# Photoluminescence of Electrochemically-Deposited Granular $Cu_2O$ Films

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Cuprous oxide ($Cu_2O$) is a well-known compound semiconductor with a relatively wide band gap (2.2 eV) and has been investigated to apply to low-cost solar cells. Although only p-type is obtained, it is used for Schottky barrier or heterojunction photovoltaic devices. It is favored to prepare high-quality $Cu_2O$ films using convenient methods. Recently, we deposited $Cu_2O$ films electrochemically on copper substrates. The thin film obtained shows four sided pyramidal grains on the surface observed by SEM and thought to be a pile of microcrystals. When we studied optical properties, we observed the weak photoluminescence at 1.36 eV, 1.51 eV and 1.72 eV from deep trapping levels. The excitation wavelength was 514 nm. These emission peaks show similar wavelengths and temperature dependences with luminescence from vacancy defects at oxygen and copper atom sites of a single crystalline sample, although the widths are quite larger than those of crystalline one. This fact suggests that relatively high quality samples can be prepared using the convenient electrochemical method, which may be comparable to the single crystalline grade. The concentration of oxygen vacancies was successfully controlled by electrochemical conditions.
Key words: $Cu_2O$, photoluminescence, electrochemical, semiconductor, SEM image.

## 1. INTRODUCTION

Cuprous oxide ($Cu_2O$) is a p-type metal oxide semiconductor with the direct bandgap of 2.2 eV, and has been studied as a candidate for solar cells [1-5]. Recently, convenient electrochemical synthesis of $Cu_2O$ films attracts the interest of many researchers. Especially, electrodeposition of $Cu_2O$ from basic copper-lactate solution is important [6-10]. Electrochemical method could control the composition and the morphology of the film. It is well known that $Cu^{2+}$ complexate with lactate ions and stabilized in alkaline solution, and $Cu_2O$ is deposited to electrode at potential between –0.35 V and –0.55 V vs SCE. Using large current density, it was found that electrochemical oscillation occurs to deposit $Cu/Cu_2O$ alternated layers [11-13].

In this study, we pay attention to the control of the composition and the morphology of $Cu_2O$ films deposited electrochemically. Photoluminescence (PL) spectra concerning the deep trap levels of the films obtained was measured at wide temperatures between 10 K and the room temperature. As a result, the concentration of oxygen vacancy in the $Cu_2O$ film can be controlled by the temperature of the electrolyte solution during electrodeposition

## 2. EXPERIMENT

The conditions for the electrodeposition of $Cu_2O$ films for the measurement of PL is as follows. Since the PL spectra of relatively thin films (~1 μm) shows prominent fringes and this interferes the analysis, thicker films (~10 μm) was prepared. The electroyte solution was prepared following the similar method of the previous reports [6]. The solution contained ~0.6 M $CuSO_4$ and ~3 M lactic acid. The pH of the solution was adjusted to 9.5 by adding several mL of saturated NaOH solution. A standard electrochemical cell with three electrodes was used. A copper disk with diameter of 18 mm and thickness of 2 mm was used as a working electrode that was rotated at 500 rpm during electrodeposition. A platinum counter electrode and a saturated calomel reference electrode (SCE) was used. The temperature of the solution was kept constant at 65 °C or 50 °C. The fluctuation of temperature was within ±2 °C. Two samples deposited at different solution temperatures was prepared. They are named as Sample-A (65 °C) and Sample-B (50 °C). The morphology of the samples depends on the temperature of the solution[7,8]. The potential of the working electrode was kept constant at –420 mV (vs. SCE) using a potentiostat (HA-151, HOKUTO DENKO Corp.). The total electroric quantity per unit area was ~5 $C/cm^2$. The pH of electrolyte solution did not change significantly. The final pH of the solution increased slightly to 9.8 for both the samples.

Secondary electron microscopic images of samples was obtained using Hitachi S-2400 microscope.

