Spectroscopic Studies of Magnetron Sputtering Plasma Discharge in Cu/O2/Ar Mixture for Copper Oxide Thin Film Fabrication

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Full paper

Spectroscopic Studies of Magnetron Sputtering Plasma Discharge in $Cu/O_2/Ar$ Mixture for Copper Oxide Thin Film Fabrication

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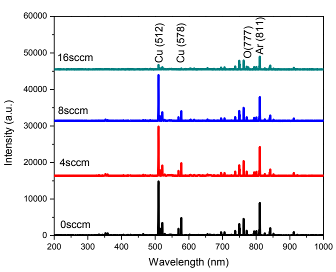
Graphical abstract



Abstract

Magnetron sputtering plasma for the deposition of copper oxide thin film has been investigated using optical emission spectroscopy and Langmuir probe. The intensity of the light emission from atoms and radicals in the plasma were measured using optical emission spectroscopy (OES). Then, Langmuir probe was employed to estimate the plasma density, electron temperature and ion flux. In present studies, reactive copper sputtering plasmas were produced at different oxygen flow rate of 0, 4, 8 and 16 sccm. The size of copper target was 3 inches. The dissipation rf power, Ar flow rate and working pressure were fixed at 400 W, 50 sccm and 22.5 mTorr, respectively. Since the substrate bias plays an important role to the thin film formation, the substrate bias voltages of 0, -40, -60 and -100 V were studied. Based on OES results, oxygen emission increased drastically when the oxygen flow rate above 8 sccm. On the other hand, copper and argon emission decreased gradually. In addition, Langmuir probe results showed a different ion flux when substrate bias voltage was applied. Based on these plasma diagnostic results, it has been concluded that the optimized parameter to produce copper oxide thin film are between -40 to -60 V of substrate bias voltage and between 8 to 12 sccm of oxygen flow rate.

Keywords: Copper oxide; optical emission spectroscopy; Langmuir probe; thin film; magnetron sputtering

Abstrak

Magnetron sputtering plasma yang digunakan untuk menghasilkan filem nipis kuprum oksida telah dikaji dengan menggunakan teknik spektroskopi pemancaran optik dan Langmuir probe. Kadar keamatan cahaya daripada atom dan radikal di dalam plasma disukat menggunakan teknik spektroskopi pemancaran optik. Kemudian, Langmuir probe digunakan untuk menganggarkan ketumpatan plasma, suhu elektron dan kadar aliran ion ke arah sampel. Dalam kajian ini, sputtering plasma kuprum aktif telah dihasilkan pada kadar aliran oksigen yang berbeza iaitu 0, 4, 8 dan 16 sccm. Saiz sasaran kuprum yang digunakan adalah 3 inci. Kuasa percikan rf sputtering, kadar aliran gas argon (Ar) dan tekanan kerja kebuk pemendapan telah ditetapkan masing-masing pada 400 W, 50 sccm dan 22.5 mTorr. Memandangkan voltan pada substrat sampel memainkan peranan yang penting dalam pembentukan struktur filem nipis, voltan berbeza pada substrat iaitu 0, -40, -60 dan -100 V telah dikaji. Berdasarkan pemerhatian kajian OES, keamatan cahaya oksigen meningkat secara mendadak apabila kadar aliran oksigen melebihi 8 sccm. Sebaliknya, keamatan cahaya kuprum dan argon menurun secara perlahan-lahan. Di samping itu, kadar aliran ion kelihatan berubah dengan ketara apabila voltan negatif dikenakan keatas substrat. Berdasarkan analisa-analisa plasma ini, telah disimpulkan bahawa parameter yang optimum untuk menghasilkan kuprum oksida yang baik adalah dengan mengunakan voltan pada substrat di antara -40 kepada -60 V dan menetapkan kadar aliran gas oksigen di antara 8 sehingga 12 sccm .

Kata kunci: Kuprum oksida; spektroskopi pemancaran optic; Langmuir probe; filem nipis; dan magnetron sputtering

1.0 INTRODUCTION

Copper oxide thin film has attracted great attention due to its potential application in various fields such as dye sensitized solar cell, photo catalysis, photochromic devices and gas sensing devices [1, 2]. As a p-type metal oxide semiconductor, copper oxide is also one of the promising candidates to replace the toxic and expensive material such as SnO_2 and In_2O_3. To date, copper oxide thin films have been deposited and growth using several methods, such as radio frequency (rf) magnetron sputtering [3-6], chemical vapor deposition[7-8], sol-gel [9] and pulse laser deposition [10]. Among those technique, rf magnetron sputtering is a potential technique to deposit the a nano-scale copper oxide thin film at low deposition rate and uniform thin films [3]. Besides, magnetron sputtering is the most popular system for industrial thin film deposition. Generally, magnetron sputtering plasma are characterized by external parameters such as radio frequency (rf) dissipation power, flow rate of sputtering and reactive gas, substrate bias voltage and working pressure. However, knowledge on the external parameters is not sufficient to produce and understand the growth of quality thin film. Therefore, in order to better understand the growth of thin film, investigation on the internal plasma properties such as atomic emission, atomic densities, electron temperature and plasma density are essential.

