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Influence of oxygen flow rate towards the rf magnetron copper sputtering plasma by means of optical emission spectroscopy

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Abstract: Copper oxide is one of the p-type metal oxide semiconductors that are suitable for gas sensing material. In addition, it is a low cost material, easy process fabrication and sensitive to ambient conditions. The copper oxide plasma was prepared by sputtering of pure copper target at different oxygen flow rate, i.e. 0 sccm, 4 sccm, 8 sccm and 16 sccm using rf magnetron sputtering technique. The argon flow rate, rf dissipation power and working pressure were fixed at 50 sccm, 400 W and 22.5 mTorr, respectively. In present study, we investigated the reactive magnetron sputtering plasma during the deposition of copper oxide thin film using optical emission spectroscopy. The measurement point was focused at 4.5 cm above the substrate holder. Copper, argon and oxygen intensities were observed at various oxygen flow rates. In general, when the oxygen flow rate increased above 4 sccm drastic changes can be observed in copper, argon and oxygen emission intensity. Copper and argon emission intensity decreased drastically after 4 sccm of oxygen gas introduced into the chamber. On the other hand, oxygen emission intensity increased with oxygen flow rate. The results suggest an optimum condition required to deposit the copper oxide thin film using solid copper target.

Keywords: Copper oxide, Reactive magnetron sputtering, Optical emission spectroscopy.

1. Introduction

Copper oxide is one of the p-type metal oxide semiconductors that are used as the material for gas sensing device. Basically, copper oxide is a much better candidates compared to those material that is toxic and expensive like ZnO, SnO_2 and In_2O_3 for application such as dye sensitized solar cell, photo catalysis, photochromic devices and gas sensing devices [1]. Furthermore, copper oxide form two type of oxides which called cuprous oxide (Cu_2O) and cupric oxide (CuO).

Cupric oxide is a monoclinic structured semiconductor with band gap range of 1.3-2.4eV [2]. In order to deposit copper oxide thin films, several method have been used, for example rf magnetron sputtering [3], chemical vapor deposition [4], sol-gel and pulsed laser deposition [5]. Therefore, in this project, rf magnetron sputtering will be the potential method to deposit copper oxide thin film due to the simplicity and repeatability performance of rf magnetron sputtering. Optical emission spectroscopy (OES) will be the technique used to investigate the plasma properties of the rf magnetron sputtering. OES is a technique that is used to study the composition of excited neutral and ionized species in the plasma produced by the rf magnetron sputtering. The excited neutral and ionized atoms in the discharge plasma will create a unique emission spectrum for each different element. The unique emission spectrum will be plotted at different wavelength in the range of 200-1000 nm. The intensity of each emission spectrum depends on the concentration of the element existed inside the plasma.

Based on the paper by A.A. Ogwu [2], which is mainly focused on the effect of varying rf power and oxygen flow rate during deposition on the electrical properties of copper oxide thin film deposited using reactive magnetron sputtering. The main point from the paper describe that the copper oxide thin film electrical sheet resistance increase with oxygen partial pressure. Besides, Drobny and Pulfrey[6] also suggested that the doping of excess oxygen will result in lowering the film resistance. This is due to the excess oxygen effectively producing more copper ion vacancies and a p-type semiconductor Cu_2O. As for this experiment, the oxygen flow rate is increased in order to perform the same effect as on the paper. Increasing the oxygen flow rate also means that the oxygen partial pressure is increases due to fixed argon flow rate.

In general, the characteristic of the deposited copper oxide thin film is influenced by the plasma properties. Various deposition parameters will affect the plasma properties such as oxygen flow rate, sputtering power, working pressure, deposition time and substrate bias voltage. However, in this paper, we report the investigation on the plasma properties of copper oxide at different oxygen flow rates. The copper, argon and oxygen emission will be accessed at different oxygen flow rate.

