffusion of the interstitial zinc.

2 Experimental procedure

Photovoltaic cells which consist of single crystalline indium phosphide (InP) and reactively deposited indium oxide ($\mathrm{In_2O_3}$) film were prepared as follows. Zinc doped p-type single crystalline InP wafers were used as substrates. Initial acceptor concentration of the InP wafer was determined by Hall measurement as $2.6 \times 10^{21}\mathrm{m}^{-3}$. The substrate was chemically etched in a solution of 1 v/o bromine in methanol. In order to make a backside ohmic contact, gold film containing small amount of zinc (about 10 wt%) was vacuum evaporated onto a surface of the InP substrate. The substrate was successively annealed in argon flow at 450°C in 10 min to achieve low resistivity contact. After the annealing, indium oxide films were deposited on the other side of the substrate by reactive evaporation of metal indium. During the deposition process, the substrate was heated at a temperature of T_{sub} between 200 and 550°C and the oxygen pressure in the chamber was maintained at 0.1 Pa. Indium oxide films deposited on glass substrates under the condition mentioned above showed resistivity of lower than 1×10^{-5} Ωm and the transmittance larger than 80% for the visible light.

The photovoltaic characteristics of the cell were measured under illumination of light from a solar simulator (AM1.5, $1\mathrm{kW/m^2}$). Current-voltage (I-V) characteristics in the dark were measured using a DC voltage source and a digital multimeter. Capacitance-voltage (C-V) characteristics at applied signal frequency of 100 kHz were measured also in the dark using an impedance analyzer. A diode factor n and a diode saturation current density J_0 were derived from semi-log plot of the measured I-V characteristics. Acceptor concentration of acceptor concentration N_{A} at a interface of the cell was derived from a slope of relation between inverse square of measured capacitance and applied voltage.

A depth profile of acceptor concentration in the InP wafer was analyzed as follows. First, an ohmic contact for the InP wafer was prepared by the same process as mentioned previously for preparing the photovoltaic cell; a gold film containing small amount of zinc was vacuum evaporated onto a surface of InP wafer and annealed in argon flow. Next, an aluminum electrode was vacuum evaporated onto the other side of the wafer to make a Schottky barrier diode. The substrate was not heated intentionally during aluminum deposition. The C-V characteristics of the Al/InP diode were measured in the dark. Then, the acceptor concentration at the surface of the InP wafer was calculated from the measured data. After the electrical measurement, the aluminum electrode was removed and the surface of the InP wafer was mechanically polished and chemically etched. The back ohmic contact was covered with apiezon wax for protection during etching process. Again, Al/InP Schottky contact was made and C-V characteristics were measured to derive the acceptor concentration at the surface of the thinned wafer. The wafer thinning and C-V measurement were repeated until the thickness of the wafer was decreased to about a half of the initial value.

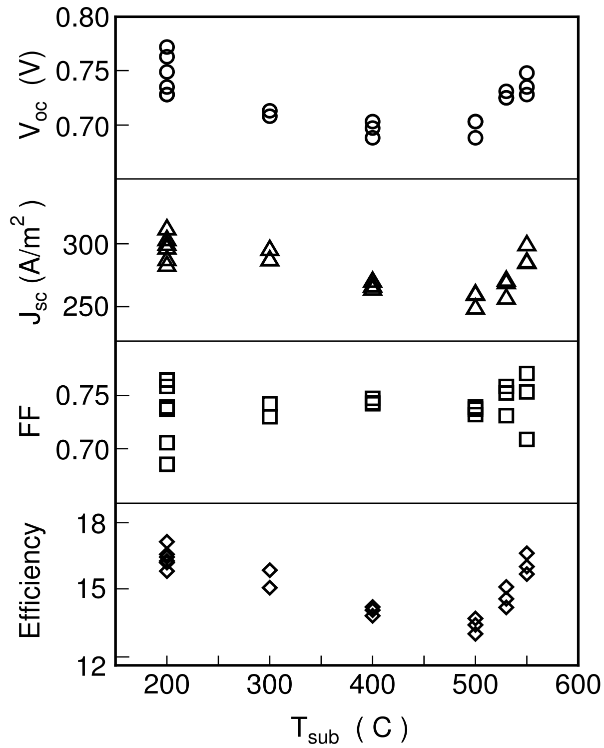

Fig. 1. Photovoltaic characteristics (under illumination of light from an AM1.5 $1\mathrm{kW/m^2}$ solar simulator) of In_2O_3/InP cells as a function of substrate temperature T_{sub} during deposition of In_2O_3 film.