For PL measurement, a cryostat cooled by a refrigerator (HE-05, Iwatani Corp.) was used. Temperature of samples was varied between 10 K and the room temperature. Optical windows used were quartz. A cw Ar ion laser (Beamlock 2060A-67 Spectra-Physics) was used as an excitation source (514 nm). Emission from the sample was collected, and transmitted using a quartz optical fiber to an monochrometer (SP-150, Acton Research Corp.). Stray light from the excitation laser was filtered by a colored glass filter (OG-570, CVI Technical Optics). Spectrographs were recorded using a liquid-nitrogen-cooled CCD camera (LNCCD-1100-PB,
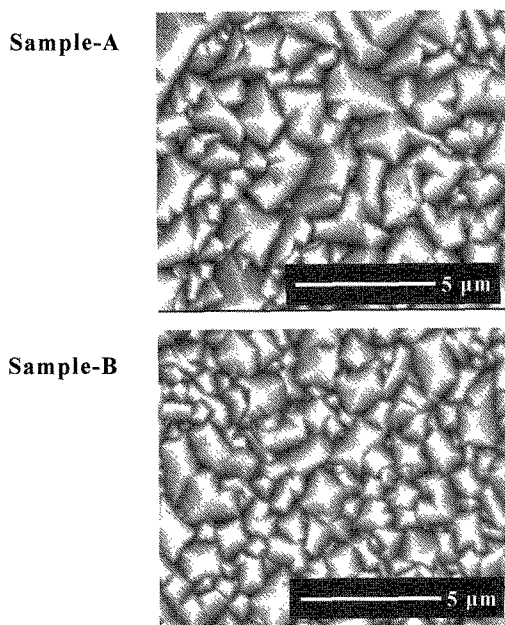
Sample-A

Sample-B



Figure 1. SEM photographs of samples deposited at 65 °C (Sample-A) and 55 °C (Sample-B).

Roper Scientific Inc.).

## 3: RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of Sample-A and Sample-B. Four sided pyramidal grains were observed in both photographs. The average size of grains of Sample-A are larger than that of Sample-B. These results are in good agreement with the previous reports [7,8]. The XRD study reports that the crystal structure of electrodeposited $Cu_2O$ films is cubic and the preferential formation of (2 0 0) surface occurs at pH 8 or 9 and temperatures between 30 and 90°C [8]. The pH and temperature range in this study fits into the conditions of the previous reports, thus the (2 0 0) faces appears at the surface.

In Figure 2, PL spectra are displayed for the two samples. The intensities was compensated and normalized for different exposure time. Sample-A showed a luminescence at 1.36 eV, that greatly increased at lower temperatures. It is well known that a $Cu_2O$ crystal is often nonstoichiometric because it ordinary contains copper and oxygen vacancies that forms deep trapping levels in the middle of the bandgap, and photoluminescence from these levels are observed [14-16]. The PL peak observed for Sample-A corresponds to the copper vacancy ($V_{Cu}$). It should be noticed that the peak width (~0.14 eV i.e. ~94 nm) was quite large. This implies that the quality of the sample is not as good as a single crystal grade. The reason for the intensity increase at low temperatures is possibly attributed to a nonradiative relaxation path or state to which a photoexcited electron thermally transitions with an activation barrier. For Sample-B, two PL peaks were observed, that correspond to PL from $V_{Cu}$ and a oxygen vacancy ($V_O^{2+}$). These peaks also became strong as temperature went down. The fact that the intensity of the $V_O^{2+}$ PL of Sample-B is much larger than that of Sample-A means that the oxygen vacancy was introduced for Sample-B under the different
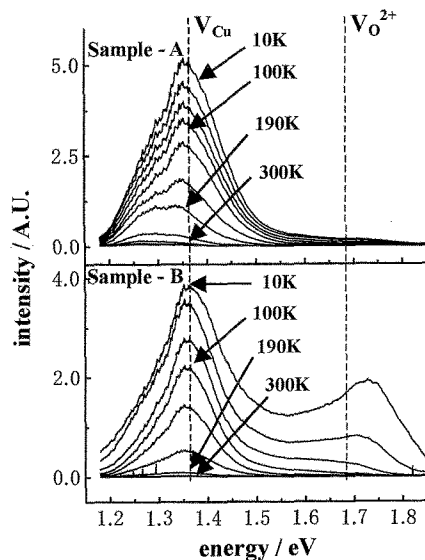


Figure 2. Photoluminescence spectra of $Cu_2O$ films. Excitation wavelength was 514 nm. Spectra were measured at elevated temperature from 10 K to 300 K with each step of 30 K.
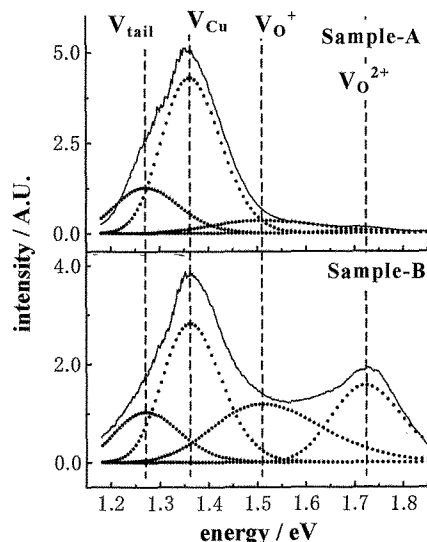


Figure 3. Deconvolution of spectra by four components of vacancy sites, $V_{tail}$ (1.27 eV), $V_{Cu}$ (1.36 eV), $V_O^+$ (1.51 eV) and $V_O^{2+}$ (1.72 eV), from the left to the right, respectively.

deposition condition. The $V_O^{2+}$ emission is also broad (0.17 eV i.e. 69 nm).

