Homojunction diode of $CuInSe_2$ thin film fabricated by nitrogen implantation

M. Nishitani, T. Negami, S. Kohiki, M. Terauchi, T. Wada, and T. Hirao
Central Research Laboratories, Matsushita Electric Industrial Co. Ltd., Moriguchi, Osaka 570, Japan

(Received 29 September 1992; accepted for publication 9 April 1993)

Rectifying homojunction have been fabricated in polycrystalline $CuInSe_2$ thin film. The *p-n* junction diode was obtained by short annealing in nitrogen atmosphere at 450 °C following the ion implantation of nitrogen with the energy and the dose of 50 keV and 1×10^{15} cm^{-2}, respectively. The properties of the near surface region in the films implanted have been studied by the Raman scattering spectroscopy. The secondary ion mass spectroscopy depth profile of the nitrogens in the $CuInSe_2$ film and the capacitive-voltage characteristics of the rectifying diode have been measured to characterize the junction properties. The photovoltaic characteristics in AM 1.0, 100 mW/cm^2 are shown with the efficiency of 0.35%.

I. INTRODUCTION

$CuInSe_2$ thin films are attractive for photovoltaic application. Several research groups have already succeeded in fabricating a highly efficient solar cell using $CdS/CuInSe_2$ heterojunction structure.[1–3] However, homojunction cells constructed of polycrystalline thin films of $CuInSe_2$ have not been reported yet. Spitzer *et al.* reported the theoretical limit efficiency for a $CuInSe_2$ homojunction cell, which discussed its dependencies on the parameters such as cell thickness, junction depth, acceptor concentration, and surface recombination velocity.[4] They showed that in the $CuInSe_2$ homojunction solar cell, the fabrication of an extremely shallow junction is an important way to realize the high efficiency. To realize such efficiency, electrical neutralization technology of grain boundaries is required for high efficiency in the homojunction solar cell constructed from polycrystalline thin films.

Electrical properties of $CuInSe_2$ thin films strongly depend on the Cu/In and (Cu+In)/Se composition ratios. The conduction type of the $CuInSe_2$ thin film can be controlled by control of the stoichiometric composition.[5] However, the conductivity and the carrier concentration of these films is difficult to control for both conduction types. Noufi *et al.*[6] showed that *p*-type $CuInSe_2$ thin films with a single phase could be obtained only in the limited composition region called "the V shaped region," where the hole concentrations ranged from 10^{14} to 10^{20} cm^{-3}, and that highly conductive films could not be obtained in *n*-type $CuInSe_2$ thin films due to compensation.

Fundamental research on doping and fabrication of homojunctions or homojunction devices has been investigated by the diffusion or the implantation of various elements into single crystals of $CuInSe_2$. The diffusion of Cd[7] or In[8] was employed for the fabrication of homojunctions based on *p*-type single crystal, and the diffusion of Cu,[9] a short anneal process in Se vapor[10] and the implantation of oxygen[11] was employed to fabricate homojunctions in *n*-type single crystals. Tomlinson *et al.*[12] showed a significant effect on the resistivity and the photoconductivity in addition to conduction type conversion in the near surface region of a $CuInSe_2$ single crystal subjected to ion bombardment using oxygen, helium, and neon. Moreover, in a polycrystalline $CuInSe_2$ thin film, Kohiki *et al.* also reported that both the conduction type and the resistivity of *n*-type $CuInSe_2$ thin films could be changed by nitrogen implantation.[13]

In the present work, we report that homojunctions based on *n*-type polycrystalline thin films of $CuInSe_2$ have been fabricated by a short annealing process following nitrogen implantation. These junctions were characterized by Raman scattering spectroscopy, secondary ion mass spectroscopy, and capacitance-voltage measurement. In addition, we show that the photovoltaic characteristics of a homojunction were measured by using a very thin Au electrode as a transparent electrode.