Study of their basic properties and behavior in sputtering discharges is essential to produce a high quality copper oxide thin film. Therefore, in this study, the sputtering discharges was characterized using two in-situ diagnostic techniques namely optical emission spectroscopy (OES) and Langmuir probe. OES is a technique that is used to monitor the excited atomic species in various plasma conditions. It can be used to investigate the emissive species within the plasma, since at different plasma condition, the amount of emissive species in the plasma will be different. Hence, it will contribute significantly to the properties of the thin film produced [11-14]. Furthermore, in order to obtain reliable understanding on production of emissive species, investigation on the plasma densities, electron temperature and ion flux are required. For this part, Langmuir probe technique will be a useful technique. This is because Langmuir probe consists of an electrode with its potential is varied to obtain a direct current-voltage (I-V) characteristics from the plasma, in which it will be later used to calculate plasma parameters.

An accurate plasma diagnostic is essential, it will not only provide better understanding of the deposition process but it also improve the control of the deposited film properties [6, 8]. Therefore, the aim of this paper is to provide a better understanding on the effect of external parameters such as substrate bias voltage and oxygen flow rate towards the plasma discharge of $Cu/O_2/Ar$ mixture. Correlation between OES and Langmuir probe result is taken into consideration to provide a better understanding on the plasma deposition.

2.0 EXPERIMENTAL SETUP

Figure 1 show the experimental setup for copper oxide plasma process using rf magnetron sputtering system embedded with the OES system and Langmuir probe system. The plasma chambers consist of six viewports and had a diameter of 16 cm and a height of 18 cm. The magnetron sputtering source was made of cylindrical permanent magnets attached to an indirect water cooling system. The sputtering plasma was produced by a 13.6 MHz magnetron sputtering discharge with an automated matching network. The sputter target was made of 3 inches pure (99.99% purity) copper target. The sputter chamber was evacuated to base pressure of 10^{-6} Torr using vacuum turbo molecular pump and backed by rotary mechanical pump. The sputtering gas, argon and reactive gas, oxygen was introduced into the chamber by using mass flow controller that was attached to the top of the chamber. The argon flow rate was fixed at 50 sccm while the oxygen flow rates were varied from 0 to 16 sccm. In order to produce negative substrate bias voltage into the chamber, a DC power supply was connected to the substrate holder and voltage within the chamber and the substrate holder were varied from 0 to -100 V. The total working pressure was fixed at 22.5 mTorr during the whole processes. The rf discharges power was fixed at 400 W. The total discharge power, chamber pressure and mass flow controller were connected with a personal computer controller unit for remote control the external parameters. A summary of the parameters used during the whole process of copper oxide plasma was tabulated into Table 1.

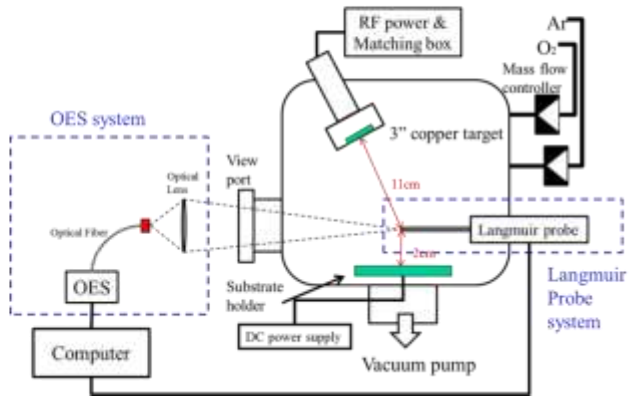


Figure 1 (Color online) Experimental setup for rf magnetron sputtering with OES system and Langmuir probe system

Table 1 Summary of the parameter used during sputtering process

Working distance from target	11 cm
Working distance from substrate holder	2 cm
Substrate bias voltage	0, -40, -60, -100 V
Argon flow rate	50 sccm
Oxygen flow rate	0, 4, 8, 16 sccm
Working pressure	22.5 mTorr
RF dissipation power	400 W
Target	3 inches pure copper target