2. Experimental Setup

Fig. 1 shows the experimental setup for copper oxide deposition using rf magnetron sputtering plasma system attached with optical emission spectroscopy attached to it via view port. The magnetron sputtering source was made of cylindrical permanent magnets attached to an indirect cooling system. The copper oxide plasma properties were obtained from the point 4.5 cm above the substrate holder and 10 cm from the Cu target. The sputter target is a 3” copper target. The chamber of the rf magnetron sputtering was evacuated to base pressure of 5×10^{-6} Torr using vacuum turbo pump and backed by rotary pump. The sputtering gas, argon, and reactive gas, oxygen was introduced into the vacuum chamber by using the mass flow controller which is attached to the top of the vacuum chamber. The Ar flow rate was fixed at 50 sccm and the working pressure also fixed at 22.5 mTorr during the process. While the rf discharge power was fixed at 400 W using a 13.6 MHz rf magnetron discharges with an automated matching network. OES system was then attached outside of the chamber via the view port. OES system consists of optical lens, optical fiber and the optical emission spectrometer. The summary of all the parameter was tabulated in table 1.

The copper oxide plasma properties were analyzed using optical emission spectroscopy from ocean optics HR4000 series. The copper oxide plasma property was measured at the range of 200 to 1000 nm wavelength.

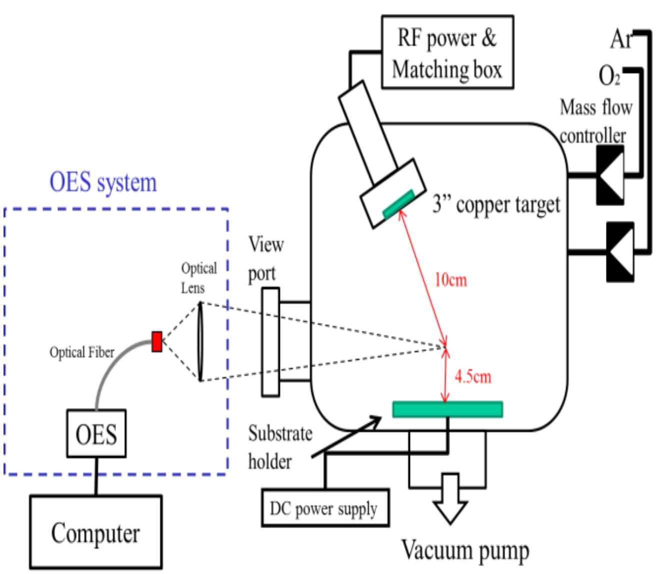


Fig. 1 RF magnetron sputtering and optical emission spectroscopy system.

Table 1 Summary of the CuO plasma sputtering parameter.

Argon flow rate	50 sccm
Oxygen flow rate	0, 4, 8, 16 sccm
Rf dissipation power	400 W
Working pressure	22.5 mTorr
Target	Cu

3. Results and Discussion

To investigate the plasma properties, the plasma emission was measured with a high resolution spectrometry (Ocean Optics) with an optical fiber that is focused using optical lens through the Pyrex glass chamber. Fig. 2 shows the typical result obtained from optical emission spectroscopy at oxygen flow rate of 0 sccm and 8 sccm. Based on the result, it is clearly shows that when oxygen is introduced into the plasma, there are various additional spectra lines observed through the OES. This is because the OES system detected the peak for oxygen emission. When 8 sccm oxygen flow rate is introduced into the plasma, the argon intensity at 811.6 nm wavelength increased from 1068.18 to 2276.39 a.u. The argon emission intensity was shown in Fig. 3(a). In addition, when the oxygen flow rate was increased, the copper intensity at 578.3 nm wavelength is also increased. The intensity only increased from 583.23 to 1015.16 a.u. It is shown in Fig. 3(b) for the copper emission intensity. As for the oxygen intensity, due to the increase of oxygen flow rate, the oxygen intensity also increases. This is notice when the graph is focus on the range of 776 nm to 779 nm wavelength which is display in Fig. 3(c).