II. EXPERIMENT

The $CuInSe_2$ films used in this experiment were coevaporated onto Mo-coated glass substrates by using a molecular beam deposition system. The substrate temperature was held at 475 °C. The preparation and the characterization of the $CuInSe_2$ are described elsewhere in detail.[5,14] The films were about 1.5 μm thick, and have a slightly In-rich composition showing *n*-type conduction. The electrical conductivity, the Hall mobility, and the electron concentration were deduced to be about 1×10^{-4} Ω^{-1} cm^{-1}, 100 cm^2/V s, and 1×10^{15} cm^{-3}, respectively, from the measurement on the film simultaneously prepared on the glass substrate.

Ion implantations of $^{14}N^+$ were performed by a scanning ion beam with an energy of 50 keV. The doses were varied from 1×10^{13} to 1×10^{15} $ions/cm^2$ by changing the implantation time and the scanning ion beam current. Reduced ion beam current densities were about 70–700 nA/cm^2. All samples used for implantation were heated up somewhat during the implantation.

III. RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) show the Raman scattering spectra as a function of the dose of the nitrogen implantation before and after annealing, respectively. The annealing of the nitrogen-implanted films was performed at 450 °C in

 0021-8979/93/74(3)/2067/4/$6.00 © 1993 American Institute of Physics

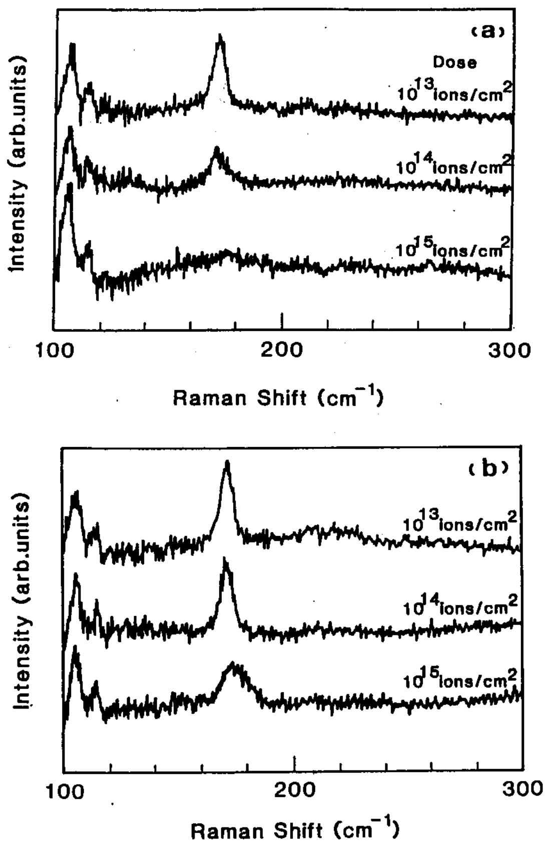

FIG. 1. Raman scattering spectra of nitrogen-implanted $CuInSe_2$ films as a function of implantation dose: (a) as ion implanted, (b) after anneal in nitrogen atmosphere at 450 °C for 1 min.

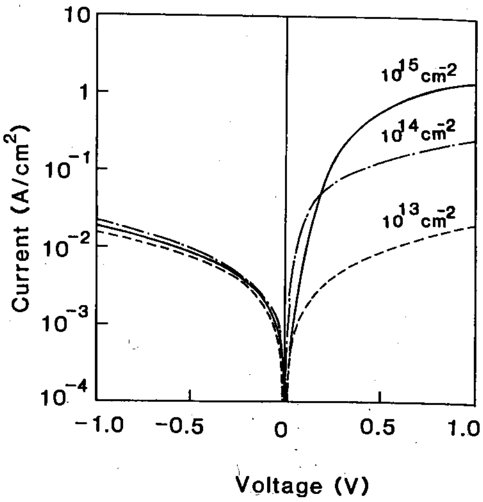

FIG. 2. Current-voltage characteristics of a $CuInSe_2$ homojunctions fabricated by implanting nitrogen into the surface of n-type $CuInSe_2$ films. The nitrogen implantation doses were 10^{13}, 10^{14}, and 10^{15} cm^{-2} at an ion energy of 50 keV.

nitrogen atmosphere for 1 min. The 514.5 nm wavelength of an Ar ion laser was used for the measurement in back-scattering configuration, so that the near surface region of the nitrogen-implanted film was probed.

