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Effect of hydrogen plasma treatment on the electrical properties of sputtered N-doped cuprous oxide films

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Abstract

Cuprous oxide (Cu_2O) is a direct-gap semiconductor with band gap energy of 2.0 eV and is regarded as one of the most promising materials for application in photovoltaic cells. The attractiveness of cuprous oxide as a photovoltaic material is due to the fact that the constituent materials are nontoxic and abundantly available on Earth, and that the cuprous oxide has a high absorption coefficient in visible regions and is cheap to produce. Practical application has not been achieved to date because of the difficulty of controlling its electrical properties. In particular, it is necessary to investigate the controllability of its electrical properties and to reduce its resistivity. From previous studies, it is known that a pure phase of cuprous oxide can be obtained by adjusting the sputtering parameters. It is also known that nitrogen doping is effective for reducing the resistivity of cuprous oxide films. N-doped cuprous oxide films have been deposited onto Corning 1737 at a constant substrate temperature of 350 °C using a magnetron cosputtering process in a mixture of oxygen and argon gases. The flow rate of nitrogen was kept at 12 ml/min, while other sputtering parameters were kept constant. It was found that the hole carrier concentration of nitrogen-doped cuprous oxide films increased from 9.0×10^{17} to 4.0×10^{18} cm^{-3} resulting in a lower resistivity of 9.1 Ω-cm after 60 s of hydrogen plasma treatment. X-ray diffraction (XRD) analysis revealed no obvious structural change, but the roughness measured by AFM is obviously reduced after hydrogen plasma treatment. Because the mobility of the carrier is almost constant, it is believed that the hydrogen plasma treatment induces point defects in the cuprous oxide, which is effective in decreasing the resistivity of the films.

Keywords: N-doped cuprous oxide; Hydrogen plasma; Cuprous oxide

1. Introduction

Cu_2O has long been considered a promising candidate for possible application in photovoltaic devices. It is a reddish, nonstoichiometric p-type semiconductor with both ionic and covalent character and a direct forbidden band gap of 2.17 eV, an acceptor level 0.4 eV above the valence band, and donor levels 1.1 and 1.3 eV below the conduction band [1]. Many attractive advantages have been pointed out for cuprous oxide [2].

(1) The starting material (Cu) is relatively cheap, nontoxic, and abundantly available on Earth.
(2) The production cost of cuprous oxide is relatively low.
(3) The Hall mobility of cuprous oxide is usually larger than 10 cm^2/V s in spite of the low formation temperature [3].
(4) Production of large area devices with cuprous oxide is possible.
(5) Cu_2O has a high absorption coefficient in visible regions and is a nonstoichiometric p-type semiconductor with an estimated theoretical efficiency of solar energy conversion approaching 12% for a top cell in a two- (or three-) solar cell stack [4].

Several techniques have been used to prepare thin films of Cu_2O, such as electrodeposition [5], spraying [6], chemical vapor deposition [7], thermal oxidation [8], molecular beam epitaxy [9], and reactive sputtering [10]. In most of these studies, a mixture of Cu_2O and CuO is

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Table 1
The sputtering parameters for the Cu_2O films

Power of Cu target	250 W
Sputter pressure	2.66 Pa
Substrate temperature	350 °C
Flow rate of argon	100 ml/min
Flow rate of oxygen	5 ml/min
Flow rate of nitrogen	4~12 ml/min
Deposition time	10 min
Film thickness	0.39–0.48 nm

generally obtained. Hence, the essential problem is to find out the specific reaction parameters for producing pure Cu_2O.

2. Experimental methods

Cuprous oxide films were deposited on to Corning 7059 glass substrates by a DC magnetron sputtering system. The sputtering was carried out with a 75-mm diameter copper target of 99.99% purity. The glass substrate was cleaned using trichloroethylene and acetone to remove grease and organic contamination then placed parallel to the copper target surface, with a substrate to target distance of 45 mm. Before deposition, the chamber was pumped to an ultimate background pressure of 1.33×10^{-4} Pa (10^{-6} Torr) for half an hour, and then a presputtering process was applied for 10 min to clean the target surface and remove any possible contamination. During sputtering, the substrate temperature was kept at 350 °C, and the flow rate of oxygen was fixed at 5 ml/min. The flow rate of nitrogen was set at a constant rate within the range 4–12 ml/min. The details of the reaction parameters are given in Table 1. The hydrogen plasma treatment was executed after the deposition N-doped Cu_2O thin films by exposing the films to hydrogen plasma generated from the gas of hydrogen with 10 ml/min flow rate and 200 W microwave power (2.45 GHz) in a microwave plasma chemical vapor deposition system. The hydrogen plasma treatment time was varied from 0 to 1 min. The phases of the deposited films were studied by X-ray diffraction (XRD). The XRD patterns of the films were determined with a Shimadzu XD-1 diffractometer using monochromatic high intensity Cu Kα radiation (λ=1.51418 A). The resistivity of the films was measured by a four-point probe system (Napson, RT-7). The mobility and carrier concentration were measured by a Hall measuring effect instrument (Lakeshore, Model 662).