The emission intensities of excited gaseous species in the plasma were collected by the optical fiber that was connected to optical emission spectroscopy from ocean optics HR4000 series. Emission light from the plasma was detected through the side view port of the magnetron sputtering system. The view port windows were made of quartz glass. In order to collect the information from the plasma at an exact point, an optical lens was used to focus the extraction point at 2 cm above substrate holder surface and 11 cm from the copper target surface. The $Cu/O_2/Ar$ mixture plasma properties were measured at the range of 200 to 1000 nm wavelength and various external parameters.

A Langmuir probe from Hiden Analytical ESPion system was used to determine the plasma densities, electron temperatures and the ion fluxes of the $Cu/O_2/Ar$ plasma. Langmuir probe was a tungsten conductor that is introduced into the plasma in order to collect the ion and electron current that flow to it in response to different probe potential. The probe tip potential ranges from -10 V until 70 V. The size of the tungsten probe is 0.15 mm in diameter and 10 mm long. The probe ceramic tube insulator was made to cover the tungsten probe and avoid disturbing the property of the plasma. The probe tip was placed at the center of the substrate holder, as the same point with OES measurement as shown in Figure 1. In addition, the probe tip was pre-clean with the negative bias for 10-20 second prior each measurement in order to remove the oxide layer on the tungsten tip. The measurement was repeated for 5 times for each conditions and averaged.

■3.0 RESULTS AND DISCUSSION

3.1 Optical Emission Spectroscopy Results

Figure 2 shows a series of optical emission spectra of rf Cu sputtering plasma at different oxygen flow rate covering the spectral region between 200-1200 nm. The argon flow rate was fixed at 50 sccm. The main features of the spectra correspond to the emission of Cu (578.213 nm), Ar (811.531 nm) and O (777.194 nm) excited radicals, which were produced directly from electron impact excitation processes. The emission of Cu was dominant when oxygen flow rate was below than 8 sccm. It is clearly shown in Figure 2 that at 16 sccm of oxygen flow rate, the rf sputtering plasma transit from the metallic mode to oxide mode. The emission from Ar and O become dominant at 16 sccm of oxygen flow rate.

At first, the effect of oxygen flow rate towards the spectral line was investigated. For this purposed, the emission intensity for the Ar (811 nm), Cu (578 nm) and O (777 nm) species were normalized at its maximum peak and plotted in Figure 3. Based on the result in Figure 3, the copper species emission gradually dropped when oxygen flow rate was increased. Similarly, Ar species emission also decreased when oxygen flow rate increased. Optical emission intensities are proportional to both the fraction of sputtered particles from the target and the percentage of particles at excited state. The later is produced generally from electron impact excitation which is proportional to the electron temperature in plasma. Therefore, one may assumes that the decrease of Ar emission is due to the lower percentage of excited Ar exist in the Ar+O_2 plasma when the oxygen flow rate increased. While the decrease on the Cu intensity with the increase of oxygen flow rate is caused by two effects. One is due to the reduction of sputter yield when the oxygen flow rate increases, causes the amount of sputtered Cu atoms to decrease. Other than that, the decreases in the Cu intensity also due to oxidation reaction in the gas phase ($Cu + O_2 \rightarrow CuO + O$) thus causes the Cu intensity to drop [18]. In contrast, the emission intensity of O increased drastically when the oxygen flow rate is above 4 sccm. Figure 3 shows that the emission intensity of O species was significantly small when the oxygen flow rate is between 0 to 4 sccm. This is due to the fact that the amount of O density is too little and there were not sufficiently produced by O_2 dissociation process. As the oxygen flow rate increased above 4 sccm, the emission intensity of O species increased drastically, indicating that there were more O species available inside the plasma for Cu oxidation processes. This is a very useful indicator to growth the copper oxide thin films.

The second part consists of investigation on the effect of substrate bias voltage. Figure 4 describes the emission species of Ar, Cu and O at various substrate bias voltages. The oxygen flow rate was fixed at 8 sccm. Based on the result, the O species increases with substrate bias voltage until -60 V and saturated when substrate bias voltage continue to decreased until -100 V. On the other hand, the emission intensities of Ar and Cu species is the opposite of the oxygen species, where it dropped when substrate bias voltage is decreased to -60 V and saturated between -60 V and -100 V. This phenomena is may be due to the thermal flux above the substrate surface that was created by the substrate bias voltages.

