

Characterization of Cu₂O thin films by photoacoustic spectroscopy

酸化銅 (I) 薄膜の光音響分光測定

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1. Introduction

Copper oxides, especially cuprous oxide (Cu₂O) is conventional and novel semiconducting material and have been studied for many applications such as rectifiers, transistors, various types of sensors and solar cells [1, 2]. This material is a p-type semiconductor with the bandgap of approximately 2.1 eV [3] and attract attention as a absorbing material of solar cells and widegap p-type contact layer. Several methods have been used to prepare Cu₂O thin films such as chemical vapor deposition, thermal oxidation, and sputtering [1, 2]. Electrochemical deposition is also one of the attractive methods to prepare Cu₂O thin films because this process is suitable for mass production. However, the electrochemical deponition technique requires a conductive substrate for film deposition. Metal, metal coated glass or transparent conductive oxide (TCO) coated glass substrates are used for the film deposition. The conductive layer influences to film characterizaitons.

The characterizaiton of optical absorption is very important for materials used in the optoelectronic devices. Optical absorption of a film on transparent glass substrate can be easily determined by transmittance measurement using an UV-vis-NIR spectrometer. However, transmittance measurements is not possible for a film on metal or other nontransparent materials. Photoacoustic spectroscopy (PAS) is one of the easy way to investigate the optical absorption of a films on nontransparent materials [4]. In addition, this method can detect weak absorption in sub-bandgap energies.

In this study, we investigate the optical properties of Cu₂O thin films by PAS method. The influence of the substrate on PAS measurements is also investigated..

2. Experimental details

Cu₂O thin films are fabricated by electrochemical deposition technique using a solution of copper sulfate pentahydrate, lactic acid, and sodium hydroxide. The bath temperature and

pH are 333 K and 12, respectively. We prepared three samples with different sample structures. In all structures, the Cu₂O thin film thickness was about 2.5 μm. The first structure was Cu₂O film on Au/glass substrate. The second one was Cu₂O film on indium-doped tin oxide (ITO)/glass substrate. The third one was Cu₂O film on epoxy. The third structure was fabricated from a film with the second structure. Nonconductive epoxy resin adhesive was put on the second structure. After drying the epoxy, the epoxy layer was detached from the substrate, resulting in the transfer of the Cu₂O film from the original ITO/glass substrate to epoxy substrate.

Absorption measurements in UV-vis-NIR regions were carried out with the setup shown in Fig. 1. It consisted of a JOBIN YVON H20 IR spectrometer (600 gr/mm), a GASERA PA 301 photoacoustic (PA) signal detector, NF 5584 mechanical light chopper, NF 5610B lock-in amplifier and halogen lamp (300W). PA spectra were measured between 400 and 1600 nm region with 5 nm resolutions. The modulation frequency was between 10 and 1000 Hz. The PA signal was detected by the cantilever in the PA cell using laser interferometer. The PA signal was normalized by the PA signal intensity of carbon black. All samples were measured at room temperature.

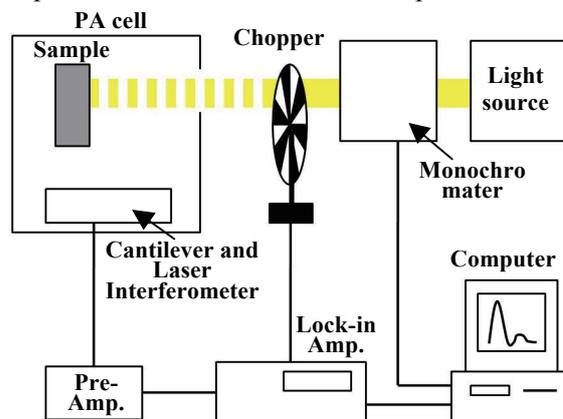


Fig. 1. Schematic diagram of PAS system.

The surface morphology of the samples was determined by scanning electron microscope (SEM; Hitachi S-6600). X-ray diffraction (XRD; Philips X'pert MRD) and Raman spectroscopy (Seishin

Syoji RA-07F) were used to evaluate the structural properties of the samples.

