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Photoacoustic Characterization of Porous Zinc Oxide Thin Films

多孔質 ZnO 薄膜の光音響分光特性

Shuzo Yamada[1†], Eiji Hosono[2], Haoshen Zhou[2], Qing Shen[1, 3] and Taro Toyoda[1]
([1]The Univ. of Electro-communications; [2]AIST.; [3]PRESTO, JST)
山田 修三 [1‡], 細野 英司 [2], 周 豪慎 [2], 沈 青 [1,3], 豊田 太郎 [1]
([1] 電気通信大学; [2] 産総研; [3]JST さきがけ)

1. Introduction

Zinc oxide (ZnO) has attracted worldwide attention because it can be used as electrode material of sensitized solar cells (SSCs). At the first step to apply ZnO to SSCs, the study on the optical absorption property of the ZnO is essential. In this study, porous ZnO thin films were prepared and investigated the influence of deposition temperature during the chemical bath deposition (CBD) procedure upon optical absorption property of porous ZnO thin films by using photoacoustic (PA) technique. PA technique is a photothermal methods and has advantages as follows [1]:

(1) available for light absorption measurement for opaque or strong scattering sample.
(2) nondestructive and noncontact method.
(3) useful for the simultaneous characterization of thermal property, optical property and carrier relaxation processes.
(4) depth profile analysis of a sample by changing incident light modulation frequency.

2. Experiments

The porous ZnO were directly assembled on fluorine doped tin oxide (FTO) substrates by a chemical bath deposition (CBD) method [2]. First, $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in methanol. The concentration of Zn was fixed at 0.15 mol/dm^3. The substrates were immersed in the above solution and were kept at 56 - 62℃ for 12 - 48 hours. Finally, the samples were heated at 450℃ for 10 min in air.

Characterization of the morphology and structure of the porous ZnO thin films were studied by using scanning electron microscopy (SEM).

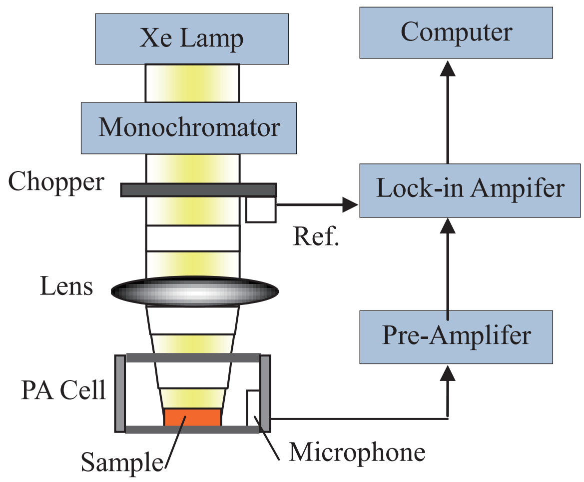

Fig. 1. Schematic diagram of PA spectrometer.

The optical absorption of the films was studied by using PA technique. The schematic diagram of the PA spectrometer used for the analysis is shown in Fig. 1. The PA measurements were carried out by using a gas-microphone PA technique. A monochromatic light beam was obtained by passing the light from a 300 W Xe arc lamp through a monochromator. This beam intensity was modulated with a mechanical chopper and focused onto the surface of a sample placed inside a sealed PA cell. Measurements of the PA spectra were carried out in the wavelength range of 300-600 nm with a modulation frequency of 33Hz at room temperature. The light absorbed by the sample is converted into heat by nonradiative relaxation processes, which result in a pressure fluctuation of the air inside the cell. The pressure fluctuation oscillating is detected as the PA signal by a microphone enclosed in the PA cell and amplified by a preamplifier and a two-phase lock-in-amplifier.