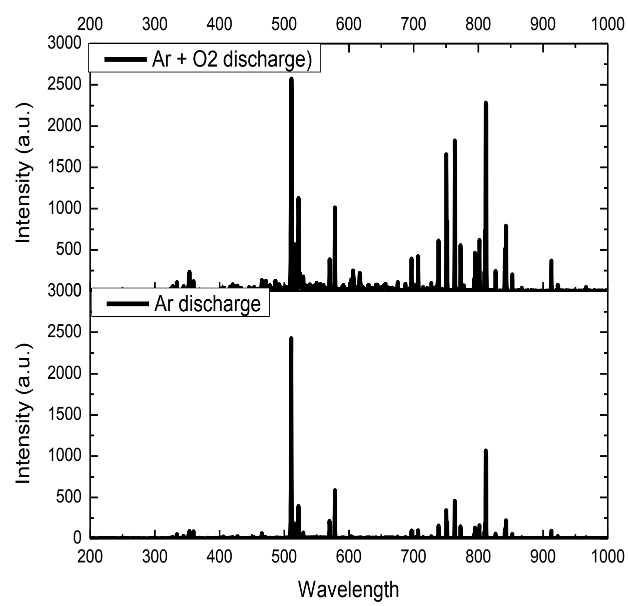
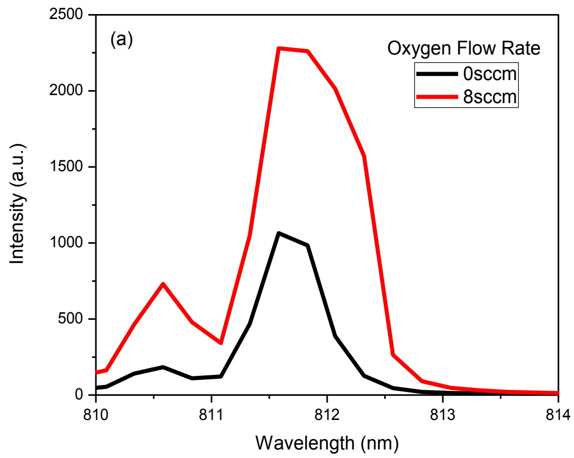
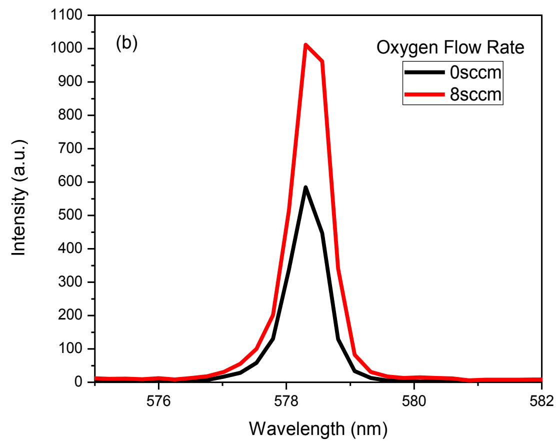


Fig. 2 Typical result of OES simulation for Ar discharge and Ar + O_2 (8 sccm oxygen flow rate) discharge.





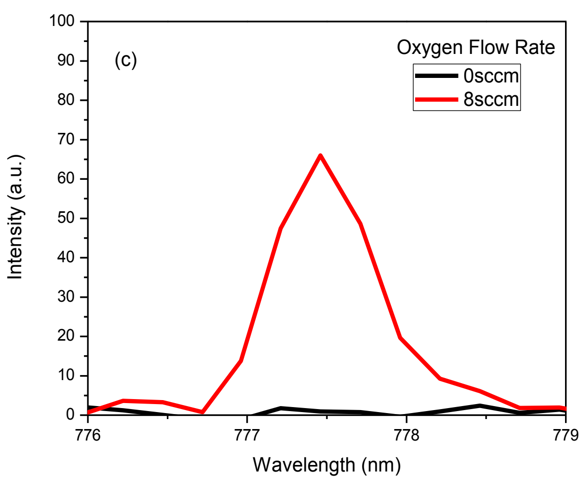


Fig. 3 The difference in intensity for element (a) argon emission, (b) copper emission and (c) oxygen emission.

