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Improvement of Photovoltaic Conversion Efficiency and also Photoluminescence Efficiency of p-Cu_2O/n-ZnO thin film heterostructures by Cyanide Treatment

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Abstract: Crown-ether cyanide (CN) treatments of the as deposited polycrystalline p-Cu_2O/i-ZnO/n-ZnO/glass heterojunction photovoltaic structures were performed with the variation of time. Effects of defect passivation and improvement of photovoltaic conversion efficiency as well as photoluminescence efficiency were demonstrated with the cyanide treated samples. Optimum time of cyanide treatment was found to be 3 minutes.

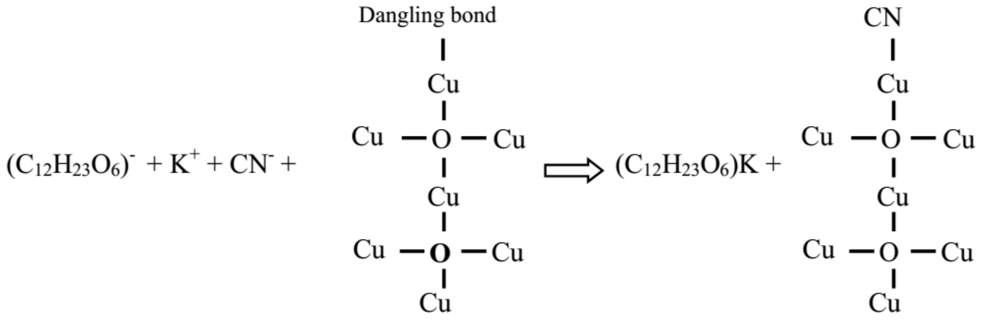
Keywords: **Cyanide treatment, Heterojunction, Photovoltaic, Photoluminescence and Defects Passivation**

I. INTRODUCTION

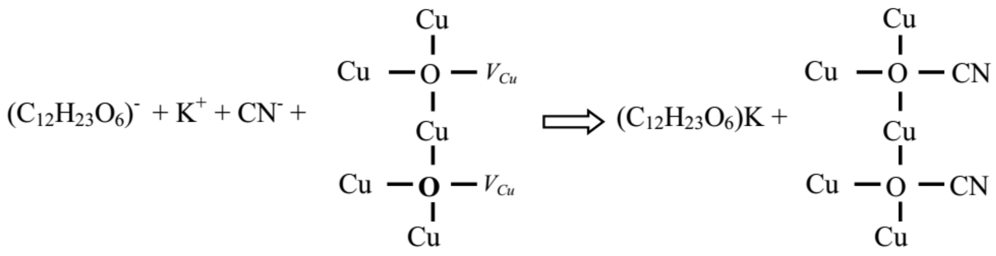
Cuprous oxide (Cu_2O) is one of the promising direct band-gap semiconductors with band-gap energy ~ 2.0 eV. It has huge potential for application to photovoltaic cells [1-3], to be more specific for the top layer in a tandem structure. This is because of the fact that has a high absorption coefficient in the visible region. Also, n-ZnO is an emerging material to be used as the window layer in solar cells [4, 5]. So, p-Cu_2O/n-ZnO thin film heterostructures provide a large area, potentially cheap, sustainable photovoltaic devices. There are reports on the fabrication of p-Cu_2O/n-ZnO heterojunction photovoltaic structures with poor conversion efficiency. The poor efficiency of this strcuture is due to the presence of defect states in the Cu_2O layer There are also reports on improvement of conversion effciency of such structures with CN treatment. This article reports fabrication of p-Cu_2O/i-ZnO/n-ZnO thin film heterojunction photovoltaic structures by radio frequency dc magnetron sputtering technique and improvement of its quantum efficiency in respect of both photovoltaic conversion as well as luminescence properties on post-deposition crown-ether CN-treatment.

II. EXPERIMENTAL DETAILS

Thin film p-Cu_2O/n-ZnO heterostructures in polycrystalline form were prepared by reactive radio-frequency magnetron sputtering on glass substrate (Corning 7059) kept at temperatures ranging from 200 ºC to 400 ºC using a Cu target (99.99 % pure), ZnO target and Ar as sputtering gas. Oxygen was introduced into the chanmber as the reactive gas during the deposition of Cu_2O through a nozzle whose end was placed near the substrate. The flow rates of O_2 and N_2, during deposition, were varied within 0 to 200 ml/min and 0 to 20 ml/min respectively. At the interface of p-Cu_2O and n-ZnO, insulating ZnO (i-ZnO) layer was deposited. The i-ZnO and n-ZnO layers were deposited using undoped and 1wt.% Al_2O_3 doped ZnO targets respectively. The thickness of n-ZnO, i-ZnO and p-Cu_2O layers were ~ 800 nm, ~ 100 nm and ~ 1700 nm respectively. The crown-ether cyanide treatment of the deposited structures was carried out by the following procedure: 0.2 mol of 18-crown-6 ($C_{12}H_{24}O_6$) was dissolved in Xylene and the solution was added to a 0.1 M KCN aqueous solution with the same volume. After keeping the solution still for 30 min, the part of the Xylene solution, which was well separated from the aqueous phase, was taken out of the separatory funnel, and the Cu_2O/ZnO heterostructure (after Cu_2O deposition) was immersed in the KCN solution of Xylene containing crown-ether for few minutes followed by successive rinses in acetone, ethanol and de-ionized water. This treatment is called “Cyanide treatment”. A set of samples was prepared with different immersion time (sample 0: 0min, sample 1: 1min, sample 2: 2min, sample 3: 3 min and sample 4: 4min). The 18-crown-molecule effectively captures a K^+ ion and consequently contamination by K^+ ion is completely prevented. That is to say, K^+ ions do not have direct contact with Cu_2O, only CN^- ions do. Details of the cyanide treatment were described elsewhere [6, 7]. The scheme of reaction for the Cyanide treatment are described below.



