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Electrical and photovoltaic properties of Cu-doped *p*-GaSe/*n*-InSe heterojunction

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GaSe(Cu)/InSe heterojunctions have been formed by bringing the cleavage surface of undoped n-InSe and Cu-doped p-GaSe into direct contact. Transport and phototransport properties are studied by the measurements of capacitance–voltage, current–voltage, and the spectral response of short-circuit current. Moreover, the efficiency parameters under illumination are estimated by using the open-circuit voltage and short-circuit current. These characteristics of GaSe(Cu)/InSe heterojunctions are compared with those of GaSe(Un)/InSe heterojunctions fabricated by undoped p-GaSe and n-InSe. The series resistance of GaSe(Cu)/InSe heterojunctions is found, the value of which is about 10^3 times lower than the corresponding value of GaSe(Un)/InSe heterojunctions. A short-circuit current density of 9.0 mA/cm^2 and an open-circuit voltage of 0.42 V on GaSe(Cu)/InSe heterojunctions are obtained under illumination of 120 mW/cm^2 of a halogen lamp. The short-circuit current of GaSe(Cu)/InSe heterojunctions is about one order of magnitude lager than that of GaSe(Un)/InSe heterojunctions. These experimental results indicate that the low-resistivity of Cu-doped GaSe is effective for the electrical and photovoltaic properties of GaSe/InSe heterojunctions. [S0021-8979(00)03712-9]

I. INTRODUCTION

Layered III–VI InSe and GaSe compounds are very interesting as materials for photoelectronic devices. As for the GaSe/InSe heterojunction, only one fabrication technique has been successful. Bakumenko *et al.*[1] and Aver'yanova *et al.*[2] have formed a p-GaSe/n-InSe heterojunction by the optical contact method. The optical contact method is a simple technique involving the direct contact of two surfaces of different semiconductors. The optical contact is formed when the distance between the two surfaces is in the order of the radius of action of intermolecular forces.

Crystals of GaSe and InSe consist of a pile of packets in which atoms are bound by covalent and ionic-covalent bonds, whereas between the packets there are only weak van der Walls forces.[3] Based on the characteristics of the layer structure, the samples are easily cleaved parallel to the layer, and the resultant surfaces are extremely smooth. The chemical bonds in the layer materials are featured so that the surfaces are inert in relation to adsorption and have a low density of surface states.[4] The requirements for the formation of the optical contact are satisfied easily by these properties of the layer structure.

Some electrical and photoelectric properties of GaSe/InSe heterojunctions formed by this method have been investigated by capacitance–voltage ($C-V$) and current–voltage ($I-V$) characteristics in the dark and under illumination. The p-GaSe(Un)/n-InSe junction was fabricated by using undoped GaSe with $\sim 10^{13}\,\text{cm}^{-3}$ hole density and undoped InSe with $\sim 7\times 10^{15}\,\text{cm}^{-3}$ electron density.[1] The high resistance connects in series with the heterojunction in order to form the GaSe layer with high resistivity. High resistivity is a disadvantageous factor for fabrication of highly efficient solar cells.

The hole concentration in Cu-doped GaSe shows a strong increase in the added impurity concentration.[5] The resistivity is about three orders of magnitude lower than the corresponding value of undoped GaSe.[6]

In this article, a GaSe(Cu)/InSe junction is formed by using undoped n-InSe and Cu-doped p-GaSe with low resistivity. We report the detailed results of the $I-V$ and $C-V$ characteristics, and the spectral response of the short-circuit current. Moreover, we discuss the mechanisms of carrier transport across the junction in the dark and under illumination.

II. EXPERIMENT

The p-GaSe and n-InSe single crystals used in this study were grown by a conventional Bridgman technique. The p-GaSe was made by doping 0.1 at. % of Cu to the stoichiometric melt of GaSe. The n-InSe was obtained from undoped stoichiometric melts. The samples were prepared by cleaving an ingot parallel to the layer which was perpendicular to the c axis.