In the Raman scattering measurement of the $CuInSe_2$ film, we can usually observe the A_1 mode of the chalcopyrite structure around 175 cm^{-1}, corresponding to the twisting mode of Se atoms.[15] As shown in Fig. 1(a), the scattering intensity of the A_1 mode decreased in the as-implanted films as the dose of the nitrogen implanted was increased to 1×10^{15} cm^{-2}. We hypothesize that for a dose of more than 1×10^{15} cm^{-2}, the crystal structure was destroyed by the implantation damage and may have changed to the amorphous phase. Mullan *et al.*[16] reported that the amorphous phase was observed in the near surface region of a $CuInSe_2$ single crystal implanted with oxygen an energy of 40 keV and a dose of 5×10^{16} cm^{-2}.

As shown in Fig. 1(b), the A_1 mode was observed in all spectra after annealing the damage suffered from the nitrogen implantation. However, the spectra also show that the A_1 mode became broader and that the peak shifted to a higher wave number as the dose of the implantation increased. According to a simplified version of the extended Keating model for the chalcopyrite structure,[16] the frequency of the A_1 mode can be described by the mass of the Se atom and the two bond-stretching force constants, corresponding to the interaction between nearest neighbors. Therefore, the broadening and peak shift of the A_1 mode suggests that the films have strain in the implanted region and that the strain changes the force constants and/or that the nitrogens implanted in the near surface region of the films occupy Se sites instead of Se atoms.

Figure 2 shows the dark static current-voltage characteristic as a function of the dose of nitrogen implantation. Au films were used for the upper electrode. The annealing conditions were the same as described above. Forward bias corresponds to positive polarity of the external bias on the ion implantation side. We can observe that the rectifying characteristic improved as the dose of the nitrogen implantation increases from 1×10^{13} cm^{-2} to 1×10^{15} cm^{-2}. This means that the near surface region of the n-type $CuInSe_2$ thin film becomes more p type as the dose increases. This supports what we observed in previous experiments.[13] In the case of the homojunction produced by a dose of 1×10^{15} cm^{-2}, a rectification ratio of 1:200 was measured at 1 V at room temperature, and a series resistance of about 1 Ω is calculated for a 1 cm^2 junction for forward bias voltages in excess of 0.25 V. The resistance is associated with the undepleted region of $CuInSe_2$ film.

Figure 3 shows a SIMS (secondary ion mass spectroscopy) depth profile of a $CuInSe_2$ film nitrogen implanted at an energy of 50 keV with a dose of 1×10^{15} cm^{-2} after short annealing in a nitrogen atmosphere at 450 °C. We used $^{133}Cs^+$ as primary ions to provide a high detection sensitivity for nitrogen. We observed secondary positive ion clusters like Se+Cs, Cu+Cs, In+Cs, N+Cs.[13] We can observe a N+Cs peak near surface in the nitrogen depth profile. The peak shows that the range of the nitrogen implantation in this experiment was about 70 nm. The content of the nitrogen in the $CuInSe_2$ film was about 10^{20} atoms/cm^3 at the peak as estimated from the dose and the depth profile of the implanted nitrogen. Mullan *et al.*[16] reported that the peak of oxygen implanted at an energy of 40 keV was at a depth of 72 nm according to a Monte

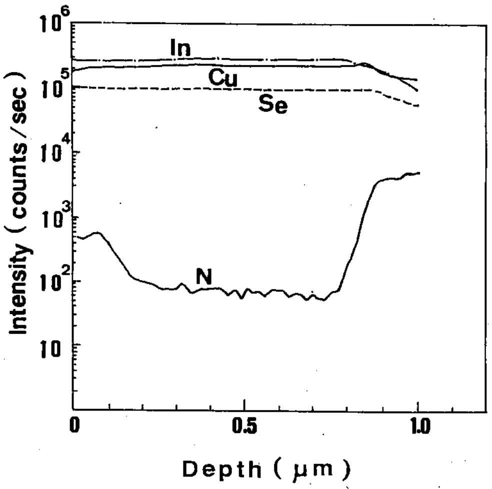

FIG. 3. SIMS depth profile of a nitrogen-ion implanted $CuInSe_2$ film after short annealing at 450 °C in nitrogen.