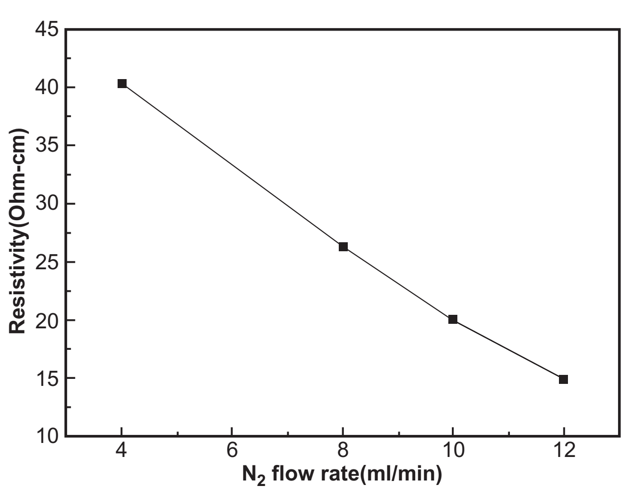

Fig. 1. The resistivity variation of N-doped Cu_2O films as a function of N_2 flow rate.

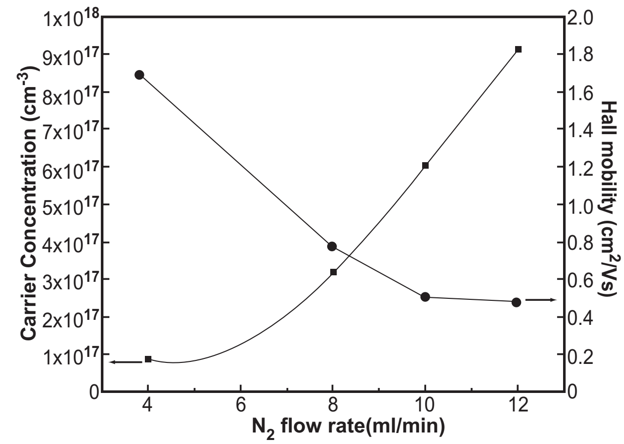

Fig. 2. The dependence of carrier concentration and Hall mobility of N-doped Cu_2O on nitrogen flow rate.

3. Results and discussion

Fig. 1 shows the room-temperature resistivity of nitrogen-doped Cu_2O films as a function of N_2 flow rate. The linearly decreasing relationship between resistivity and nitrogen flow rate suggests that the nitrogen can be effectively incorporated in the lattice sites of Cu_2O and

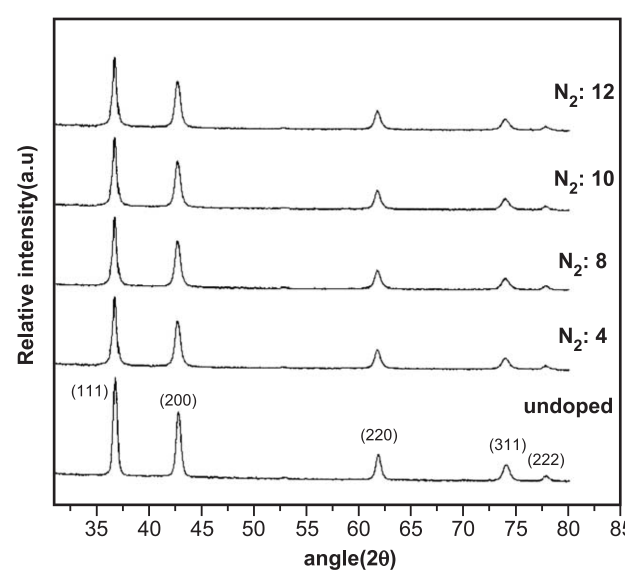

Fig. 3. The XRD patterns of N-doped Cu_2O films under different nitrogen flow rates.