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The study of bandgap energies of $Cu(In,Ga)Se_2$ thin films grown by a sequential evaporation method using a photothermal spectroscopy

連続成膜法によるCIGS薄膜の光熱変換分光法を用いたバンドギャップの評価

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1. Introduction

Chalcopyrite $Cu(In,Ga)Se_2$ (CIGS) is a promising material for thin film solar cells with high conversion efficiency by its high optical absorption coefficient and adjustable bandgap. Its bandgap energy (E_g) varies from 1.04 to 1.68 eV from $CuInSe_2$ to $CuGaSe_2$, respectively. To date, the best CIGS thin film solar cell has reached a confirmed conversion efficiency of about 20%. The Ga/(In+Ga) and E_g of its CIGS film are about 0.3 and 1.15 eV, respectively. Theoretical analysis of the photovoltaic performance of single junction solar cells indicates that much higher efficiencies can be expected for E_g of about 1.4 eV, where a Ga/(In+Ga) is 0.6. However, it is difficult to obtain a single phase CIGS with high Ga/(In+Ga) because of the unintended phase separation into $CuInSe_2$ and $CuGaSe_2$ or phase gradation due to the difference in the reaction rates of the two compounds.[1)] In addition, the open-circuit voltage (V_{OC}) and the efficiency of the CIGS solar cells do not increase proportionally with E_g due to the low crystal quality.[2)]

Currently, device-quality CIGS thin films are prepared by three-stage process using a molecular beam epitaxy (MBE).[3)] On the other hand, we proposed a new process using a vacuum deposition apparatus with three evaporation boats, which was the sequential evaporation technology from $CuInSe_2$ and $CuGaSe_2$ ternary compounds.[4,5)] Proposed process has advantages to be able to easily control Ga/(In+Ga) in CIGS thin films by changing the amount of $CuInSe_2$ and $CuGaSe_2$ evaporating materials in the first step. This enables us to obtain inexpensive equipment for preparation of the absorbing layer.

In this study, we investigate the optical properties of CIGS thin films with high Ga/(In+Ga) fabricated by sequential evaporation method. Although it is usually important to measure the optical absorption spectrum in order to estimate E_g, a conventional optical absorption technique for measuring the ratio of incident and transmitted light cannot be performed because of strong absorption of Mo layer as a back contact. Hence, in order to estimate E_g of CIGS thin films, we have adopted the photoreflectance (PR) and the photothermal (PT) technique using a transparent transducer.

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2. Experimental Procedure

The CIGS thin film samples were prepared on Mo/soda-lime glass (SLG) by sequential evaporation method as follows.[4,5)] In the first step, Cu-In-Ga-Se layer was evaporated from $CuInSe_2$ and $CuGaSe_2$ compounds onto the Mo/SLG substrate. In the second step, In-Ga-Se layer was deposited from In_2Se_3 and Ga_2Se_3 compounds. Finally, only Se was effused.

The PR measurement was carried out using a standard experimental setup.[6)] An Ar^+ (488 nm) of 3 mW was used as the excitation source to generate an electric field. The ratio of AC and DC components of the optical reflection signal from the sample surface ($\Delta R/R$) were detected. E_g was estimated by fitting the third derivative Aspnes' function to $\Delta R/R$ spectrum.[7)]

For the PT measurements, the transparent transducer was attached on CIGS surface and probing light was incident on the same side. All the PT measurements were carried out at room temperature.

3. Results and Discussion

Obtained $\Delta R/R$ spectrum of sample with Ga/(In+Ga) of 47% at 4.7 K is shown in **Fig. 1** by the solid curve. As shown in the figure, signal modulations accompanied by peak and dip were observed in the $\Delta R/R$ spectrum. To check the interference effect within CIGS thin films, we calculated the theoretically expected reflection spectrum from CIGS surface using the refractive indices.[8)] We ascertained the consistency of the photon energy positions of the maximum and minimum intensities between the calculated and obtained reflection spectra shown in Fig. 1 by the

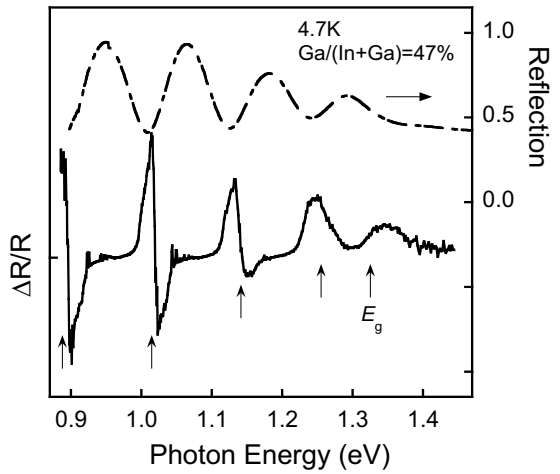

Fig. 1 ΔR/R spectrum of Ga/(In+Ga) of 47% at 4.7 K.