It is shown that the oxygen intensity increased around 70 arbitrary units. when the oxygen flow rate is increased to 8 sccm.

Fig. 4 shows the normalized intensity for argon, copper and oxygen element. The emission intensity for the three elements was normalized for the sake of comparison on the influence of oxygen flow rate towards argon, copper and oxygen element. First of all, it is notice that the copper emission increased between 0 and 4 sccm of oxygen flow rate. Based on this, there are two reasons to describe the enhancement of the copper emission intensity in this region. The first reason is that it is due to the enhancement of electron temperature where the electron impact excitation process causes the production of more excited state copper, thus increases the copper emission. Besides, electron temperature is also closely related to the ionization of argon and oxygen element. This is because the energy required to ionize the argon element with energy level of 15.75eV is much higher compared to the ionization of the oxygen element with energy level 13.6eV. The second reason is that when a small amount of oxygen is introduced into the plasma, the sputter rate will be higher. The sputter rate of the copper element is due to the sputtering gas that is applied into the plasma. In this case, the sputtering gas used is the argon gas. Therefore, changes in the amount of oxygen flow rate will affect the argon element and in turn affected the copper element.

It has been reported that, the sputter rate increased with the addition of small amount of oxygen in the plasma [7]. When oxygen flow rate is increased from 4 sccm to 8 sccm drastic changes can be observed from the graph. The copper emission decreased while oxygen emission increased when oxygen flow rate is increased above 4 sccm. Based on this, it is certain that copper was oxidized into copper oxide by oxygen. The transition point for the copper oxide deposition was observed at 8 sccm. It is notice that there is excess of oxygen element when oxygen flow rate is increased above 8 sccm. The results show that OES is a good indicator to monitor the excess of oxygen content during the growth of copper oxide thin film.

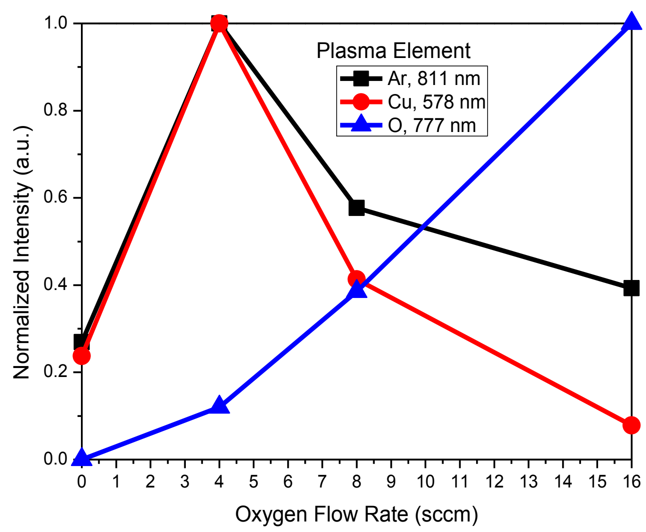


Fig. 4 Normalized result for argon, copper and oxygen intensity.

4. Summary

The optical emission spectroscopy result was successfully investigated with the argon, copper and oxygen emission were related to the oxygen flow rate. By relating the optical emission spectroscopy result with the electrical properties of the copper oxide thin film which is stated in A.A. Ogwu, Drobny and Pulfrey, it is observed that increase in the oxygen flow rate will affect the copper element intensity to drop which in turn causes the thin film to form lower film resistance copper oxide thin film. Therefore, based on the result, an optimized oxygen flow rate was obtained in order to produce copper oxide thin film that have the higher film resistance and the optimized oxygen flow rate was 8 sccm. The copper oxide thin film will later be optimized for gas sensing element.

Acknowledgement

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