In $Cu_2O$ samples of single crystalline grades, several photoluminescences due to the vacancy sites of copper and oxygen are known; $V_{Cu}$ at 1.36 eV(~910 nm), $V_O^{2+}$ at 1.51 eV(~720 nm), and $V_O^+$ at 1.72 eV(820 nm). Moreover, a luminescence tail ($V_{tail}$) appears at the longer wavelength side of $V_{Cu}$ although the origin of this tail is not known yet [15]. Since our spectra cannot be represented by single Gaussian profile, they are deconvolved as an overlap of these four known peaks. Figure 3 shows the PL spectra of Sample-A and Sample B at 10 K and their deconvolved Gaussian peaks. The position of the component peaks are fixed to known values, and the peak width and the intensities are varied. These fitted values are listed in Table 1. As is

Table 1. Observed PL wavelengths, widths and integrated intensities.

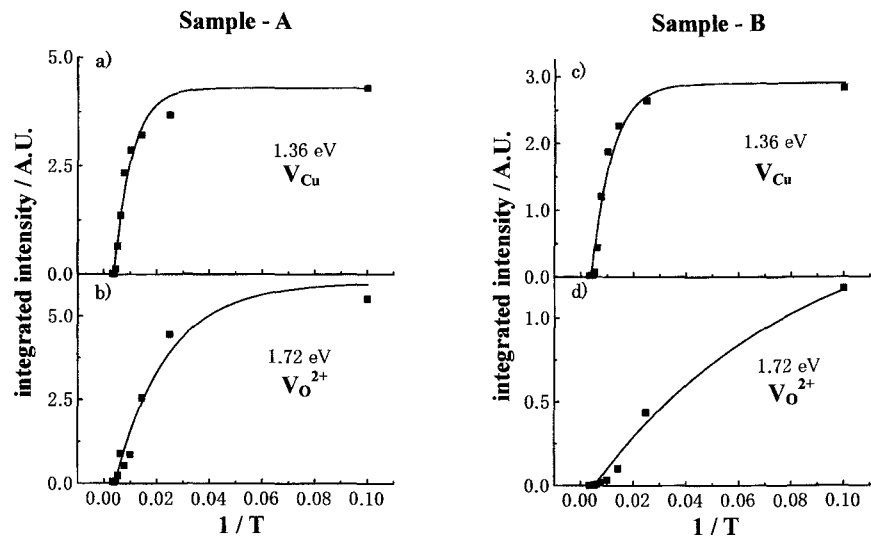| vacancy type | Sample-A | | | Sample-B | | | Literature* | |
|---|---|---|---|---|---|---|---|---|
| | peak / eV | fwhm / eV | intergrate intensity / A.U. | peak / eV | fwhm / eV | intergrate intensity / A.U. | peak / eV | fwhm / eV |
| $V_{tail}$ | 1.27 | 0.15 | 0.20 | 1.27 | 0.15 | 0.16 | — | — |
| $V_{Cu}$ | 1.36 | 0.14 | 0.65 | 1.36 | 0.14 | 0.43 | 1.36 | 0.097 |
| $V_O^+$ | 1.51 | 0.26 | 0.10 | 1.51 | 0.26 | 0.33 | 1.51 | 0.12 |
| $V_O^{2+}$ | 1.72 | 0.17 | 0.013 | 1.72 | 0.17 | 0.28 | 1.72 | 0.11 |

* ref.14



Figure 4. Integrated intensities plotted against inverse temperatures. Black squares are experimental data and solid lines are the fitted curves using simple three state relaxation. The upper panes and the lower panels correspond to $V_{Cu}$ (1.36 eV) and $V_O^{2+}$ bands.
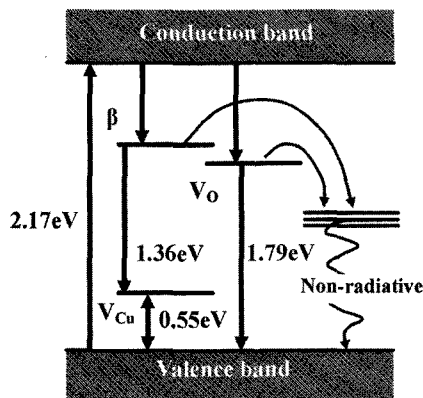


Figure 5. Model kinetics for temperature dependence of $V_{Cu}$ and $V_O^{2+}$.

described above, the peak widths are larger than single crystalline samples. This indicates quite a short lifetime of excited states or an inhomogeneous environment surrounding the trapping sites.

