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Amorphous $Cu_xGa_{1-x}O$ film deposition by ultrahigh vacuum radio frequency magnetron sputtering

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1. Introduction

Oxide semiconductor β-gallium oxide (β-Ga_2O_3) single crystal has wide band gap (about 5.0 eV) and high transmissivity in the visible light (400 nm-800 nm), UV-A (320 nm-400 nm), and UV-B (280 nm-320 nm). Doping allows the variation of the conductivity for both p- and n-type over a wide range. Ga_2O_3 is being expected as transparent conducting oxides (TCOs), but most TCOs show n-type conductivity[1]. This has limited their applications since functional semiconducting devices require a pn-junction. But, Hosono group reported $CuAlO_2$ which had delaffossite structure as a transparency p-type TCOs in 1997[2]. They also succeeded in preparing the p-type $CuGaO_2$[3]. Here we report on the preparation of amorphous $Cu_xGa_{1-x}O$ films grown by a ultrahigh-vacuum radio frequency magnetron sputtering at room temperature[4]. Prominent bowing characteristics of amorphous $Cu_xGa_{1-x}O$ films have been found. The local density of states at valence band edge is also investigated. A variety of methods, FE-SEM for surface morphologies and cathode luminescence, atomic force microscope for morphology are used for characterization of grown films.

2. Experimental results

Preparation of Ga_2O_3 films

Amorphous gallium oxide thin films were prepared by the ultrahigh vacuum (UHV) radio frequency (RF) magnetron sputtering using the gallium oxide ceramic target of 99.999 % purity. Base pressure of the system is lower than $2x10^{-7}$ Pa and depositions are carried out at a deposition rate as low as 0.1 nm/s. Different sputtering gas compositions of argon and oxygen are employed by using mass flow controller. Figure 1 shows the plot of optical band gap energy of amorphous GaO films versus sputter gas composition. The sputtering gas composition dependence on the deposition rate and optical band gap energy suggest that the stoichiometric chemical composition can be obtained when the oxygen gas composition is higher than approximately 20 %. No discernible diffraction peaks are observed in X-ray diffraction measurements (XRD), indicating that the grown films are amorphous.

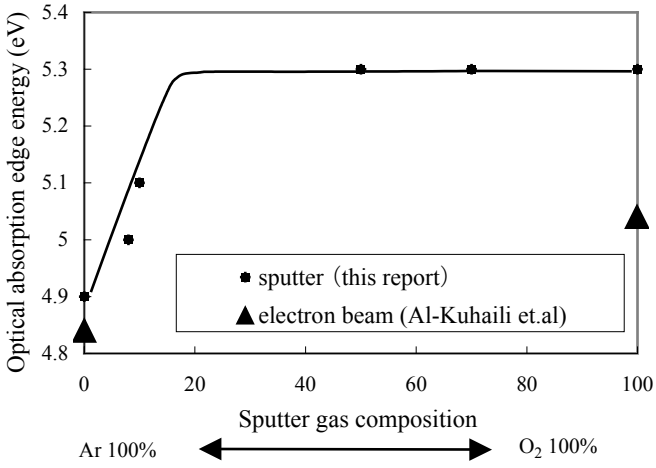

Figure 1. Optical absorption edge energy of amorphous gallium oxide films deposited at room temperature. Reference results are from Al-Kuhaili et.al[5].

Preparation and characteristics of $Cu_xGa_{1-x}O$ films

Next, the growth and characteristics of amorphous $Cu_xGa_{1-x}O$ layer are investigated. The doping of Cu is here done by putting a small piece of Cu plate on the Ga_2O_3 target. The doping level is controlled by changing the Cu plate area.

The copper compositions are evaluated from the Energy Dispersion X-ray Spectrometry (EDS) and X-ray Photoelectron Spectroscopy (XPS). Figure 2 demonstrates optical absorption edge energies of alloy $Cu_xGa_{1-x}O$ films as a function of copper compositions obtained from EDS data. The optical absorption edge energies are estimated from optical absorption coefficients of optical transmittance and optical reflectance. Other optical constants such as refractive index and extinction coefficient are estimated by ultraviolet spectroscopic ellipsometry.

