



Characterization of Cu₂O and Cu₂O–Ag₂O thin films synthesized by plasma oxidation



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ABSTRACT

Cu₂O and Cu₂O–Ag₂O thin films were synthesized by a plasma oxidation process on uncoated as well as Cu and Cu–Ag(4 at.%) thin-film coated Cu sheets, using an inductively coupled plasma system equipped with four internal antennas. During oxidation, a plasma probe and an optical emission spectrometer were used to characterize the plasma with the variation of O₂/(Ar + O₂) flow ratios. After oxidation, the structural phases and the growth rate of the oxidized layer were first examined. To compare the photoelectrical properties of Cu₂O and Cu₂O–Ag₂O, the incident-photon-conversion-efficiency of the samples was measured. The results shows that the oxidation rate was increased with the increase of oxygen radicals (O*), which is attributed to the increase of plasma density. Deposited in low oxygen ratio, the oxidized films would have high deposition rate but with more complex structure. The coupling of Ag₂O phase into Cu₂O can enhance light absorption and create more electron–hole pairs due to the narrower band-gap structure of Ag₂O. The effect of Ag₂O phase on the enhanced photocurrent is discussed.

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1. Introduction

Cuprous oxide (Cu₂O) has been considered as a promising candidate for possible application in photovoltaic devices. It is a reddish p-type semiconductor with a direct forbidden band-gap of 2.17 eV [1]. Cu₂O has a high optical transparency at wavelengths above 500 nm, and with a high absorption coefficient at the wavelength below. Besides non-toxicity and low production cost of Cu₂O films, the theoretical energy conversion efficiency of 20% make it possible to be used as an absorber layer in thin film heterojunction solar cells [2]. The Cu₂O films can be prepared using various deposition techniques such as electro deposition [3], thermal spraying [4], chemical vapor deposition [5], thermal oxidation [6], molecular beam epitaxy [7], reactive sputtering [8], and atomic layered deposition [9]. Plasma oxidation is known to be a possible way to produce oxide in many areas, including semiconductor industries. According to the recent report by Saburi et al. [10,11], the

oxidation rate of copper in an oxygen containing plasma might be far faster than thermal oxidation within the low temperature region.

Regarding the application of Cu₂O-based photoelectrical devices, there is an inherent problem which needs to be overcome. The problem is the low carrier concentration and mobility in Cu₂O films, which often cause the reduction of photocurrent. According to previous reports, this problem can be improved by embedding other oxide nanoparticles in the oxide matrix [12]. Recently, some studies have shown that the opto-electrical properties of certain Cu₂O-oxide composites may be improved [13–14] due to the aforementioned reasons.

In the present study, Cu₂O and Cu₂O–Ag₂O thin layers were synthesized by a plasma oxidation process directly on pure Cu sheet, as well as on Cu and Cu–Ag(4 at.%) thin-films deposited Cu sheets. The plasma oxidation was carried out using an inductively coupled plasma (ICP) system attached with four internal antennas. During oxidation, a plasma probe and an optical emission spectrometer (OES) were used to characterize the plasma with the variation of O₂ flow ratio (O₂/(Ar + O₂)). It is believed that the oxidation rate and oxide quality should be related to the characteristics of the processing plasma [15–17].

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2. Experimental methods

To study the effects of oxygen concentration on plasma characteristics and their relationship to oxidation rate, annealed Cu plates (>99.995 wt.%, 25 mm × 20 mm × 1 mm) were first oxidized in a ICP system with the $O_2/(O_2 + Ar)$ flow ratio varied from 9% to 50%. During plasma oxidation, the ICP power was controlled at 2000 W, while the working pressure was maintained at 40 mtorr (5.33 Pa). The oxidation time was two hours. The schematic drawing of the ICP system is shown in Fig. 1. The detailed plasma oxidation parameters are presented in Table 1. During oxidation, a Langmuir probe (ESPION, Hiden Analytical) and an OES (PLASUS EmiCon) were attached to the plasma chamber, and used to characterize the plasma generated with the variation of $O_2/(Ar + O_2)$ ratio. The resolution of OES was 0.1 nm. Under the described processing conditions, the plasma density was around $5 \times 10^{10} \sim 1 \times 10^{11}/cm^3$. The phases of the oxidized layers were examined by X-ray diffractometry. The X-ray diffractometer (Phillips PW 1830) used monochromatic high intensity Cu K α radiation ($\lambda = 0.1514$ nm). The scanning angle was from 25° – 2θ to 65° – 2θ , with a step size of 0.02° and a measuring time of 1.25 s per step. For the investigation of the cross-sectional morphology and thickness of the oxide layers, the samples were examined using field-emission scanning electron microscopy (JEOL 6701F). Due to the extremely softness of Cu substrates, to examine the thickness of the oxide layers, the samples had to be cold-mounted using epoxy first. These samples were then going through grinding and polishing. The surface may look pretty rough afterward. These cross-sectional photos were taken, after grinding and polishing. The thickness of oxide layer was first confirmed by checking the SEM image using back-scattered electron function, which could show very significant difference in contrast. The thickness was measured five times in a sample. Normally, three samples were used, and average value was calculated.