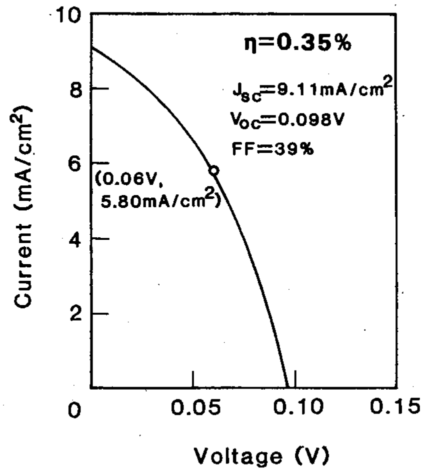

FIG. 5. Current-voltage characteristics of a $CuInSe_2$ thin film *p-n* junction of 0.04 cm^2 area under AM1.0, 100 mW/cm^2.

Carlo type TRIM-89 algorithm in which an amorphous $CuInSe_2$ structure with a density of 5.78 g/cm^3 was assumed. Considering that in our experiments nitrogen was implanted at an energy of 50 keV, the nitrogen range obtained from the SIMS profiling is in reasonable agreement with the Mullan's results for oxygen.

Figures 4(a) and 4(b) show the result of capacitance versus voltage measurement in a rectifying homojunction diode. In Fig. 4(a) we show a $1/C^2$ versus voltage plot, which is meaningful for an abrupt homojunction. The $1/C^2$ vs V plot is linear over the voltage range from -2.0 to -0.75 V. If we assume that reverse bias voltage makes the depletion layer extend almost exclusively into the *n*-type region, we would calculate the carrier concentration as a function of the depth from the edge of the depletion layer. The result is shown in Fig. 4(b). The carrier concentration, N, was calculated from the equation, $N=(2q/\epsilon)\times[d(1/C^2)/dV]^{-1}$, where q and ϵ are the unit charge and the dielectric constant, respectively.[17] The value of the carrier concentration obtained from this analysis was comparable to the value of 1×10^{15} cm^{-3} obtained by the Hall effect measurement.

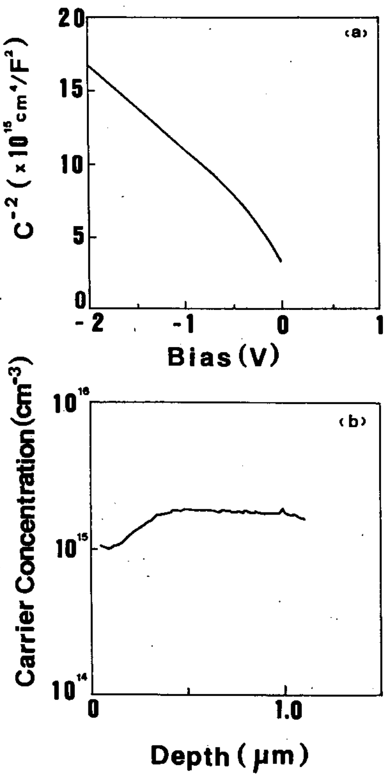

FIG. 4. Results of capacitance vs voltage measurements at 1 MHz on a rectifying diode fabricated by nitrogen implantation at an energy and dose of 50 keV and 1×10^{15} cm^{-2}, respectively: (a) a plot of $1/C^2$ vs bias voltage, and (b) the carrier concentration as a function of depth from the edge of the depletion layer at 0 V, obtained by analyzing the *C-V* data.