3 Results

3.1 Photovoltaic characteristics

Figure 1 shows characteristics of In_2O_3/InP cells under illumination as a function of substrate temperature T_{sub} during deposition of the In_2O_3 film. Open circuit voltage V_{oc} and short circuit current density J_{sc} decreased with the increase of substrate temperature. Consequently, the conversion efficiency of the cell was decreased from 16.5% for the cell fabricated at the condition of $T_{sub} = 200$°C to 13.5% for the cell of $T_{sub} = 500$°C. As compared with the changes of the open circuit voltage and the short circuit density, the value of fill factor less depended on the substrate temperature. When the In_2O_3 film was deposited at higher substrate temperatures, T_{sub} >500°C, the conversion efficiency of In_2O_3/InP cells were improved with the increase of substrate temperature. The conversion efficiency of the cell fabricated at the highest temperature of T_{sub}=550°C became up to 16.7%.

Junction capacitance C of the cell in the relation of applied reverse bias voltage V was measured in the dark. Inverse square of measured capacitance ($1/C^2$) was a linear function of the

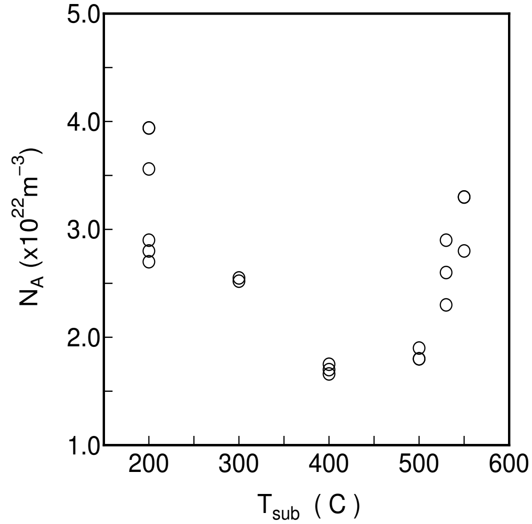

Fig. 2. Acceptor concentration N_{A} at the interface of $\mathrm{In_2O_3/InP}$ cell as a function of substrate temperature T_{sub} during deposition of $\mathrm{In_2O_3}$ film.

applied voltage. Figure 2 shows the acceptor concentration N_{A} which was derived from the dark C-V characteristics as a function of substrate temperature T_{sub}. Change of acceptor concentration depends on the value of substrate temperature. The tendency of the relation between the acceptor concentration N_{A} and the substrate temperature T_{sub} can be divided in two parts at the temperature T_{sub}=500°C. This is similar to the relation between the photovoltaic characteristics of the cell and the substrate temperature which was shown in Fig. 1. However, the value of acceptor concentration scattered for the cell fabricated at higher substrate temperatures of $T_{\mathrm{sub}} > 500$°C.

Figure 3 shows the relation between the open-circuit voltage V_{oc} and the acceptor concentration N_{A} for the cell fabricated at various substrate temperatures. Annealing temperature T_{ann} for forming an ohmic contact was 450 or 500 °C. It is clear that the open-circuit voltage increases linearly with the increase of the acceptor concentration. Consequently, the dependence of the cell characteristics on the substrate temperature which was shown in Fig. 1 was thought to be caused by the change of the acceptor concentration.

A value of open-circuit voltage V_{oc} is described by the following well known equation,

$$V_{\mathrm{oc}} = \frac{nkT}{q} \ln\left(1 + \frac{J_{\mathrm{sc}}}{J_0}\right), \tag{1}$$

where n is a diode factor, k is Boltzmann's constant, T is the absolute temperature, q is electronic charge magnitude and J_0 is diode saturation current density. This equation means that the change of the open-circuit voltage depended on that of the diode factor n and the saturation current density J_0. Figure 4 shows a relation between the diode saturation current density J_0 derived from the measured I-V characteristics in the dark and the acceptor concentration N_{A}. It

