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Study of Terahertz Emission from Surfaces of $Cu(InGa)Se_2$ Layers

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In this contribution, we report on investigations of THz emission from $Cu(In,Ga)Se_2$ layers, deposited from a single copper-deficient sputtering target. Emission from $Cu(In,Ga)Se_2$ layer surface and from multilayer structure with transparent ZnO layers were studied. It was determined that additional undoped ZnO layer reduces the amplitude of THz emission, while additional n-type ZnO layers increase the emission amplitude again. This effect can be attributed to stronger electric field in the heterostructure between p-type $Cu(In,Ga)Se_2$ and n-type ZnO layers.

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1. Introduction

The efficiency of $Cu(In,Ga)Se_2$ (CIGS) solar cells have recently reached a 20.3% record [1] for small solar cells. Such a number means that CIGS technology is already competitive with silicon solar cells and could be one of the most promising technologies for cost reduction of photovoltaics. However, one of the remaining challenges for the production of CIGS solar cells is the lack of diagnostics tools that could provide rapid feedback for adjusting real-time processes. In this paper, we report on investigations of THz emission from $Cu(In,Ga)Se_2$ layers in various steps of production, and the influence of additional transparent oxide layers.

2. Experiments

In our experiments, we have used two THz time domain spectroscopy (TDS) setups with different femtosecond lasers. The first laser was more powerful (650 mW), while the second one gave a possibility change of the excitation wavelength at a fixed power of 5 mW. These setups are presented in Fig. 1.

For initial measurements, a setup with femtosecond mode-locked Ti:sapphire laser (800 nm wavelength, 150 fs pulse duration, 76 MHz repetition rate, 650 mW average power) was used (Fig. 1b) [2]. The laser beam was divided into two parts. More powerful part was directed to the CIGS sample, which in turn emits THz radiation. THz radiation was detected by the low temperature grown (LTG) GaAs photoconductive detector, which was gated by small part of laser radiation ($\approx$ 45 mW). The sample was attached to a 2-axis stage mount, with which we could measure THz emission from different sample parts. By changing the delay line position, we change the delay only of the THz pulse which arrives at the THz detector and therefore induces the current, which is measured with a lock-in amplifier. Thus we determine the entire THz pulse transient.

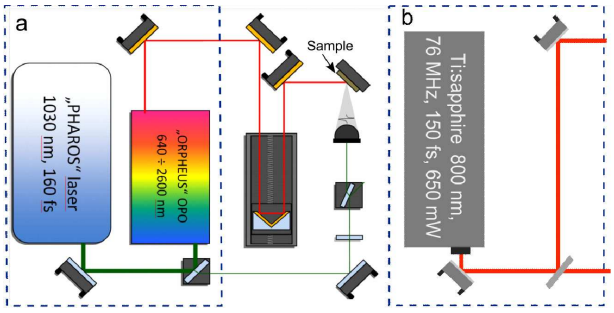

Fig. 1. Measurement setup. Parts of the setup indicated by a dashed line rectangle were interchanged based on the experiment requirements. Part (a) was used for tunable spectrum measurements, part (b) for a fixed excitation measurements at higher power levels.

For experiments with variable quantum energy, a more complex system was used (Fig. 1a). Here, as the optical source, amplified ytterbium-doped potassium gadolinium tungstate (Yb:KGW) laser system (Pharos, Light Conversion Ltd.) was used. It emits 1030 nm, 160 fs optical pulses with 200 kHz repetition rate. The major part of laser radiation ($\approx$ 6 W) was directed to the optical parametric amplifier (OPA Orpheus, Light Conversion Ltd.), which generates tunable 640–2600 nm wavelengths and approximately 140–160 fs long pulses. This setup is similar to the setup that we described previously except that the THz radiation was detected by the photoconductive THz detector manufactured from a GaAsBi epitaxial layer, which was excited by a small part of laser radiation ($\approx$ 5 mW).