A 2×2 mm^2 homojunction, fabricated for the measurement of the photovoltaic properties, has some of its characteristics shown in Figs. 1 and 2. This *n*-type $CuInSe_2$ film (Cu:In:Se=23.3:26.6:50.1) was implanted with $^{14}N^+$ at an energy of 50 keV and a dose of 1×10^{15} cm^{-2}. It was annealed in nitrogen at 450 °C for 1 min. Figure 5 shows the current-voltage characteristics of a 2×2 mm^2 solar cell under AM1.0, 100 mW/cm^2 illumination. The open circuit voltage, short circuit current density, and fill factor are 0.098 V, 9.11 mA/cm^2, and 39%, respectively, corresponding to a conversion efficiency of 0.35%.

IV. CONCLUSION

We succeeded in fabricating rectifying homojunctions in polycrystalline $CuInSe_2$ film by nitrogen implantation, and fabricating a photovoltaic device with an efficiency of 0.35%. This work shows that homojunctions can be fabricated by ion implantation even in a polycrystalline thin film of $CuInSe_2$, and that photovoltaic cells can be produced by this process.

ACKNOWLEDGMENTS

This work was supported by the New Energy and Industrial Technology Development Organization as a part of the Sunshine Project under the Ministry of International Trade and Industry. The authors acknowledge Dr. T. Nitta and Dr. K. Kanai for support. Dr. Y. Mizutani for useful discussions on the ion implantation, and the staff of the Ion Engineering Center Corporation for assistance, and Mr. Tukamoto for SIMS analysis and useful discussions on the SIMS data in this work.

[1] R. A. Mickelsen and W. S. Chen, *Proceedings of the 16th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1982), p. 781.

[2] K. Mitchell, C. Eberspacher, J. Ermer, and D. Pier, *Proceedings of the 20th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1988), p. 1384.

[3] B. M. Basol, V. K. Kapur, and A. Halani, *Proceedings of the 22nd IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1991), p. 893.

[4] M. Spitzer, J. J. Loferski, and J. Shewchun, *Proceedings of the 14th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1980), p. 585.

[5] M. Nishitani, T. Negami, M. Terauchi, and T. Hirao, Jpn. J. Appl. Phys. **31**, 192 (1992).

[6] R. Noufi, R. Axton, C. Herrington, and S. K. Deb, Appl. Phys. Lett. **45**, 668 (1984).

[7] P. W. Yu, S. P. Faile, and Y. S. Park, Appl. Phys. Lett. **26**, 384 (1975).

[8] J. Parkes, R. D. Tomlinson, and M. J. Hampshire, Solid-State Electron. **16**, 773 (1973).

[9] R. D. Tomlinson, E. Elliott, J. Parkes, and M. J. Hampshire, Appl. Phys. Lett. **26**, 383 (1975).

[10] P. Migliorato, B. Tell, J. L. Shay, and H. M. Kasper, Appl. Phys. Lett. **24**, 227 (1974).

[11] G. A. Medvedkin, V. Yu. Rud, and M. V. Yakushev, Cryst. Res. Technol. **25**, 1299 (1990).

[12] R. D. Tomlinson, A. E. Hill, M. Imanieh, R. D. Pilkington, A. Roodbarmohammadi, M. A. Slifkin, and M. V. Yakushev, Proceedings of 9th EC Photovoltaic Solar Energy Conference, Freiburg, 1989, p. 149.

[13] S. Kohiki, M. Nishitani, T. Negami, K. Nishikura, and T. Hirao, Appl. Phys. Lett. **59**, 1749 (1991).

[14] S. Kohiki, M. Nishitani, T. Negami, K. Nishikura, and T. Hirao, Thin Solid Films **207**, 265 (1992).

[15] H. Neumann, Helvetica Physica Acta. **58**, 337 (1985).

[16] C. A. Mullan, C. J. Kiely, A. Rockett, M. Imanieh, M. V. Yakushev, and R. D. Tomlinson, Proc. MRS Spring Meeting, San Francisco, 1992 (to be published).

[17] P. H. Mauk, H. Tavakolian, and J. R. Sites, IEEE Trans. Electron Devices **37**, 422 (1990).