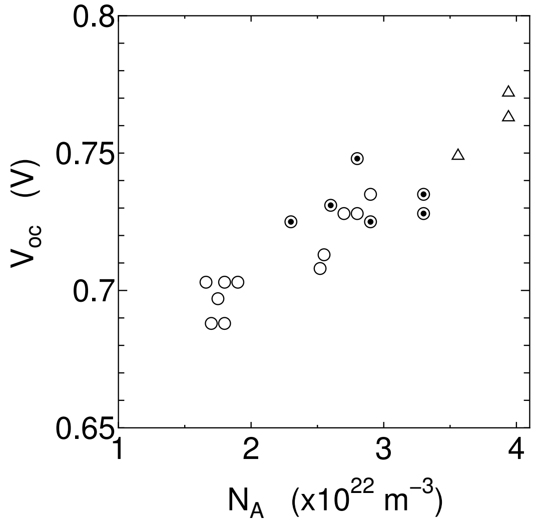

Fig. 3. Relation between open-circuit voltage V_{oc} under illumination and acceptor concentration N_A of In_2O_3/InP cells prepared at annealing temperature of T_{ann} for forming an ohmic contact and at various substrate temperatures T_{sub}. $\circ$: T_{ann}=450°C and T_{sub} $\leq$500°C, $\odot$: T_{ann}=450°C and T_{sub} >500°C, $\triangle$: T_{ann}=500°C and T_{sub}=200°C.

is observed that the saturation current density J_0 decreases strongly depending on the increase of the acceptor concentration N_A, except when the samples annealed at high temperatures (higher than 500°C). On the other hand, the values of diode factor n were almost constant (about 1.5) over the same range of the acceptor concentration change, as shown in Fig.5. Consequently, the dependence of the open-circuit voltage on the variation of acceptor concentration could be explained mainly by the change of the diode saturation current density. The short-circuit photocurrent density J_{sc}, another term in equation (1), also increased with the increase of acceptor concentration. However, the magnitude of improvement of the open-circuit voltage by change of the short-circuit current density is thought to be much smaller than by that of the saturation current density, in present case. A good photovoltaic characteristics was obtained also for the cell fabricated at high substrate temperature, T_{sub}=550°C. However, the short-circuit current density, the diode factor and the acceptor concentration for the cell fabricated at higher substrate temperatures of $T_{sub} > 500$°C were scattered in wide range. Courses of improvement of the open-circuit voltage of these cells in high heat treatment temperature range are not well known yet.

3.2 Effects of heat treatment on acceptor concentration of InP bulk

The acceptor concentration at the interface of the In_2O_3/InP junction was depended on the substrate temperature as shown in Fig. 2. However, it is noted that even the smallest acceptor concentration value for the cell which fabricated at the substrate temperature of $T_{sub} = 400$°C was about ten times as large as the bulk acceptor concentration value derived from the measured

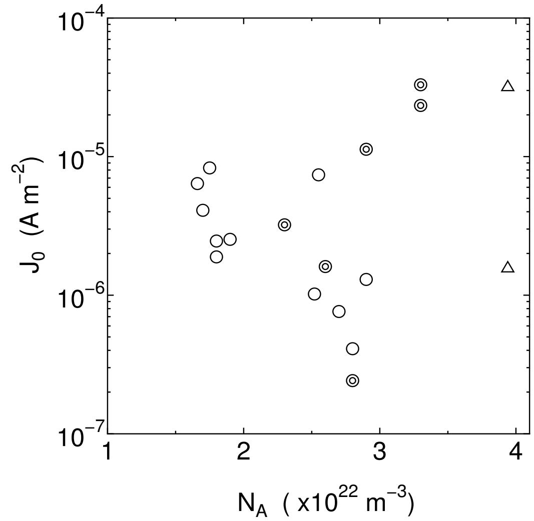

Fig. 4. Diode saturation current density J_0 as a function of acceptor concentration N_A of $\mathrm{In_2O_3/InP}$ cells prepared at annealing temperature of T_ann for forming an ohmic contact and at various substrate temperatures T_sub. $\circ$: T_ann=450°C and T_sub $\leq$500°C, $\odot$: T_ann=450°C and T_sub >500°C, $\triangle$: T_ann=500°C and T_sub=200°C.

Hall constant. It is thought that the acceptor concentration increased drastically during the ohmic contact fabrication process by heat treatment. In order to analyze the cause of the increase of acceptor concentration in detail, depth profiles of that in the bulk were measured. The analyzing method used in this study was described in the section 2.