(1)



(2)

$V_{Cu} \Rightarrow$ Cu vacancy in Cu_2O

The hole concentration of Cu_2O was in the range between $1x10^{17}$ cm^{-3} and $5x10^{18}cm^{-3}$ and the electron concentration of n-ZnO was kept constant at $1x10^{20}$ cm^{-3}. Ohmic contacts were prepared on Cu_2O by thermal evaporation of gold (Au) with diameter of 0.3 cm, as reported earlier [8]. The surface topology of the films was investigated by using atomic force microscope (AFM) (Topometrix-Accurex-II). The Current-voltage (I-V) characteristics and photoluminescence (PL) spectra of the as-deposited heterostructures and also of the cyanide treated samples were extensively studied. The PL spectra of the samples with and without CN treatment were recorded at liquid nitrogen temperature by varying the CN treatment time.

III.RESULTS AND DISCUSSION

The density of trap states was found to depend strongly on the CN-treatment time. The said densities were found to increase initially when the CN-treatment time was small and subsequently decreased for larger value of CN-treatment time. The results suggest that the CN^- ions passivate non-radiative recombination centers in and/or on polycrystalline Cu_2O grains as reported earlier [9 -11]. Thus, the CN-treatment of Cu_2O/ZnO hetero-structure affects the Cu_2O layer of the structure, not only the surface of Cu_2O, since probable reactions occurring in CN-treatment are illustrated before. Fig.1 shows the surface morphology of Cu_2O surface. The surface shows polycrystalline structure with well defined grain boundaries but the sizes of the grains have a dispersion centred on an average value of ~ 200 nm.

Fig.2 depicts the variation of hole concentration with N_2 flow rate before and after the Cyanide treatment. This figure clearly shows that the concentration of hole increases linearly with N_2 flow rate and also the rate of increase is a bit higher in the CN treated samples, as it should be.

From the I-V characteristics (not shown here) of the as-deposited structure and also of the CN treated samples it was found that the optimum time for CN treatment is 3 minutes in respect of the photovoltaic conversion efficiency. Fig. 3 shows the photoluminescence spectra for a representative sample recorded at 77K with and without CN treatment. The figure clearly shows that quantum efficiency of photoluminescence of Cu_2O gets enhanced on CN treatment. It was also observed that the photoluminescence efficiency of Cu_2O is maximum at CN treatment time of 3 minutes, same as that of the photovoltaic conversion. From these results, it is very clear that the quantum efficiency of photovoltaic conversion as well as photoluminescence properties of the cyanide treated heterostructures has been increased to a great extent compared to that of the as-deposited samples. The polycrystalline p-Cu_2O thin layer in the above mentioned heterostructure is expected to have large number of dangling bonds, which act as non-radiative recombination centers or carrier traps, on the surface of polycrystalline grains. The non-radiative recombination centers on and in polycrystalline grains were obviously passivated by Crown-ether CN-treatment since with CN^- treatment carrier concentration showed marked increase from 10^{17} to 10^{18} cm^{-3}. It is generally believed that the dangling bonds of Cu act as donor-like defects in Cu_2O, which compensate acceptors. It is, therefore, supposed that the hole carriers generated by nitrogen acceptors are compensated by such defects. Consequently, the increase in the hole concentration by the cyanide treatment may be caused by the termination of the dangling bonds of Cu. Therefore, the improvement of efficiency in respect of both of the prepared heterostructures is mainly due to the reduction of defect densities by the CN-treatment.