†E-mail address: shuzo.y@jupiter.pc.uec.ac.jp

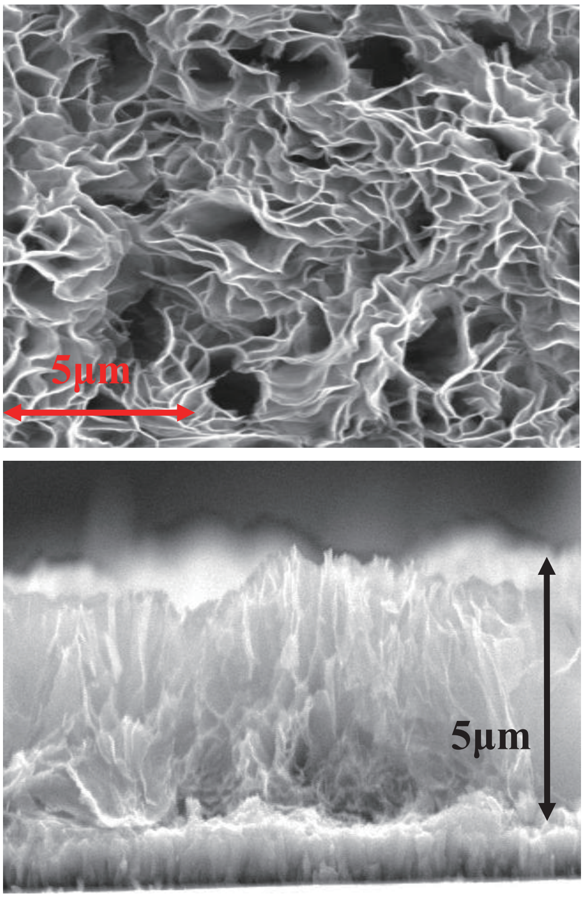

Fig. 2. SEM images of porous ZnO thin films deposited after immersion at 56℃ for 36h (a) surface and (b) cross section.

3. Results and discussions

Figure 2 shows SEM images of ZnO films ((a) surface and (b) cross section ; deposition: 56℃ for 36h). Highly porous nanostructures in the ZnO films could be demonstrated from the SEM observations. The film thicknesses of the porous ZnO thin films increased with the decreases of the deposition temperature during the CBD procedure.
Figure 3 shows the PA spectra of porous ZnO thin films having three different deposition temperatures during the CBD procedure from 56℃ to 62℃ (film thickness: 2-5μm). The PA intensity spectra gradually increase and show peaks at around 3.3 eV for all sample. In the PA spectra, the exponential slope of the spectrum increases with the increase of the deposition temperature during the CBD procedure. PA intensity (P) is assumed with the following equation (1) on the assumption that the PA intensity is proportional to the absorption coefficient α,

$$P = P_o \exp\left[-\sigma (E_o - E) / k_B T\right]. \quad (1)$$

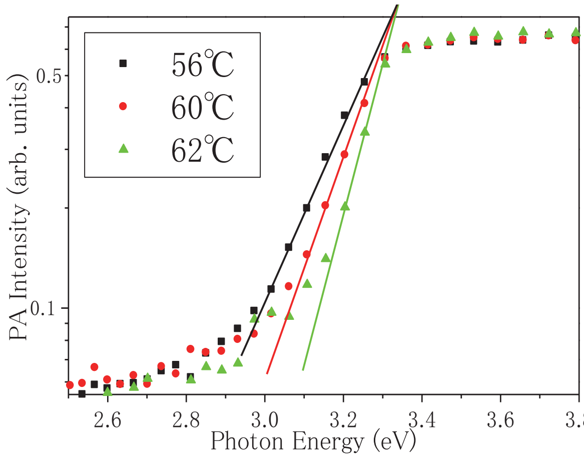

Fig. 3. photoacoustic spectra of porous ZnO thin films with different the deposition temperatures during the CBD procedure (■: 56℃, ●: 60℃, ▲: 62℃)

In eq. (1), σ is steepness factor [3], P_o and E_o are constant, E, k_B, and T are photon energy, Boltzmann constant, and room temperature, respectively. These values of steepness factor σ are shown at Table 1. It is found that the steepness factor σ increases with the increase of the deposition temperatures during the CBD procedure. Usually, the optical absorption in the region with photon energy lower than bandgap can provide information on disorders, defect and characteristic of electron- phonon interactions for semiconductor samples. One possibility for the increase of the steepness factor σ with increasing the deposition temperatures during the CBD procedure could be supposed to result from the decrease of defects and/or disorders in ZnO during the CBD procedure.

deposition temperatures (℃)	56	60	62
steepness factor σ	0.075	0.090	0.12

Table 1. Steepness factor for different deposition temperatures.

References

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