Figure 6 shows depth profiles of the acceptor concentration for the InP bulk wafers which were annealed in argon flow at temperatures of 400, 450 or 500°C in 10 min. It was revealed by means of the repetition of removing the bulk surface by etching and C-V measurement that the acceptor concentration value was gradually decreased from the surface to that in the deep of the wafer. The acceptor concentration near the surface was about ten times as large as that at inside in the bulk. With the increase of annealing temperature, the acceptor concentration near the surface became large. The value of acceptor concentration at the InP surface shown in Fig.6 is almost the same as that observed at the interface of the $\mathrm{In_2O_3/InP}$ cell shown in Fig.2. The acceptor concentration at deep inside of the bulk is saturated at about 1×10^{21} m^{-3} and is regarded as the initial doping density in the bulk. This value is different from the acceptor concentration derived from the measured Hall constant (2.6×10^{21} m^{-3}) for the same InP bulk. The reason why this difference occurred is explained as follows. Acceptor concentration values calculated from the measured Hall constants stand for the average of magnitude of entire bulk. Since Hall measurement was done after the heat treatment of deposited gold film to make a van der Pauw electrode, in this case, acceptor concentration at surface of the bulk was increased compared to the initial doping value. So, the calculated value from the Hall constant, which shows the mean value of entire bulk, is expected larger than initial doping value.

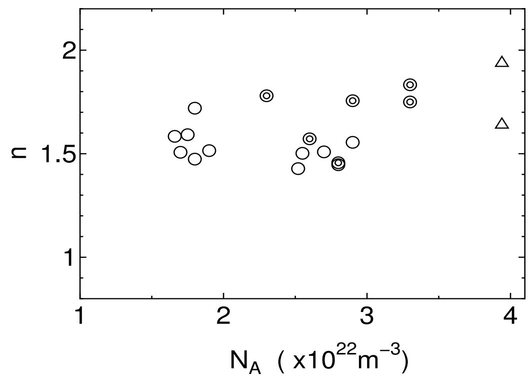

Fig. 5. Diode factor n as a function of acceptor concentration N_A of In_2O_3/InP cells prepared at annealing temperature of T_{ann} for forming an ohmic contact and at various substrate temperatures T_{sub}. ∘: T_{ann}=450°C and T_{sub} ≤500°C, ⊙: T_{ann}=450°C and T_{sub} >500°C, △: T_{ann}=500°C and T_{sub}=200°C.

Figure 7 shows the depth profiles of acceptor concentration in the InP wafers which have different initial doping density after annealing in argon flow at 450°C in 10 min. Hall measurement was also made for the nonannealed wafer. Relatively low resistive ohmic contact could be made on the wafer which was initially doped to the order of 10^{22} m^{-3}. The obtained acceptor concentration value of $N_A = 1.7 \times 10^{22}$ m^{-3} was smaller than that for the annealed wafer (2.2×10^{22} m^{-3}), but was fairly well coincide with the value for the deep inside of the bulk ($\sim 1.5 \times 10^{22}$ m^{-3}) derived from the C-V measurement. The magnitude of the increase in the acceptor concentration was very small for the wafer with high initial doping density on the order of 5×10^{23} m^{-3}. The depth profile of the acceptor concentration for the wafer, which initially doped to 10^{22} m^{-3}, after annealing in 60 min at 450°C is also shown in Fig. 7. The concentration at the surface became lager with the increase of the annealing time.

4 Discussion

The experimental results shown in Figs. 6 and 7 suggest that the acceptor concentration of the InP wafer was modified due to diffusion of some kind of impurities during heat treatment process. In order to explain the cause of the concentration change, two types of diffusion process were considered. One is a indiffusion process of impurities from surface to inner bulk. The other is a process of outdiffusion of interstitial zinc atoms which were initially contained in the InP bulk.

Firstly, an indiffusion process, which can describe by the complementary error function, for any impurities such as heavy metal atoms was considered. By assuming a pair of parameters for two different impurities which will be diffusing into the InP wafer, a successful curve fitting to the experimental data was achieved by the sum of these two diffusion processes. The chosen pair of diffusion constant for the profile of the wafer annealed at 450°C in 10 min were 2.3×10^{-12} m^2/s and 1.2×10^{-13} m^2/s. To our best knowledge, however, there are no heavy metal atoms which has such a diffusion constant. Only copper seems to have a similar value of