To study the donor and acceptor concentrations in the bulk of n-InSe and p-GaSe, Hall coefficient measurements were carried out by a conventional dc method. The current was flowed parallel to the layer plane and a magnetic field of 0.5 T was applied perpendicular to the plane. The Hall con-

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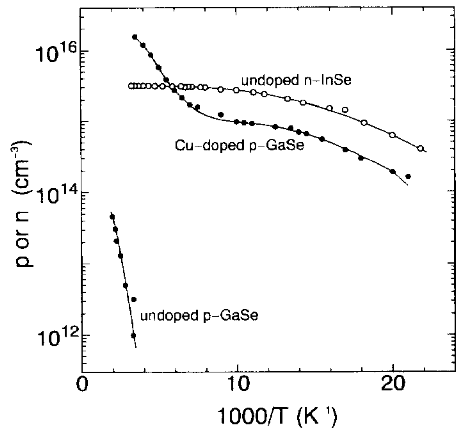

FIG. 1. Carrier concentrations as a function of reciprocal temperature for undoped p-GaSe, Cu-doped p-GaSe, and undoped n-InSe. The solid lines show the calculated hole and electron concentrations with the parameters in Table I.

tact was formed by evaporating In through a mask onto the samples. The indium contact was near Ohmic for the undoped GaSe and Ohmic in the case of the Cu-doped samples with low resistivity.

The heterojunctions were produced by bringing the natural cleavage surfaces of the uniform layer planes of n-InSe and p-GaSe into direct contact. These surfaces were mirror-like and no further etching treatment was necessary to make the optical contact. The thickness of n-InSe was about 200 μm and the thickness of p-GaSe was changed from 20 to 150 μm. The contacted planes were rubbed together. Then, the samples were placed between microscope slide glasses and left under a load of about 200 g/cm^2 for about 3 h. The four sides of the samples were cut. The contacts on both sides were formed by In evaporation.[5,7] The typical dimensions of the contact area were 3×3 mm^2. $C-V$ characteristics in the dark were performed at a modulation frequency of 10 kHz. $I-V$ measurements were carried out by a typical direct current method.

The spectral responses of the short-circuit current for photocells were obtained by a low-level monochromatic illumination of 5×10^{-2} mW/cm^2 using a grating monochrometer. The incident light intensity was normalized by a thermocouple detector. To prevent the influence of the In electrode, we used a ring-shaped upper electrode on the illuminated layer of photocells. The illuminated layer was the p layer of GaSe and the window size of the photocell was 9×10^{-2} cm^2. Solar efficiencies were measured under a halogen lamp with 120 mW/cm^2 and calibrated against a standard silicon photocell.

III. RESULTS AND DISCUSSION

Figure 1 shows the behavior of carrier concentrations as a function of the reciprocal temperature in n-InSe and p-GaSe. The carrier concentrations of holes p and electrons n were calculated from the Hall coefficient by assuming a Hall factor of unity. Analyses of experimental data for undoped InSe and undoped GaSe were already carried out by using the single-donor–single-acceptor model.[8,9] The best-fit curve is drawn by the solid line. The values of the parameter obtained from this model are summarized in Table I. The carrier transports of undoped n-InSe and p-GaSe are dominated by the shallow donor level at 0.025 eV below the conduction band and the deep acceptor level at 0.49 eV above the valence band, respectively.

After Cu doping to the GaSe, stoichiometric melt, p increased more than that of the undoped sample, displaying two slopes for p above and below 100 K. We analyzed the experimental result by using a compensated nondegenerate two-acceptor model.[5] The best-fit curve is drawn by the solid line. The values of the parameters for fitting also are shown in Table I. The positions of the deep and shallow acceptor energy levels evaluated by fitting are about 0.12 and 0.038 eV above the valence band. The shallow acceptor level of 0.038 eV is attributed to Cu atoms, whereas the deep acceptor level of 0.12 eV is governed by the defects or defect complexes. The acceptor concentration of the Cu-doped GaSe is about three orders of magnitude larger than the value of the undoped sample. On the other hand, a resistivity of 1.1×10^1 Ω cm was obtained in the Cu-doped sample and was about three orders of magnitude lower than the corresponding value of undoped GaSe.[6] Therefore, the low resistivity of the Cu-doped sample is caused by the increase of the acceptor concentration.

Figure 2 shows the $C-V$ characteristics at reverse biased voltage for the GaSe(Cu)/InSe and GaSe(Un)/InSe junctions. Since the dependence of C^{-2} on V is followed by the straight line, the step junction model is applicable for the GaSe/InSe junctions. The value for the diffusion voltage V_d obtained from the intersection of the straight line with abscissa was found to be in the range from 0.60 to 0.71 eV, as shown in Table II.