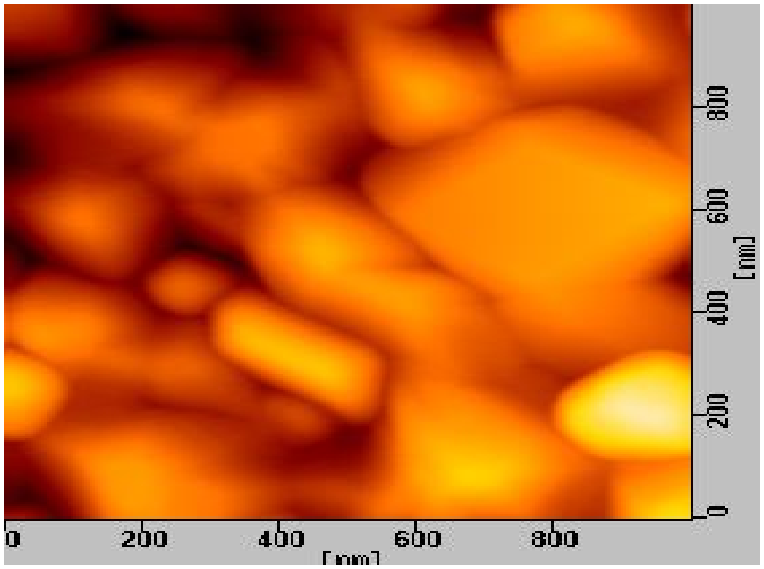


Fig.1: AFM image of Cu_2O

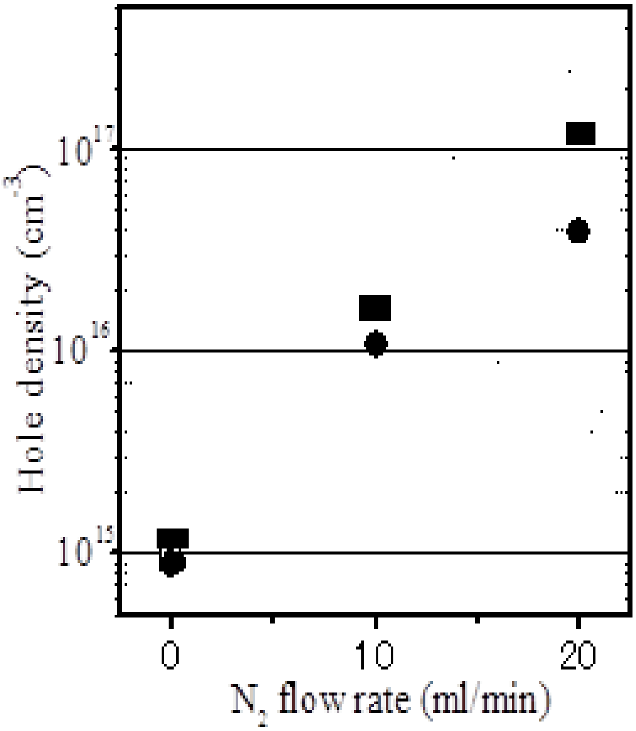


Fig.2: Variation of hole density with N_2 flow rate (● represents data point before CN treatment and ■ represents data point after CN treatment)

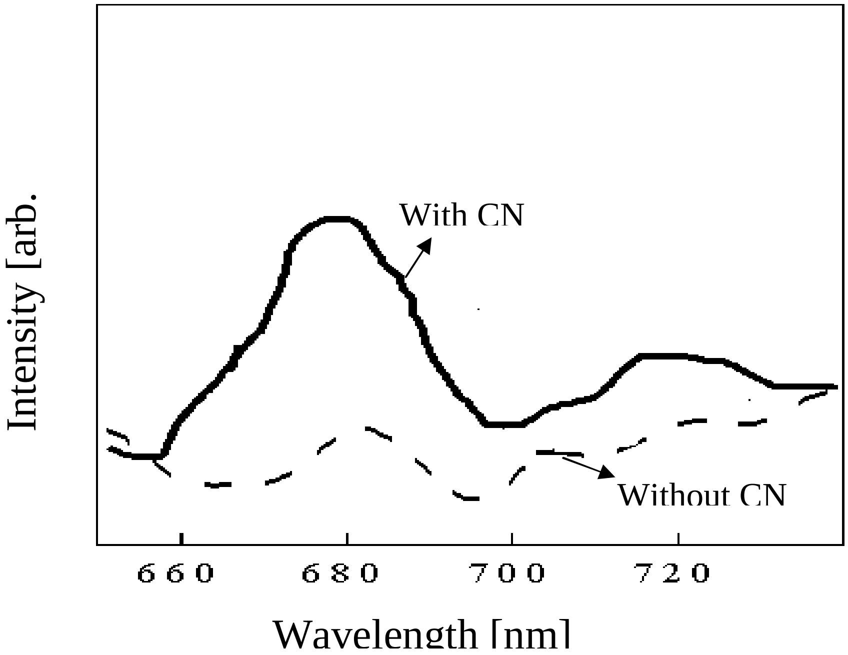


Fig.3: Photoluminescence response of the samples with and without CN treatment.

IV. CONCLUSIONS

In this article we have reported a study of p-Cu_2O/i-ZnO/n-ZnO thin film heterostructures prepared by dc reactive magnetron sputtering and subsequently subjected to various CN-treatment times, clearly showing the enhancement of photovoltaic conversion efficiency as well as photoluminescence properties.

V. ACKNOWLEDGMENT

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