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Nitrogen Doping into Cu_2O Thin Films Deposited by Reactive Sputtering Method

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1. Introduction

Cuprous oxide (Cu_2O) is one of the materials expected for applications to solar cells. However, the difficulty of controlling electrical and optical properties prevents the practical applications at present. However, Cu_2O is still attractive material because it has advantages of nontoxicity, high absorption coefficient and low cost producibility. For the practical applications, it is necessary to establish a deposition method which enables to control various properties of Cu_2O. We have investigated the controllability of structural and optical properties in Cu_2O deposited by reactive sputtering method, and the substrate temperature was found to be important to get high quality films[1]. As for the controlling of electrical properties of Cu_2O, it may be a key point to select dopant atoms suitable for Cu_2O. It was reported that Cd or In are effective as p-type dopants and the lowest resistivity of 9 Ω cm was obtained in case of Cd-doping into bulk Cu_2O[2]. Chlorine was reported to have a effect of increasing mobility[3]. However, there are few reports concerned with doping into Cu_2O as yet.

In this paper, nitrogen doping into Cu_2O thin films is reported. Nitrogen is well known as a nontoxic, low cost and easily available material, however, to the best of our knowledge, the investigation of nitrogen doping into Cu_2O thin films has never been reported. We tried nitrogen doping into Cu_2O thin films deposited by sputtering method and studied the effects on electrical properties of Cu_2O.

2. Experimental

The nitrogen-doped Cu_2O thin films were prepared by reactive radio-frequency (rf) magnetron sputtering method on barium borosilicate glass (Corning 7059) substrates using a Cu target with 99.99% purity and Ar as a sputtering gas. The oxygen gas and the nitrogen gas were introduced through the nozzles, which were set near the substrate. The flow rate of oxygen gas was fixed at the range of 210~225ml/min, in which single phase of Cu_2O were obtained, and the flow rate of nitrogen gas was varied from 2ml/min to 15ml/min. The substrate temperatures during deposition were 400℃ and 500℃, and the output power of rf-plasma was kept constant at 60W. The film thickness and deposition rate were typically 2 μ m and 3 μ m/h which were determined by scanning electron microscope (SEM).

The electrical properties of Cu_2O thin films were measured by van der Pauw method using BIO-RAD HL5500PC. The structural properties were studied by X-ray diffraction (XRD) in θ-2θ mode using Cu-Kα radiation, and the optical properties were studied by measuring absorption spectra at room temperature using JASCO V570 spectrometer.

3. Result and discussion

Fig.1 shows the results of XRD from films deposited at 500℃ under various flow rate of nitrogen. We can see the $Cu_2O(200)$, and $Cu_2O(111)$ diffraction indicating single phase of Cu_2O with poly-crystalline. It seems that the composition and structure of Cu_2O are not changed by nitrogen doping into Cu_2O, because the full width at half maximum (FWHM) of the intensity of $Cu_2O(200)$ reflection peaks were almost constant with increasing N_2 flow rate, and the distances between (200) facets of Cu_2O (d-value) calculated from the peak position were also almost constant as well. From these results of XRD, it can be said that the structural properties of Cu_2O were not influenced by nitrogen doping at the flow rate until 15ml/min at least.

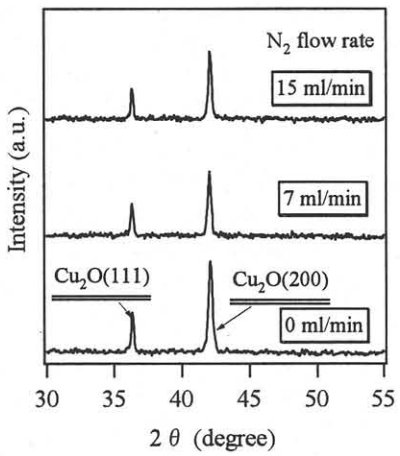

Fig. 1 XRD profiles of Cu_2O thin films for various N_2 flow rates deposited at 500℃.

Fig.2 and 3 show the resistivity and hole concentration, respectively, determined by van der Pauw method at room temperature. As can be seen in these figures, resistivity of thin films decreases and hole concentration increases with increasing N_2 flow rate. The nitrogen was found to have an effect of increasing hole concentration and to be act as acceptor in Cu_2O. The nitrogen doped into Cu_2O can be expected to be incorporated in oxygen lattice site, and this may be the reason for nitrogen acting as acceptors. The decrease of the resistivity may be caused by the increase of hole concentration.