The following discussion focus on the $V_{Cu}$ and $V_O^{2+}$ PL peaks, since they are prominent at low temperatures.

Although $V_O^{2+}$ PL peak of Sample-A is very weak compared to the $V_{Cu}$ peak, the $V_O^{2+}$ of Sample-B is as strong as the half of the $V_{Cu}$ peak. That is, the $V_O^{2+}$ peak of Sample-B is ~20 times stronger than that of Sample-A. The main difference between two samples is the temperature of the electrolyte solution; i.e. 65 °C for Sample-A, and 50 °C for Sample-B. It is reported that under galvanostatic deposition, the potential-time transients shows the clear separation of nucleation and growth phases [7]. They shows that the growth rate become important at higher temperatures while nucleation increases at lower temperatures. This may leads to the increase of the extent of grain boundaries, and also defects and vacancies at lower temperatures. On the while, the reason why the intensity of $V_{Cu}$ emission is not affected by the solution temperature is not clear at this time, although the morphology of the samples is significantly different.

Figure 4 shows integrated intensities of $V_{Cu}$ and $V_O^{2+}$ luminescence plotted against temperature for Sample-A and Sample-B. Black squares indicate the experimental data, and solid lines show fitted curves that assume a simple three state relaxation process as is shown in Figure 5. Ea values in electron volts shown

Table 2. Fitted Ea values.

| Vacancy type | Sample-A Ea / meV | Sample-B Ea / meV |
|---|---|---|
| $V_{tail}$ | 20 | 4.8 |
| $V_{Cu}$ | 13 | 11 |
| $V_O^+$ | 6.1 | 2.2 |
| $V_O^{2+}$ | 4.3 | 1.1 |

in the figure are an activation barrier that electrons transition to nonradiative processes. These values are listed in Table 2. The behaviors of the $V_{Cu}$ emission are almost identical for Sample-A (Fig. 4a) and Sample-B (Fig. 4c). The activation energy are also similar values (13 meV for Sample-A and 11 meV for Sample-B) The $V_{Cu}$ level is higher than the edge of the valence band by 0.55 eV [17]. The $V_{Cu}$ emission occurs when the excited electron relaxes from 'β-state' to the $V_{Cu}$ level [15]. The β-state is supposed to exist below the edge of the conduction band by 0.26 eV, and is considered to be a trapped excitonic state at the $V_{Cu}$ site [15,17]. The above results indicate that the formation of the copper vacancy site is insensitive to the deposition conditions of this study. The PL spectra of single crystal grade samples reported by Ito et al [15]. shows a similar tendency below 150 K, that the $V_{Cu}$ luminescence decreases with increasing temperature. Above 150 K, this emission increases again and shows a maximum at ~240 K according to the literature [15]. This behavior is not observed in our sample. The above results may mean that the relaxation process exists that is similar to the one of single crystals involving a copper vacancy, although the quality of the sample is not so good. On the other hand, the $V_O^{2+}$ emission shows quite different temperature dependence between Sample-A and Sample-B. In Sample-A, the experimental data agree with the fitted curve well as is shown in Fig. 4b, while in Sample-B the fitting quality is poor (Fig. 4b). It should be noted that the $V_O^{2+}$ radiation in Sample-B is quite strong, and therefore the oxygen vacancy concentration is higher in Sample-B than that in Sample-A. The temperature dependence, however, seems different from the one of single crystalline sample reported by Harukawa et al[14]. This implies that Sample-B contains a different type of oxgen vacancies from Sample-A and the single crystalline one.

4. Conclusion

Pure Cu₂O films electrodeposited from an aqueous copper lactate basic solution is characterized by the measurement of photoluminescence spectra from the copper and oxygen vacancies at different deposition conditions. As the deposition rate is increased by increasing solution temperature from 50 °C to 65 °C, the vacancy concentration of $V_O^{2+}$ is increased significantly lthough that of $V_{Cu}$ is unchanged.

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