The THz excitation spectrum was determined by changing the wavelength of the excitation laser beam and measuring the peak to peak value of THz waveform. Measurements were performed at constant optical power ($\approx$ 5 mW), where the THz amplitude is linearly propor-

tional to the optical power. All spectra were normalized to a constant photon number. More detailed instructions of this experiment can be found in Ref. [3].

Test samples were prepared using Alcatel SCM 650 sputtering equipment. First, approximately 1 μm thick molybdenum layer was deposited on top of the polished and cleaned glass plates. Afterwards, approximately a 0.36 μm thick layer was deposited from a single quaternary chalcogenide CIGS target (Pioneer Materials, 20 cm diameter, 6.35 mm thickness, composition: Cu — 22.8 at.%, In — 20 at.%, Ga — 7 at.%, Se — 50.2 at.%). After deposition, the sample was annealed in argon atmosphere for 20 min at 250 °C and for 40 min at 530 °C.

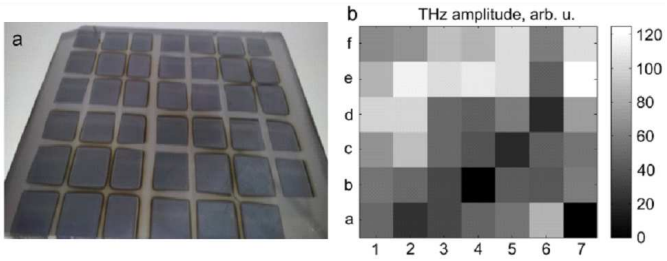

Fig. 2. Photo of the sample (a); peak THz amplitude map of CIGS surface without additional ZnO layer (b). Amplitude values correspond to peak photocurrent of THz detector, measured in pA. Numbers and letters on the axis are used later to indicate the position of the sample square (e.g. a1, b3 etc.), from which THz waveform is recorded.

Photograph of the obtained sample is presented in Fig. 2a. Each of the squares corresponds to a CIGS layer segment with slightly different properties due to a relatively large glass size (approximately 9×12 cm^2) causing non-uniformity during the deposition step and thermal gradients during the thermal processing step.

3. Results

Firstly, an entire sample array was scanned with first THz TDS setup. An obtained photocurrent map is presented in Fig. 2b. As one can see, a rather random map is obtained. Recorded THz pulse wave forms and spectra from one row (b row) of a sample are presented in Fig. 3. Pulse wave forms and shapes of the spectra are similar. Difference in peak amplitude and spectra width can be explained by different properties of CIGS layer.

After deposition of an undoped 50–60 nm thick ZnO layer, the amplitude map becomes more uniform, with an amplitude reduction in the average (Fig. 4a,b). Such a result can probably be attributed to a modification of internal fields near the surfaces of CIGS crystals by deposition of an undoped wide-gap semiconductor ZnO.

One of the "brightest" (in THz) sample fields (b2) was selected for further characterization after a step-by-step growth of doped ZnO:Al layers. First, the THz amplitude was recorded for various quantum energies of the

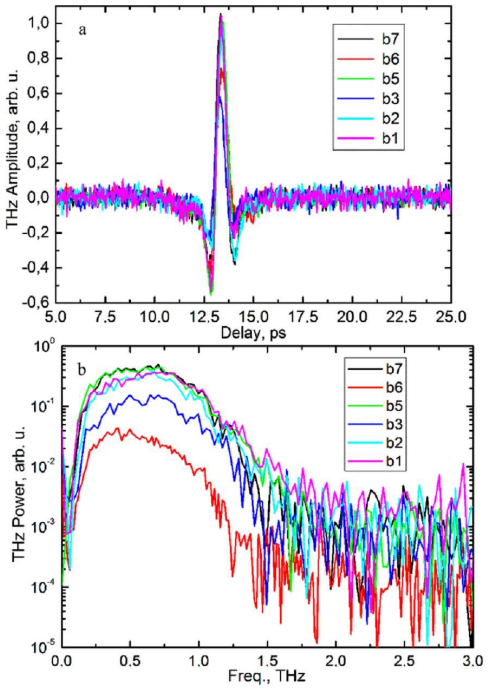

Fig. 3. Recorded THz pulse wave forms (a) and their spectra (b) from b row of a sample.

