$CuInSe_2$ homojunction diode fabricated by phosphorus doping

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Homojunction diodes were fabricated by doping of phosphorus to *n*-type Cu-In-Se thin films. The junction prepared by P implantation at the energy of 50 keV with the dose of 1×10^{15} ions/cm^2 showed a rectification ratio of more than 100. Conduction in Cu-In-Se thin films, whose crystal structure is of the chalcopyrite type, changes from *n*- to *p*-type in such a way that group V elements (N, P, Sb, or Bi) substitute for Se in the film.

Since $CuInSe_2$ is a promising material for realization of thin-film solar cells, chalcopyrite structure Cu-In-Se thin films have been studied extensively. We have reported the change from *n*- to *p*-type conduction of the film deposited by molecular beam method with doping of N[1,2] or another group V element; i.e., P, Sb, or Bi.[3] The doped N atoms substitute for Se atoms in the Cu-In-Se crystal,[2] which causes the change in conduction type. (We call this mechanism "valence manipulation".) We have proposed fabrication of homojunction diode based on the valence manipulation.[1] We fabricated the *n*-$CuInSe_2$:N homojunction diode whose rectification ratio exceeds 200.[4] We have also succeeded in fabricating the Cu-In-Se thin-film homojunction diode by using P ion implantation and short time annealing process.

Shing *et al.*[5] have converted the conduction-type of the single-crystalline $CuInSe_2$ from *n*- to *p*-type by the thermal diffusion process of P. Homojunction diodes have been reported only in the *p*-$CuInSe_2$:In,[6] *n*-$CuInSe_2$:Se,[7] *n*-$CuInSe_2$:Cu,[8] and *p*-$CuInSe_2$:Cd.[9] As reported in Refs. 10–12, the conduction type changed from *n*- to *p*-type with the ion implantation of He, Xe, or O, and heterojunction diode was fabricated by the O ion implantation to *n*-type chalcopyrite structure Cu-In-Se crystals. Formation of In_2O_3 at the surface by thermal annealing,[13] which causes the conversion of conduction type, gives the impression that the O implantation is a reasonable choice for the formation of *p-n* junction. Although some characteristics of the heterojunction diode fabricated by the O implantation into the *n*-type Cu-In-Se single crystal were reported,[10] no experimental data on the Cu-In-Se homojunction diode doped with the group V elements has been published.

The films of 2 μm thick were deposited onto Mo electrodes formed on quartz substrates at 770 K in a vacuum better than 1×10^{-9} Torr. The temperatures of the molecular beam sources were 1400–1450 K for Cu, 1100–1150 K for In, and 400–450 K for Se. The composition of the films, determined by inductively coupled plasma optical emission spectroscopy, was near-stoichiometric but slightly In rich. Uniform distribution of the elements over the film surfaces was confirmed by electron probe microanalysis. The chalcopyrite structure of the films was confirmed by both x-ray diffraction and Raman scattering spectroscopy. The conduction type and the conductivity of the films without implantation, measured by Hall measurement, were *n*-type and ranging from 10^{-4} to $10^{-5}/\Omega$ cm. Seebeck coefficient measurement was also used to confirm the conduction type of the films.

A 400 keV ion implanter (installed at Ion Engineering Center Co., Osaka, Japan) was used for the P doping. P ions were implanted at 50, 100, 200, and 300 keV into the *n*-type Cu-In-Se films on Mo electrodes. The dose level ranged from 1×10^{13} to 1×10^{16} ions/cm^2. Current density of the implantation was in the order of 10^{-5} A/cm^2, and the temperatures of the samples did not exceed 300 K during the implantation. The films were annealed at 723 K in N_2 at 1 atm pressure for 1 min after the implantation.

All of the P implanted Cu-In-Se films showed rectification. The largest rectification ratio (-1 to $+1$ V) of more than 100 at 300 K was observed in the film P implanted at 50 keV and 1×10^{15} ions/cm^2 as shown in Fig. 1. The nonlinear characteristic of the current density at the region over $+0.5$ V may be due to series resistance in the *n*-type Cu-In-Se film. Larger conductivity of the film will provide larger rectification ratio.

It is well known that the valence band of the chalcopyrite Cu-In-Se crystal consists of Cu-Se *d-p* hybridization. The valence band maximum (VBM) is dominated by the characters of Se *p* orbital. In the valence manipulation the change in conduction type from *n*- to *p*-type is resulted from the introduction of holes at the VBM. Se substitution by P introduces holes into the VBM and then changes the type of conduction.

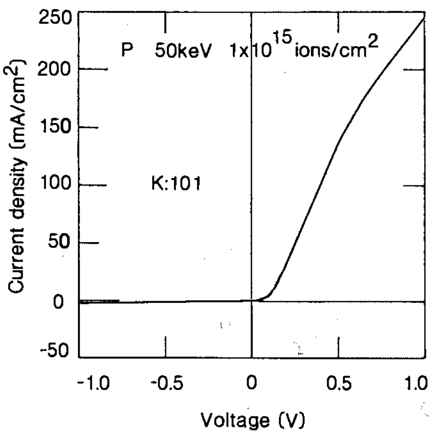

FIG. 1. Dark current-voltage characteristic of the homojunction diode of the P doped chalcopyrite structure Cu-In-Se thin film. The rectification ratio: K.

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Homojunction is more favorable than heterojunction because the former avoids the influence of lattice mismatch and reduces the density of recombination center of the carriers in the film. The valence manipulation is effective for the formation of high performance solar cells since the homojunction diode can be fabricated by implantation of N, P, Sb, and/or Bi into the *n*-type chalcopyrite Cu-In-Se thin films.

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