3.2 Langmuir Probe Results

Figure 5 display example of I-V curve obtained directly from Langmuir probe for 400 W rf power, 22.5 mTorr working pressure, 50 sccm Ar flow rate and 8 sccm oxygen flow rate. This curve represents the ion and electron current as a function of probe potential. I-V characteristics curve is divided into three regions to calculate different plasma parameters. There are namely ion saturation region, transition region and electron saturation region. As the name imply, ion saturation region is the area where the probe only collects the positive ions, while electron saturation region is the area the probe collects the electrons. The transition region is where the plasma density and plasma potential were calculated. Then, electron temperature and ion flux were obtained directly by analysis of the I-V characteristic using the ESPsoft software [11].

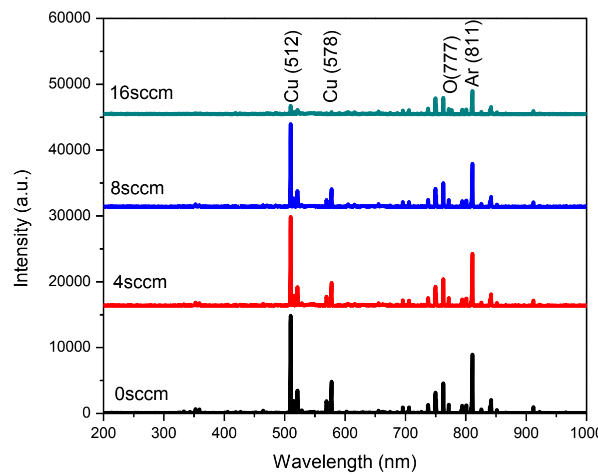


Figure 2 (Color online) Typical results for optical emission spectroscopy

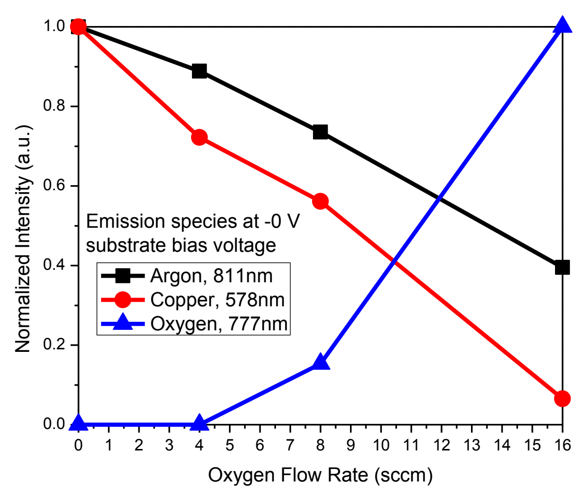


Figure 3 (Color online) Normalized result of -0 V substrate bias voltage emission at various oxygen flow rate

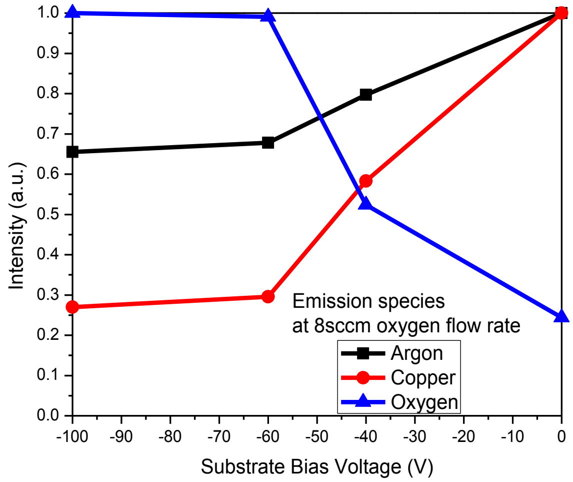


Figure 4 (Color online) Normalized result of 8sccm oxygen flow rate emission at various substrate bias voltages

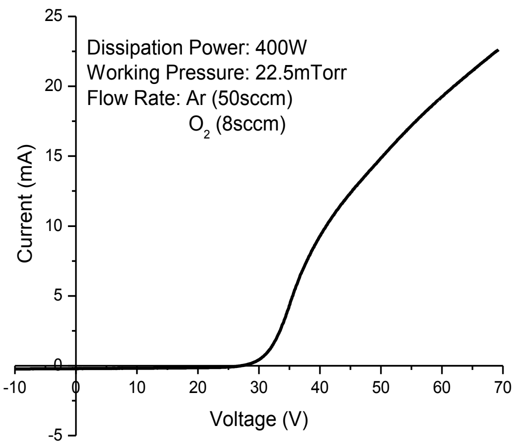


Figure 5 Typical current-voltage (I-V) characteristic result for Langmuir probe measurement

One can also interpret the I-V curve in Figure 5 by understanding the floating plasma potential, which is given by the transition point when the current increased exponentially. The floating plasma potential in Figure 5 indicates that the potential between plasma and sample substrate is approximately 30 V. As a result, the ions in the plasma will bombard the deposited thin film at this potential energy and thus alter the surface morphology of deposited thin film.