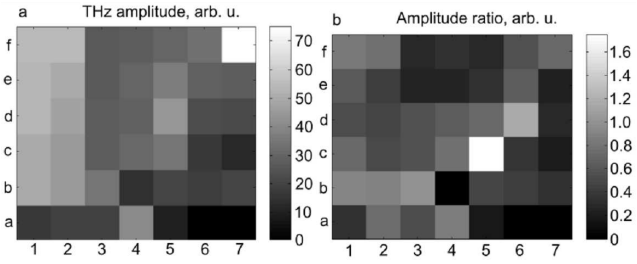

Fig. 4. Peak THz amplitude map of CIGS samples with an undoped ZnO layer (a); ratio of peak THz amplitudes without (Fig. 2b) and with (Fig. 4a) additional undoped ZnO layer (b). Amplitude values correspond to peak photocurrent from the detector, measured in pA.

excitation beam. Measurement results are presented in Fig. 5. Here, as one can clearly see, the THz emission amplitude growths steadily, starting from approximately 1.2 eV. The signal was too low to record the emission below 1.2 eV. For the given composition of CIGS layer, 1.2 eV is an expected band-gap value, and growth of the emission amplitude with increased photon energy is expected for direct band-gap materials [3].

Afterwards several ZnO:Al_2O_3 (standard 2% doping) layers were deposited in the same sputtering equipment in order to check the influence of doped n-type semiconducting layers on THz emission properties. The overall thickness of layers was 800 nm, deposited in 4 steps of 200 nm each. The results are summarized in Fig. 5. As one can clearly see, a steady amplitude growth is ob-

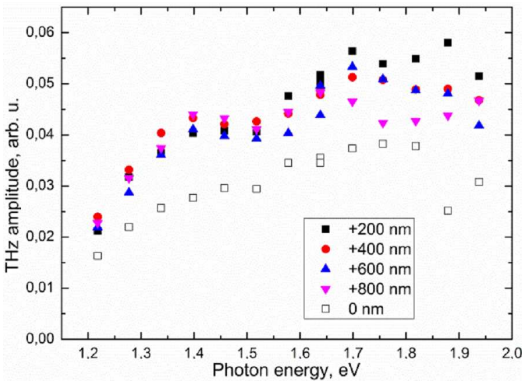

Fig. 5. THz amplitude dependence on photon energy of the excitation beam for the sample with additional n-ZnO layer of different thickness.

served for all excitation energies and thicknesses in comparison with the layer having only undoped ZnO. This effect can be attributed to an increased electric field near the CIGS/ZnO/ZnO:Al_2O_3 junction. The Cu deficient CIGS is usually a p-type material, while ZnO:Al_2O_3 is an n-type wide band-gap semiconductor. Due to heavy doping of ZnO:Al_2O_3 layer, the depleted area in such heterostructure should extend mostly into layers below. This also means that 200 nm is a sufficient thickness to screen any dc electric fields within this layer. Due to wide band-gap of ZnO, it is also transparent for all photon energies in the investigated range and partially transparent in THz [4].

4. Conclusions

The spectra of THz emission from Cu(In,Ga)Se_2 layers, grown by the sputtering technique from a single chalcogenide target, was studied by means of THz TDS spectroscopy. It was determined that for large area samples, THz emission may vary by nearly an order of magnitude, probably because of imperfections in grown layers and the influence of surface defects. However, a well pronounced average reduction of the amplitude was observed when an undoped ZnO layer was deposited. The THz amplitude increased as a result of ZnO:Al positioning. This effect can be attributed to stronger electric fields in the heterostructure with the p-type CIGS and the n-type transparent contact. The growth of the THz amplitude was observed for photon energies of the fs beam above 1.2 eV, confirming an expected direct band gap of deposited material.

Acknowledgments

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