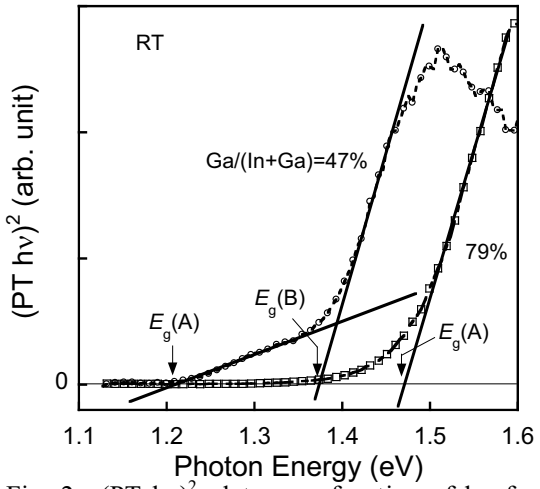

Fig. 2 $(PT\ h\nu)^2$ plots as a function of hν for Ga/(Ga+In) of 47 and 79%

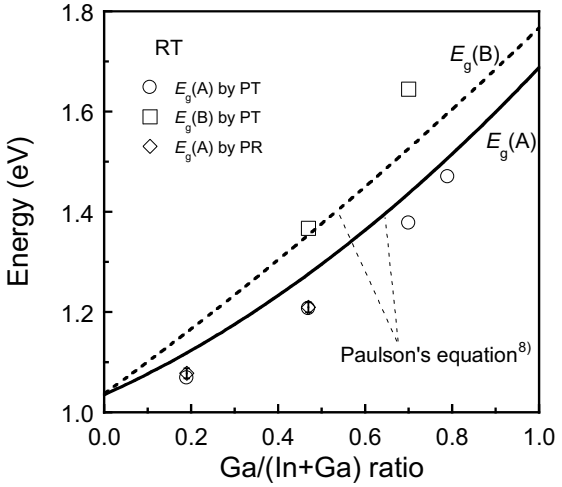

Fig. 3 Change of E_g estimated by PT as a function of Ga/(In+Ga) in film

dashed curve. We then concluded that signal modulations observed around 0.90, 1.00, 1.15, and 1.25 eV were not due to E_g but the interference effect within CIGS thin films. Therefore, E_g of sample with Ga/(In+Ga) of 47% at 4.7 K was estimated to be 1.325 eV. However for high Ga/(In+Ga) more than 70%, the ΔR/R spectrum could not be obtained because of weak signal intensity arising from the low crystalline.

For samples with high Ga/(In+Ga), we adopted the PT method. In case of a detector and an incident light configuration of the present study, the PT signal intensity is expected to be proportional to its optical absorption coefficient α.[9)] Since the CIGS is a direct bandgap semiconductor, we plotted the $(PT\ h\nu)^2$ as a function of the photon energy (hν) in place of $(\alpha\ h\nu)^2$ to estimate E_g of these films. **Fig. 2** shows $(PT\ h\nu)^2$ plots of the samples with Ga/(In+Ga) of 47 and 79%. The values of E_g of CIGS thin film were estimated from the extrapolation of the straight lines to $(PT\ h\nu)^2 = 0$, as shown in the Fig. 2.

Estimated values of E_g by PR and PT were plotted on **Fig. 3**. We found that E_g shifted to higher energy side with increasing of Ga/(In+Ga). In this figure, variation in fundamental absorption edges were also shown, where E_g(A) and E_g(B) are the non-degenerate levels formed by the crystal field and spin-orbit interaction.[8)] Obtained E_g by PR and PT well coincided with the value of Paulson's calculation. As a result, present experimental results implied that the Ga/(In+Ga) of CIGS thin films can easily controlled by using the proposed sequential evaporation method, and that the PT is a powerful method for determining the E_g of low crystallinity sample.

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