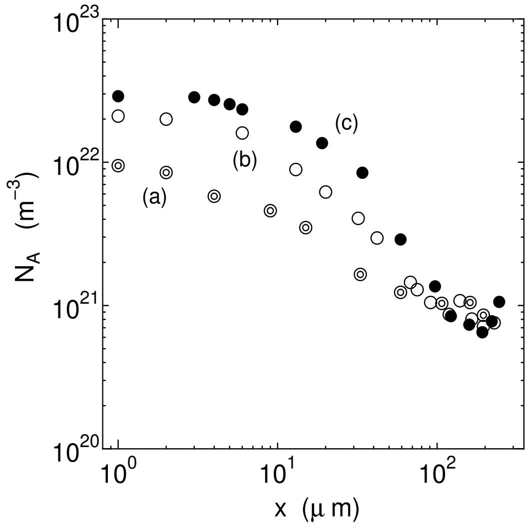

Fig. 6. Depth profiles of acceptor concentration N_{A} in InP single crystal wafers after heat treatment in argon flow at various temperature T_{ann}=(a)400, (b)450, (c)500°C. Initial doping density of the crystal was on the order of $10^{21}\ \mathrm{m}^{-3}$.

diffusion constant in InP [7] but the solid solubility of copper in InP [7] is too small to explain the observed large increase of the acceptor concentration.

Wang and Bube [5] investigated the heat treatment effect on the InP crystals. They concluded that the effect could be described by the outdiffusion of interstitial zinc during heat treatment, reducing the compensation of substitutional zinc acceptors. After the reference [5], the following equation was adopted to simulate the data,

$$\frac{S}{S_0} = \operatorname{erf}\left(\frac{x}{2(Dt)^{1/2}}\right) + \exp\left(\frac{\alpha x}{D} + \frac{\alpha^2 t}{D}\right) \times \operatorname{erfc}\left[\frac{x}{2(Dt)^{1/2}} + \alpha\left(\frac{t}{D}\right)^{1/2}\right], \qquad (2)$$

where S is the concentration of interstitial zinc, S_0 is the original dopant density in the solid, t is the length of heat treatment time and x is the depth into the bulk. D is the diffusion constant of the interstitial zinc, α is the surface evaporation constant of the interstitial zinc,

In Fig. 8, lines show the curve fittings for experimental results in terms of the outdiffusion of interstitial zinc by annealing. The diffusion constant D and surfaces evaporation ratio α of the interstitial zinc which were chosen here to calculation are shown in Table I.

The larger value of D and α were chosen to simulate the data for the wafer annealed at higher temperature. The effect of annealing time on acceptor concentration was able to simulate only by change the term of annealing time t using the same value of D and n. The change of normalized acceptor concentration $(S_0 - S)/S_0$ into bulk wafers, which have different initial doping densities, were able to simulate by the same theoretical curve. Consequently, it is thought that the acceptor concentration change can be explained in terms of the outdiffusion of interstitial zinc.

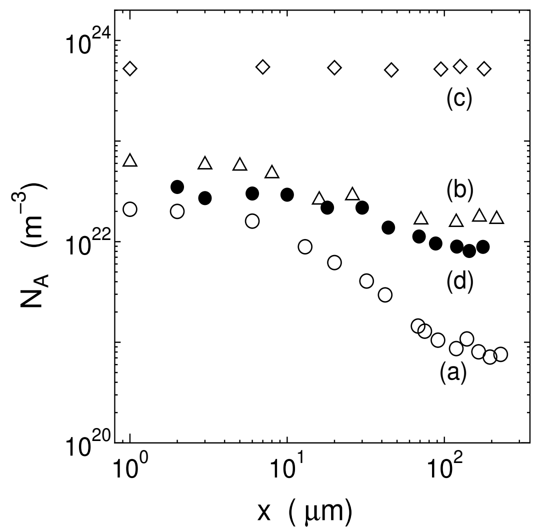

Fig. 7. Depth profiles of acceptor concentration N_A in InP with various initial doping density, after heat treatment in argon flow at $T_{ann} = 450°C$ in 10 min (a)–(c) or 60 min (d). Initial doping densities are (a) and (d) $2.6 \times 10^{21} m^{-3}$, (b) $2.2 \times 10^{22}\ m^{-3}$, (c) $5.9 \times 10^{23}\ m^{-3}$.

In the process of fabrication of the In_2O_3/InP heterojunction cell, the InP substrate was heat treated not only during fabrication of ohmic contact but also during the deposition of In_2O_3 film. The change of acceptor concentration is thought to be affected by both of these two heat treatment processes. Namely, the value of acceptor concentration is increased by the first annealing and then modified (decreased) by the second substrate heating. The latter modification of the acceptor concentration may be occurred as follows. Since the In_2O_3 film is deposited on the surface during the second heat treatment, the evaporation of outdiffused zinc is prevented by this surface layer. Thus the interstitial zinc pile up near the In_2O_3/InP interface to increase the compensation of substitutional zinc acceptor.