The dependence of C on V in the given range can be expressed as[10]

TABLE I. Electrical properties of undoped GaSe, Cu-doped GaSe, and undoped InSe. The acceptors (N_{a1},N_{a2}), donor (N_d) concentrations, and the thermal ionization energies of the acceptors (E_{a1},E_{a2}) and donor (E_d) were obtained from the Hall effect in Refs. 8 and 9

Sample	N_d ($\times10^{13}$ cm^{-3})	E_d (eV)	N_{a1} ($\times10^{14}$ cm^{-3})	E_{a1} (eV)	N_{a2} ($\times10^{14}$ cm^{-3})	E_{a2} (eV)
n-InSe (undoped)	460	0.025	14			
p-GaSe (undoped)	0.030		0.72	0.49		
p-GaSe (Cu-doped)	3.1		210	0.12	11	0.038

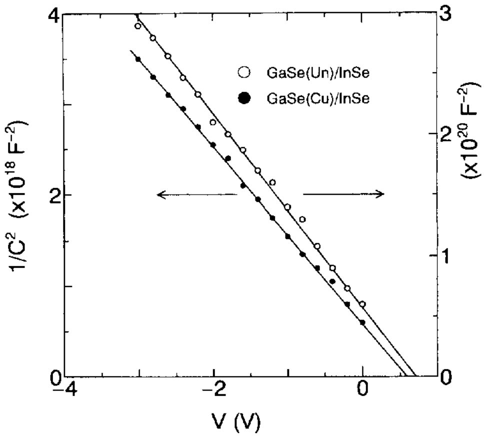

FIG. 2 Capacitance–voltage characteristics of the GaSe(Cu)/InSe and GaSe(Un)/InSe heterojunctions. The solid lines indicate the calculated C^{-2} from Eq. (1) with the parameters in Table I.

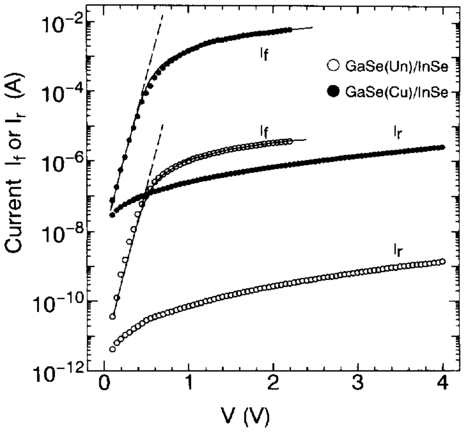

FIG. 3. Current–voltage characteristics of the GaSe(Cu)/InSe and GaSe(Un)/InSe heterojunctions. The solid lines indicate the plot of Eq. (2) with the parameters in Table II.

$$\frac{1}{C^2}=\frac{2(\epsilon_n N_{dn}+\epsilon_p N_{ap})}{S^2 q N_{dn} N_{ap} \epsilon_n \epsilon_p}(V_d-V), \qquad (1)$$

where S is the contact area, q is the electronic charge, and N_{dn} and N_{ap} are the concentrations of noncompensated ionized donor in the n layer and the acceptor in p layer, respectively. ϵ_n and ϵ_p are the static dielectric constant equal to $6.5\epsilon_0$ for InSe and $8.45\epsilon_0$ for GaSe,[1] and $\epsilon_0=8.85\times 10^{-14}$ F/cm. The values of calculated C^{-2} are drawn by the solid lines. For the fit, the values of N_{dn} and N_{ap} are given by $N_{dn}=N_d-N_{a1}$ and $N_{ap}=N_{a1}+N_{a2}-N_d$ and use the results of the Hall effect in Table I. The experimental results of C are in agreement with the calculated values. The value of V_d for the GaSe(Un)/InSe junction is higher than that of the GaSe(Cu)/InSe junction. It would be expected that V_d decreases with increasing the impurity concentration. The anomalous effect has been observed in Si junction.[11] One possible origin is considered to be the change of the density of the interface states. In Fig. 2, the experimental slope agrees with that from the calculated result. The concentrations of the ionized donor and acceptor in the space-charge region appear the same as the concentrations of the donor and acceptor in bulk materials. Since the $C-V$ characteristic can be accounted for by normal diode theory, it is expected that the direct contact of the GaSe and InSe layers behaves as a reasonably good step junction.

