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We report here upon the electroluminescent properties of CdS p-n junction produced by nitrogen ion implantation into highly conductive n-type crystals.

CdS is usually an n-type compound semiconductor and its p-n junction can be formed by neither growth nor thermal diffusion. Although there have been many reports on electroluminescence in CdS crystals whose injection mechanisms are double injection in highly resistive crystal, tunnel injection, hetero-junction etc., there has been only one paper by Chernow et al.¹⁾ on electroluminescence which is believed to be due to p-n junction by bismuth ion implantation.

We reported previously the formation of p-n junction by nitrogen ion implantation and the properties of implanted layers²⁾, and it is here successfully demonstrated that CdS electroluminescent diodes caused by p-n junction have been produced by the nitrogen ion implantation. The external quantum efficiency is still low and the luminescence spectrum is not yet controllable.

Ion implantation was carried out at room temperature with energy of 50 to 200 keV, at a dose level of 10^{15} to 5×10^{16} cm⁻². After annealing at 400 °C for 10 minutes, electrodes of diodes were made by evaporation method. The electroluminescence was observed at diode current density >100 mA/cm² at 100 K. The threshold voltage was around 2 volts. The diodes were classified into three groups according to the luminescence spectra. Group A shows green luminescence, group B shows orange-yellow, and group C dark red. This classification has not, however, clear dependence on the implantation conditions mentioned above. Group A and C have Au contacts to the p-type layer (implanted layer) and group B has Ag contact, although electron injecting contacts were equally provided on n-type substrate by In vacuum deposited films. Figure 1 shows the typical luminescence spectra of these groups. Group A has a peak at 5000 Å and the shape of the spectrum is not symmetrical. The spectrum is reasonably resolved into two peaks at 4990 Å and 5070 Å. These peaks correspond well to the LO-phonon replicas of A-exciton of CdS at about 120 K. The peak of group B is located at about 6000 Å. It must be pointed out that only in this group does each diode have an Ag contact to the implanted layer and that only this group was alloyed at 200 °C for 10 minutes. It is well known that Ag in a CdS crystal forms a luminescence center at about 6100 Å.

The origin of the luminescence of group B is, therefore, thought to be Ag impurities. The peak position of the luminescence spectrum of group C is at around 8000 Å, which corresponds to the peak of the photovoltage spectrum of the implanted CdS diodes²⁾. The origin of the photovoltage peak is the impurity center caused by the implanted nitrogen.

The dependence of electroluminescence intensity of diode current and voltage shows the injection mechanisms of the CdS diodes. The I-V characteristic of group A where electroluminescence is observed can be expressed by $I \propto V^2$. And the luminescence is observed in spots. From these facts the emission of group A is believed to be due to a double injection in a p-i-n structure. On the other hand, the intensities of electroluminescence of group B and C depend exponentially on diode bias, that is, $L \propto \exp(\alpha V)$, and the I-V characteristic can also be expressed by $I \propto \exp(\alpha' V)$. The intensity of luminescence is, therefore, related to diode current as $L \propto I^{1.6-2.7}$. These properties of group B and C are similar to those of the usual injection luminescence from p-n junction.

It is not easy to obtain an estimate of the external quantum efficiency of the CdS diodes, but rough estimates fall in range of 10^{-8} - 10^{-6} for dc current levels of 1 to 10 A/cm².

In conclusion, we made CdS electroluminescent diodes by nitrogen ion implantation, and from studies of their electrical and optical properties the origin of luminescence and the structure of the CdS diodes were revealed.

References

- 1) F.Chernow et al., Proceedings of the National Electron Conference, 1969 p.220
- 2) Y.Shiraki et al., J. Appl. Phys 43, 710 (1972)

Fig.1