3. Results and Discussion

Figure 2 shows the Raman spectra of the three samples. Two peaks at around 217 and 630 cm^{-1} are observed. The peak at around 217 cm^{-1} originated from the second-order overtone mode of Cu_2O crystal. The other peak at around 630 cm^{-1} originated from the oxygen vacancy-related defect in Cu_2O crystal. We investigated the ratio of the peak intensity at around 630 cm^{-1} to that around 217 cm^{-1} (I_{630}/I_{217}) to evaluate the defect in Cu_2O . The I_{630}/I_{217} of the samples on Au and ITO substrates was about 0.23. On the other hand, the I_{630}/I_{217} of the sample on epoxy resin was about 0.17. These results suggest that the oxygen-related defect density at the interface between Cu_2O and ITO is lower than that at the surface of Cu_2O .

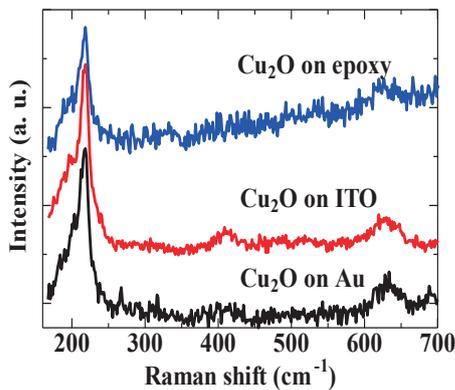


Fig. 2. Raman spectra of Cu_2O thin films on different substrate.

Figure 3 shows the PA spectra of the three samples. The onset of the decrease of the PA signal is located at photon energy of about 2.2 eV for all samples. This photon energy corresponds to the bandgap of Cu_2O . No clear absorption edge near 1.4-1.5 eV which corresponds to CuO is observed from all samples, indicating that the all films are pure Cu_2O .

The spectra in the sub-bandgap region are influenced by the substrate. The samples on Au/glass substrate show a gradual decrease of PA signal with decreasing photon energy compared with other two samples. This gradual decrease is attributed to the absorption of Au. The periods of the interference is corresponding to the Cu_2O film thickness. The shape of PA signal obtained from the Cu_2O thin film on the ITO substrate shows similar behavior to the shape of signal obtained from the Cu_2O on the epoxy resin substrate from 3.0 eV to 1.7 eV. The broad peak at around 1.0 eV is

attributed to the free carrier absorption in the ITO layer. These results indicate that PAS measurement is useful for optical characterization of Cu_2O films on conductive substrates.

4. Conclusion

We demonstrated the PAS measurements of Cu_2O films deposited on conductive substrates. The observations revealed that no CuO phase exist in our Cu_2O films. We also confirmed that the defect density of the surface attributed from oxygen vacancy is higher than the defect density near the interface between Cu_2O and ITO.

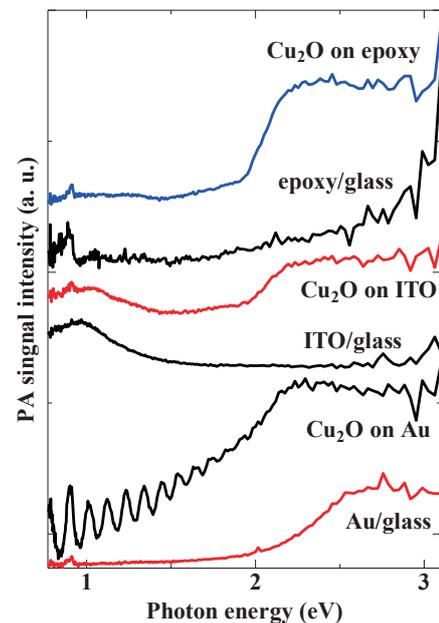


Fig. 3. PA spectra of Cu_2O thin films on different substrate. The peak at around 0.9 eV originates the adsorbed water on the sample surface. The PA spectra of Au, ITO, and epoxy on glass are also shown for reference.

Acknowledgment

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References

1. H. A. Al-Jawhari: Mater. Sci. Semicond. Process. **40** (2015) 241.
2. L. C. Chen: Mater. Sci. Semicond. Process. **16** (2013) 1172.
3. S. Haller, J. Jung, J. Rousset and D. Lincot: Electrochim. Acta. **82** (2012) 402.
4. H. Miyazaki, J. Morimoto, K. Toda, S. Onoda and T. Ohshima: Jpn. J. Appl. Phys. **50** (2011) 07HB07.