Figure 3 shows the $I-V$ characteristics of the GaSe(Cu)/InSe and GaSe(Un)/InSe junctions whose $C-V$ characteristics are given in Fig. 2. The forward and reverse currents of the GaSe(Cu)/InSe junction were about three orders of magnitude larger than that of the GaSe(Un)/InSe junction and were significantly influenced by adding an amount of Cu.

TABLE II. Electrical parameters for GaSe(Cu)/InSe and GaSe(Un)/InSe heterojunctions.

Junction	V_d (V)	n	I_0 ($\times 10^{-10}$ A)	R_s ($\times 10^5\ \Omega$)
GaSe(Cu)/InSe	0.60	1.9	90	0.0025
GaSe(Un)/InSe	0.71	1.8	0.042	4.0

The forward current–voltage (I_f-V) characteristics have an exponential behavior at the voltage region with $V<0.4$ V. At the voltage region $V>0.5$ V, the I_f-V characteristics deviate from the linear relation between $\log I_f$ and V. The degree of deviation of the GaSe(Cu)/InSe junction is lower than that of the GaSe(Un)/InSe junction.

The I_f-V characteristic can be expressed as[12] .

$$V=\frac{nkT}{q}\ln\left(\frac{I_f}{I_0}+1\right)+I_f R_s, \qquad (2)$$

where n is a diode factor, I_0 is the saturation current, and R_s is the series resistance. Using Eq. (2), the fits for experimental values were made with I_0, R_s and n as parameters. The best-fit curves of I_f are shown by the solid lines in Fig. 3. The estimated values of the parameters are listed in Table II. The value of R_s obtained in the GaSe(Cu)/InSe junction was about three orders of magnitude lower than that of the GaSe(Un)/InSe junction. This behavior is due to the low resistance of the bulk material of Cu-doped GaSe because the carriers increase in the Cu-doped samples. The obtained n value of about 1.9 suggests recombination either through the level in the depletion region[13] or through the interface states,[14] both of which are capable of yielding values between 1 and 2.

The temperature dependence of I_0 of the GaSe(Cu)/InSe junction is shown in Fig. 4. The plot of I_0 varied with temperature is in accordance with the law $I_0 \propto \exp(-\Delta E/kT)$, where ΔE is the activation energy. The value of $\Delta E=0.14$ eV was derived from the slope of the straight line and almost agrees with the activation energy of the deep acceptor level at 0.12 eV in the Cu-doped GaSe, as shown in Table I. It is found that the carrier transport of the GaSe(Cu)/InSe junction is dominated by the impurity level in the band gap.

The reverse currents I_r for the GaSe(Cu)/InSe and GaSe(Un)/InSe junctions increase gradually with increasing V, as shown in Fig. 3. A similar I_r-V characteristic has been observed in the Si junction under small and medium bias lower than 6 V.[15] The current for small reverse bias is due to the generation and recombination of carriers in the space-charge region. Moreover, the current for medium bias is

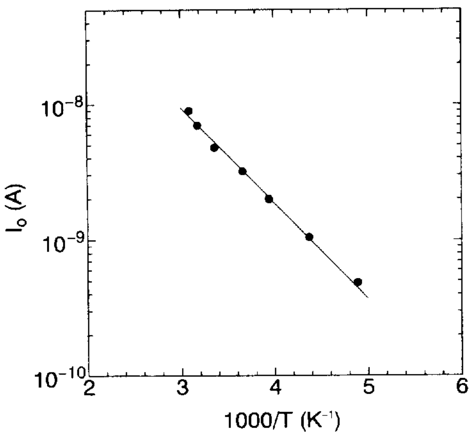

FIG 4 Saturation current I_0 as a function of reciprocal temperature for the GaSe(Cu)/InSe heterojunction.

caused by the surface leakage or defects in the junction. The variation of the reverse current with V for the GaSe(Cu)/InSe junction is smaller than that of the GaSe(Un)/InSe junction. This result indicates that the $I_r - V$ characteristic of the GaSe(Cu)/InSe junction approaches the ideal diode behavior, which includes a saturation of current with reverse bias.