Acceptor concentration at the interface is preferable being high, after two heat treatment processes, to improve the open-circuit voltage of the In_2O_3/InP cell. Since the condition of forming an ohmic contact is not able to choice in wide range, the photovoltaic characteristics seems to be affected rather significantly by the substrate temperature during the In_2O_3 film deposition. The experimental results indicates that higher acceptor concentration is obtained when the cell was fabricated at the substrate temperatures of $T_{sub} = 200$ or 550°C. However, the large acceptor concentration of the cell fabricated at the higher substrate temperature of $T_{sub} > 500°C$ cannot explain in terms of the way mentioned above. In order to fabricate a good performance In_2O_3/InP heterojunction cell, the lower substrate temperature during deposition of the In_2O_3 film is thought to be preferable according to following observations; (1) No deposit of In_2O_3film on the InP substrate was observed when the substrate was heated to 570°C during deposition. (2) It was reported [8] that the InP surface was decomposed by annealing in vacuum at higher than 475°C. (3) The characteristics of the cell fabricated at the substrate temperature higher than

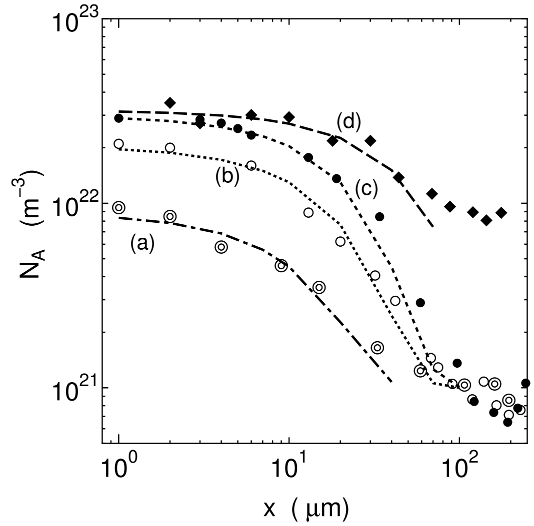

Fig. 8. Depth profiles and calculated curves of acceptor concentrations for InP single crystals after heat treatment. (a)$T_{\rm ann} = 400°$C, 10min, (b)450°C, 10min, (c)500°C, 10min and (d)450°C, 60min.

500°C showed a tendency of fluctuation. However, In_2O_3 film deposited at the substrate temperature lower than 150°C is not suitable to use in window material due to its low transmittance (lower than 40% in visible light range) compared with those for the film deposited at the temperature of $T_{\rm sub} > 200°$C.

5 Summary

Photovoltaic characteristics of the In_2O_3/InP heterojunction cell was found to depend on the acceptor concentration at the interface. High value of acceptor concentration was preferable to obtain the high performance cell because the larger open-circuit voltage can be achieved due

Tab. 1. Sets of diffusion constant D and surfaces evaporation ratio α of the interstitial zinc chosen to calculation in this study.

Annealing temperature (°C)	D ($m^2 \cdot sec^{-1}$)	α ($m \cdot sec^{-1}$)
400	2.5×10^{-13}	3.5×10^{-9}
450	5.5×10^{-13}	1.7×10^{-8}
500	7×10^{-13}	4×10^{-8}
*500 (in H_2)	$*3 \times 10^{-13}$	$*3 \times 10^{-8}$

* data in Ref.[5]

to decrease of diode saturation current of the cell with the increase of acceptor concentration. The value of acceptor concentration was modified by two steps of annealing. Firstly, the acceptor concentration at the interface is increased by annealing to form an ohmic contact to InP. Secondly, the increased acceptor concentration value is modified further by the substrate heating during deposition of transparent conductive surface layer of In_2O_3 film. The increase of acceptor concentration by former annealing was able to explain in terms of outdiffusion of the interstitial zinc in the InP bulk.

It is thought that highly efficient In_2O_3/InP heterojunction solar cell can be obtained by controlling the value of acceptor concentration at the interface. For this purpose, the low temperature deposition of In_2O_3 by reactive evaporation of indium is preferable.

Acknowledgement: The author would like to thank Prof. K. Ito (Shinshu Univ.) for valuable discussion, and Mr. M. Okeya for experimental assistance.

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