In order to compare the opto-electrical properties of Cu_2O and Cu_2O – Ag_2O oxide layers formed during plasma oxidation, the Cu and Cu–Ag(4 at.%) films prepared by sputtering were deposited on Cu plates, then plasma oxidized using the optimized plasma processing parameters. The Cu and Cu–Ag(4 at. %) thin films were prepared with Cu (>99.995 wt. %) target, and with Cu and Ag (>99.995 wt. %) dual targets. Each target has a diameter of 50 mm and was tilted by 30° to the substrate base. The distance of target-to-target and target-to-substrate is 150 mm and 100 mm respectively. For the sputtering deposition, the chamber was first pumped down to 7×10^{-4} Pa, and, then, Ar gas (35sccm) was introduced to fill the chamber up to 0.65 Pa. During deposition, the power of Cu target was kept at 84 W while the power of Ag was kept at 6 W. The thickness of these films was about 600 nm. The substrates were Cu sheet (25 mm × 20 mm × 1 mm). The photo-induced current of the films was measured by an incident-photon-conversion-efficiency (IPCE) (MSSS-330, Hong-Ming Tech.) system. The light source for

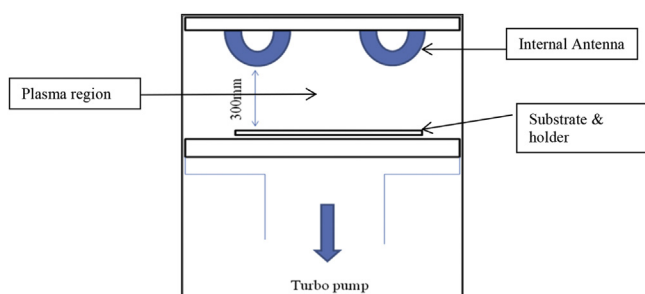


Fig. 1. Schematic drawing of the ICP system with four internal antennas.

Table 1

Plasma oxidation parameters for the samples used in this study.

Sample designation	RF power (W)	Ar gas (sccm)	O ₂ gas (sccm)	O ₂ /Ar + O ₂ flow ratio	Oxidation temperature (°C)
1	2000	100	10	9%	RT
2	2000	100	20	17%	RT
3	2000	100	45	31%	RT
4	2000	100	100	50%	RT
Cu film	2000	100	100	50%	RT
Cu–Ag(4 at. %) film	2000	100	100	50%	RT

Note.

1. RT = room temperature.
2. The total time of plasma oxidation was 2 h.
3. The working pressure was 52 mbar.

IPCE measurement was Xe lamp at 1000 Watt with irradiation intensity at AM1.5G. During the measurement, the bias voltage was set at 0.005 V. No special preparation of electrode was needed.

3. Results and discussion

3.1. Plasma characterization with OES and Langmuir probe

Fig. 2 shows the optical emission spectra obtained from the plasma generated with various O_2 flow ratios. Several common wavelengths corresponding to atomic transitions in plasma containing argon and oxygen are normally used to analyze the plasma emission spectra. The most significant oxygen peaks under our experimental conditions were the 777.4 nm and 845 nm peaks. These peaks correspond to the de-excitation of oxygen atom in the state 5P (O^*), whose creation is predicted by the following ways $e + O_2 \rightarrow e + O^* + O$ and $e + O \rightarrow e + O^*$, i.e. dissociative excitation or direct impact excitation of oxygen atom, respectively [18]. The most outstanding argon peak in our experiment conditions is the 751.4 nm line. This main mechanism of this Ar_1 emission line is caused mostly due the direct electron-impact excitation from the ground state. These spectra clearly show the change of O^* (845 nm) and Ar^* (751.4 nm) when O_2 flow ratio was varied. According to this figure, it can be found that the O^* intensity decreases with the increase of O_2 flow ratio. Apparently, the decrease of O^* intensity is related to the addition of O_2 . To better understand atomic oxygen density in the plasma containing oxygen and argon, it is useful to plot the intensity ratio of O_1 845 nm to Ar_1 751.4 nm vs. oxygen flow

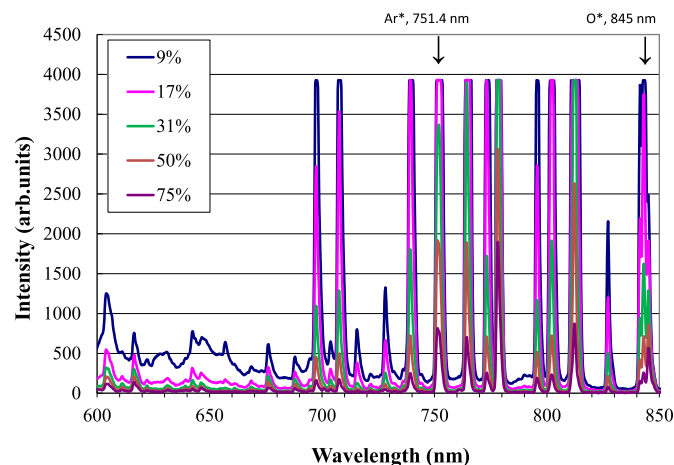


Fig. 2. Optical emission spectra recorded during plasma oxidation with various O_2 flow ratio.

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