Figure 5(a) shows the spectral responses of the short-circuit current of GaSe(Cu)/InSe photocells with the p-GaSe layer thickness as a parameter. The spectral responses of GaSe(Un)/InSe photocells are also indicated by a comparison in Fig. 5(b). The spectral distribution of the photosensitivity of the photocells covers a wide range of photon energies between the band gaps of the InSe ($E_g = 1.26\,\mathrm{eV}$) (Ref. 16) and GaSe ($E_g = 2.02\,\mathrm{eV}$) (Ref. 17) single crystals. The short-circuit current decreases with increasing thickness of the GaSe layer. Moreover, the photocurrent at the short-wavelength region larger than the band-gap energy is much more influenced by the absorption of GaSe layer. When the GaSe layer for the GaSe(Un)/InSe photocell was thick, there was no significant photosensitivity, as shown in Fig. 5(b). This result indicates that the larger part of the contact potential drop occurred in GaSe with high resistivity. The photosensitivity of the GaSe(Cu)/InSe photocell was larger than that of the GaSe(Un)/InSe photocell. The main reason for this high intensity is the large reduction in the series resistance brought about by the doping effect of Cu atoms.

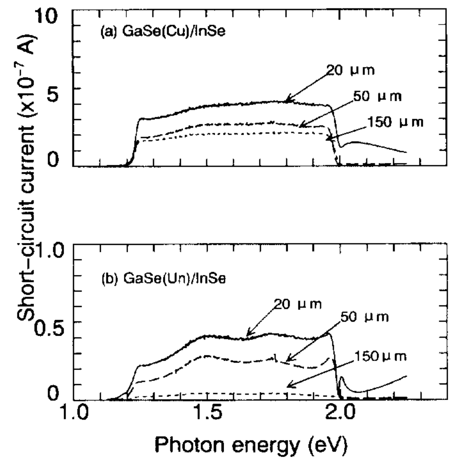

FIG 5. Spectral responses of the short-circuit current of (a) GaSe(Cu)/InSe and (b) GaSe(Un)/InSe photocells under low-level monochromatic illumination for 5×10^{-2} mW/cm^2. The illuminated layer of photocells is the GaSe layer. The thickness of the GaSe layer was changed from 20 to 150 μm.

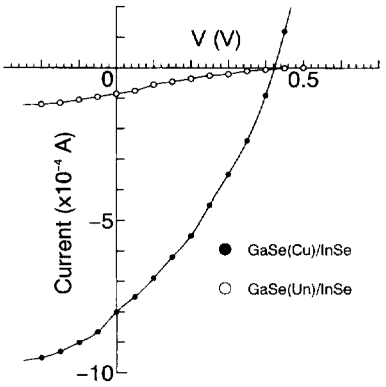

FIG. 6 Current–voltage characteristics of GaSe(Cu)/InSe and GaSe(Un)/InSe photocells under illumination for 120 mW/cm^2 of a halogen lamp.

Figure 6 shows a typical $I-V$ characteristic under illumination from the side of the wide-band-gap GaSe layer at 120 mW/cm^2 by a halogen lamp. The open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), solar efficiency (ζ), and fill factor (ff) are listed in Table III. The value of V_{oc} is independent between the GaSe(Cu)/InSe and GaSe(Un)/InSe photocells. However, the values of I_{sc} and ζ of the GaSe(Cu)/InSe photocell are about one order of magnitude larger than those of the GaSe(Un)/InSe photocell. The high efficiency of the GaSe(Cu)/InSe photocell is due to the large reduction in the series resistance by Cu doping and creates a strong influence on the photocurrent in GaSe. The solar cell characteristic is improved very greatly for the GaSe(Cu)/InSe photocell.

IV. CONCLUSION

Using Cu-doped p-GaSe with low resistivity, GaSe/InSe heterojunctions were formed by a simple direct contact method. The carrier transport of the forward current is due to the recombination through the level in the depletion region or through the interface states. The reverse current is controlled by the generation and recombination of carriers and the surface effect. The series resistance of the GaSe(Cu)/InSe junction was about three orders of magnitude lower than that of the GaSe(Un)/InSe junction. We found that the low resistivity of Cu-doped GaSe is useful for the electrical and photovoltaic properties of the GaSe/InSe junction.

TABLE III Efficiency parameters for GaSe(Cu)/InSe and GaSe(Un)/InSe photocells The thickness of the illuminated GaSe layer is 20 μm.

Photocell	V_{oc} (V)	I_{sc} (mA/cm^2)	ζ (%)	ff (%)
GaSe(Cu)/InSe	0.42	9.0	1.1	34
GaSe(Un)/InSe	0.42	1.0	0.056	16

ACKNOWLEDGMENT

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