The band gap energy of alloy $Cu_xGa_{1-x}O$ is expressed as equation (1), where C is the bowing parameter defining the parabolic nonlinearity of the alloy. The amorphous GaO band gap is taken to be 5.3 eV and amorphous CuO band gap is assumed to be the same value as crystalline Cu_2O 2.0

eV[6]. A least squares fit to the data of Fig.2 results in bowing parameter of C=9.1 eV.

$$Eg_{(CuGaO)} = xEg_{(CuO)} + (1-x)Eg_{(GaO)} - Cx(1-x) \quad (1)$$

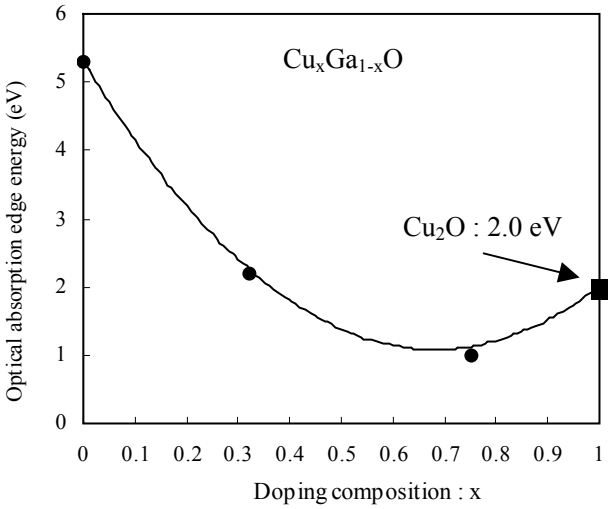

Figure 2. Optical absorption edge energy of amorphous copper gallium oxide films.

High Resolution X-ray photoelectron spectra

Higher resolution X-ray photoelectron spectra were measured with PHI Quantera SXM under a vacuum of $1.5x10^{-7}$ Pa at room temperature. Figure 3 shows valence band spectra of amorphous GaO and $Cu_xGa_{1-x}O$ (x=0.36) measured using AlKα (hν=1486.6 eV) with acceleration voltage of 15 kV. The beam diameter is approximately 100 μm. Electrostatic charging of samples is compensated for using an additional low energy electron gun. The error in the determination of electron binding energy value does not exceed 0.1 eV. Also the gold, silver and copper metals are referred at the determination of Fermi energy level in the binding energy.

It is observed that the experimental result in Fig.3 clarify shows that the top of valence band shifts to higher energy region and that the density of states of valence band increases when Cu is doped.

3. Conclusions

The high quality amorphous gallium oxide films are prepared with the UHV RF magnetron sputtering. The presence of the stoichiometry point at the sputter gas compositions is suggested. The bowing parameter of amorphous $Cu_xGa_{1-x}O$ films is obtained (C=9.1 eV). XPS data reveals that the top of valence band is sifted by Cu doping.

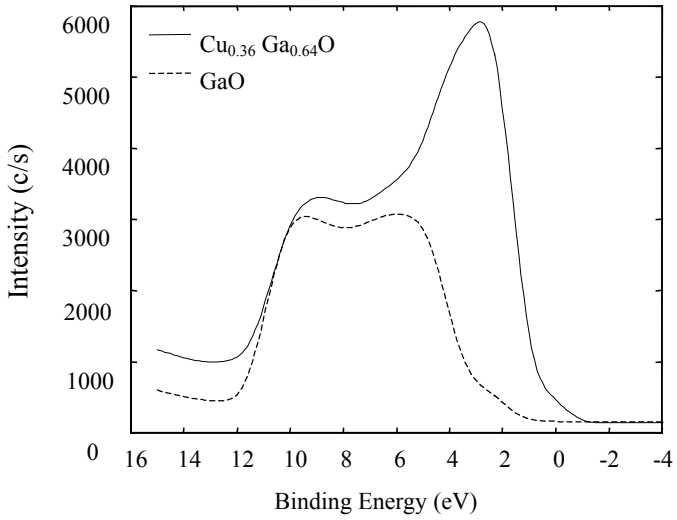

Figure 3. Valence band spectra of amorphous gallium oxide film and amorphous copper gallium oxide film (x=0.36).

Acknowledgements

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