According to Figure 6(a), the electron density doesn't show any drastic changes, the electron density range between 1.5×10^{-16} to 2.25×10^{-16} m^{-3}. As for the ion density in Figure 6(b), slight changes in the flow is observe when the oxygen flow rate increased above 4 sccm. Hence, it is consistent with the optical emission spectroscopy result that when the oxygen flow rate is increased above 4 sccm, the oxygen emission intensity increased.

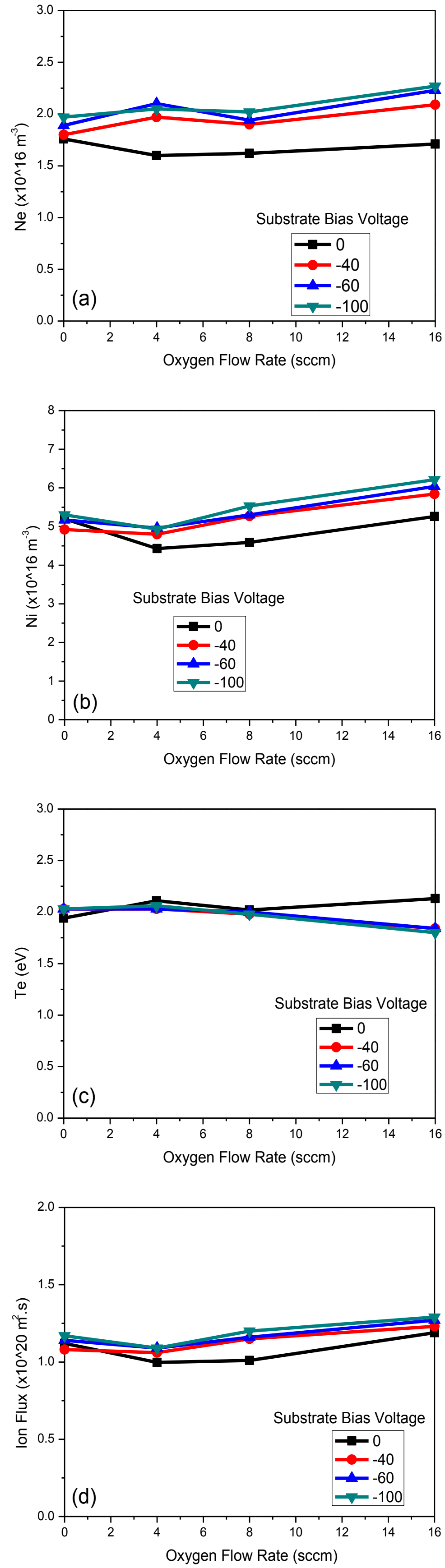


Figure 6 Langmuir probe result for (a) electron density, (b) ion density, (c) electron temperature and (d) ion flux at various oxygen flow rate

The ion density varied from 4×10^{-16} to 6.5×10^{-16} m^{-3}. Considering on the electron temperature of Figure 6(c), the changes in oxygen flow rate does not affect much on the electron temperature . The electron temperature only varied at 1.75 to 2eV. Finally, the ion flux which shown in Figure 6(d) varied in between 1×10^{20} and 1.25×10^{20} m^2·s. At 8 sccm of oxygen flow rate, the ion flux was influenced by the substrate bias voltage. The ion flux increased when the negative bias was applied. This may be due to the thermal energy on the substrate surface that was produced by the bias voltage. This phenomena will change the property of deposited thin film to form CuO or Cu_2O thin films.

■4.0 CONCLUSION

Plasma diagnostic is useful to understand the deposition process and plasma properties, so thus it will provide a better control of the deposited film properties. In present works, optical emission spectroscopy and Langmuir probe analysis were successful measured in copper sputtering plasma at various oxygen flow rate and substrate bias voltage combination. Based on the results, in order to produce a good structure on the thin film, it is suggested that -40V to -60V of bias voltage and 8 to 12 sccm of oxygen flow rate are proposed.

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