The resistivity of the film deposited at 400℃ is lower

than 500℃. This difference may be caused by desorption of nitrogen from Cu_2O surface at higher substrate temperature.

The lowest resistivity with 17.9 Ω cm was obtained when deposited at 400℃ and N_2 flow rate was 10ml/min. The record of the lowest resistivity was 9 Ω cm in case of Cd-doping into bulk Cu_2O[2], however, the lowest resistivity of Cu_2O thin films reported is 25 Ω cm [4], so the obtained value of 17.9 Ω cm in this work is the lowest resistivity of polycrystalline Cu_2O thin film reported so far. These results suggest that the nitrogen doping into Cu_2O is very effective to control electrical properties in p-type conduction.

The variation of hole concentration by nitrogen doping was only one and half order of magnitude as shown in Fig.3. Such small variation may be caused by a small sticking coefficient of nitrogen or an existence of hole trap at grain boundary. Further detailed study is necessary to clarify such a small variation of hole concentration.

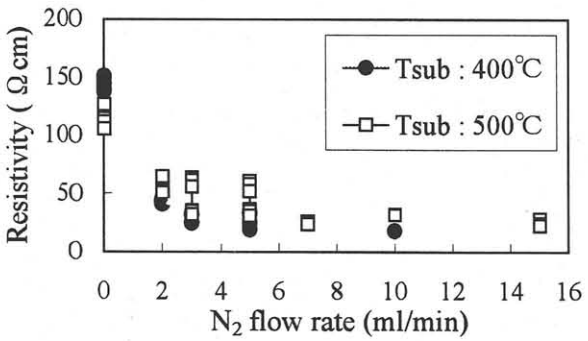

Fig. 2 Resistivities determined by Hall effect measurements for Cu_2O thin films deposited at various N_2 flow rates.

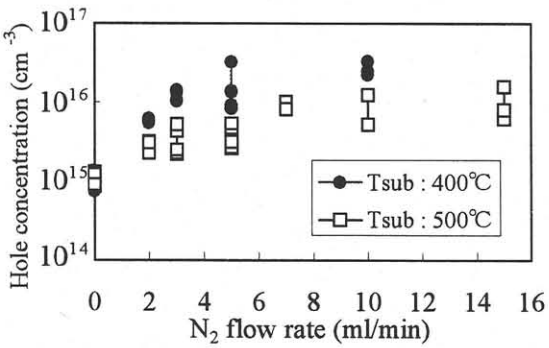

Fig. 3 Hole concentration determined by Hall effect measurements for Cu_2O thin films deposited at various N_2 flow rates.

Fig.4 shows absorption spectra of films deposited at 500℃ with various nitrogen flow rates. The photo-absorption of each films steeply increased at almost the same photon energy around 2.0eV as indicated by dotted line. The band gap energy of each Cu_2O can be estimated to be about 2.0eV in good agreement with that of the bulk crystal, and any shifts or new peaks were not observed in the spectra with increasing N_2 flow rate. It can be said that the optical properties of nitrogen-doped Cu_2O are not so degraded and significant midgap levels are not generated by nitrogen doping.

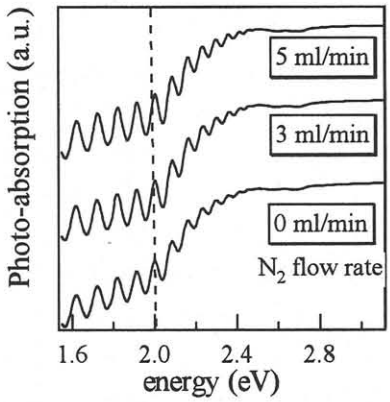

Fig. 4 Photo-absorption spectra measured at room temperature of Cu_2O thin films for various N_2 flow rates deposited at 500℃.

4. Conclusion

Effects of nitrogen doping into Cu_2O film deposited by reactive rf-magnetron sputtering method were studied. The nitrogen was found to have an effect of increasing hole concentration and to be act as acceptor in Cu_2O. The resistivity decreases with increasing N_2 flow rate and the obtained minimum resistivity was 17.9 Ω cm which is the lowest value reported so far for Cu_2O thin films.

References

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