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Semitransparent *p*-CuI and *n*-ZnO thin films prepared by low temperature solution growth for thermoelectric conversion of near-infrared solar light

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ABSTRACT

In this work by means studying the crystal structure, optical, electrical, and thermoelectric properties of chip, available and safe for the environment copper iodide CuI, zinc oxide ZnO and indium-doped zinc oxide ZnO:In films we have developed and improved low temperature solution growth Successive Ionic Layer Adsorption and Reaction (SILAR) technique, which allows to deposit these materials over large areas. Output thermoelectric parameters were analyzed for several single *p*-CuI, *n*-ZnO and *n*-ZnO:In thin film thermolegs. The possibility of combining of the obtained *p*-CuI and *n*-ZnO:In thin film thermolegs into a thermocouple is shown for the use in new semitransparent planar solar thermoelectric generator working at near-room temperatures through harvesting near-infrared solar light as an energy source to supply electric power to the wireless sensors and microscale devices.

1. Introduction

Although near-infrared (NIR) light, which is approximately 42% of solar light, cannot be efficiently converted into electric energy using the photovoltaic effect, it can be harvested with the use of thin film thermoelectric (TE) materials in thermoelectric generators (TEGs) of a new generation (Moraes et al., 2015; Mizoshiri et al., 2012a; Zhu et al., 2015a; Ito et al., 2017). Bulk thermoelectric materials are foremost applied in high power and high temperature regimes, but TE thin films have their main field of application in low temperature and low power consumption electronic devices. It is difficult to improve the generation performance of the vertical type thin film TEGs, because a large temperature gradient ΔT cannot be generated in the thin films in the thickness direction, but ΔT in the planar TEGs can be controlled facilely by changing the length and shape of the thin film thermolegs (Mizoshiri et al., 2012a; Zhu et al., 2015a; Ito et al., 2017). Along with a reduction in material usage, thin film TE materials have also other advantages when compared to the bulk, specifically, the higher degrees of freedom as the in-plane geometry can be adapted to the application requirements. In the designs of thin film solar TEGs presented in Mizoshiri et al. (2012a, 2012b), solar light is focused by cylindrical lens on the one side of the banded *p*-$Bi_{0.5}Sb_{1.5}Te_3$ and *n*-$Bi_2Te_{2.7}Se_{0.3}$ thermolegs in the center part of the planar thermoelectric module and heats them up to 45–53 °C creating in this way a temperature gradient $\Delta T \approx 20$ K between hot and cold edges of the thermolegs. In the proposed by Zhu et al. (2015a, 2015b) thin film solar TEGs, the central area is the absorber for solar light, from which thin *p*-$Bi_{0.5}Sb_{1.5}Te_3$ and *n*-$Bi_2Te_{2.7}Se_{0.3}$ semiconductor strips extend across the TE module plane to the metal contacts on its rim. When solar irradiation heats up central area (it is also the hot side of the TEG) up to 52 °C, a temperature difference $\Delta T \approx 20$ K is established across the *p*-$Bi_{0.5}Sb_{1.5}Te_3$ and *n*-$Bi_2Te_{2.7}Se_{0.3}$ thermolegs, as the outer rim is maintained at the surrounding temperature. In above mentioned configurations, the solar illumination area, heat conduction area, thermolegs, and electrodes are all placed in the same plane. The devices (Mizoshiri et al., 2012a, 2012b; Zhu et al., 2015a, 2015b), which generate several hundreds of microwatts, convert waste energy in the environment into electric energy. Authors Ito et al. (2017) have demonstrated a fabrication of thin film thermoelectric generator with ball lenses, which separated visible light and near-infrared solar light using a chromatic aberration. So, the transmitted visible light is used as daylight and the NIR light is used for thermoelectric generation by semicircular sections of opaque *p*-$Bi_{0.5}Sb_{1.5}Te_3$ and *n*-$Bi_2Te_{2.7}Se_{0.3}$ thin films as thermolegs. Evaluation of the thermoelectric properties of this TEG with ball lenses when solar

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light (A.M.1.5) was irradiated at 298 K has shown (Ito et al., 2017) the temperature difference between the hot and cold sides (distance 374 μm) $\Delta T \approx 0.58$ K, open circuit voltage $U_{oc} \approx 0.88$ mV and maximum output power $P_{max} \approx 1.0$ nW.

Common drawbacks of the all above designs of thin film solar TEGs, which can turn NIR light into electricity, is toxicity and extremely scarce in the Earth's crust of tellurium, and also an opaqueness of $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Te_{2.7}Se_{0.3}$. Therefore, it is necessary to develop alternative materials which involve cheaper and abundant wide bandgap semiconductor elements. If thin and visibly transparent solar TEGs on the base of abundant and environmental friendly materials, especially, *p*- and *n*-type TE wide bandgap semiconductors, will be available, the NIR light can be used as an energy source for micro- and nano-energy application. Along with this, the visible light can be used as daylight when these solar TEGs are set on transparent or semitransparent substrates (Loureiro et al., 2014; Fan et al., 2015; Mondarte et al., 2016; Ito et al., 2017; Yang et al., 2017). The prospect of a using of low cost thin film solar TEGs based on the earth abundant semitransparent TE materials on large areas, for example, in the building's glazing, has led to the idea of self-powering, wherein devices are driven by heat from their working environment (Jiménez-Gonzaílez and Nair, 1995; Khallaf et al., 2009; Tubtimtae and Lee, 2012; Gaspera et al., 2015; Jantrasee et al., 2016; Mondarte et al., 2016; Edinger et al., 2017; Klochko et al., 2017). In these TEGs the thermal energy of the terrestrial heat produced by sunlight can create a temperature gradient ΔT of several Kelvin degrees, which is converted to electric energy through TEGs thus ensuring the recycling of this waste heat. For instance, recently energy-harvesting devices have attracted attention in the Internet of Things (IoT) and Roadmap for the Trillion Sensors Universe to supply electric power to the IoT sensors.

Lately, large thermoelectric figure of merit and high value of Seebeck coefficient were theoretically predicted (Yadav and Sanyal, 2014) and experimentally obtained (Yang et al., 2017; Klochko et al., 2017; Kneiß et al., 2018; Rabinal and Mulla, 2018) for a new wide bandgap thermoelectric material copper iodide (γ-CuI). According to Yang et al. (2017), Klochko et al. (2017), Kneiß et al. (2018), Rabinal and Mulla (2018), γ-CuI is a promising candidate for the *p*-type counterpart in the semitransparent thermoelectrics due to its high bandgap $E_g \approx 3$ eV at room temperature and intrinsically *p*-type conducting due to copper vacancies always present in the material. Again, *n*-type oxide TE materials, in particular ZnO and its solid solutions, are promising candidates for the use in thin-film solar TEGs (Loureiro et al., 2014; Fan et al., 2015; Hung et al., 2015; Jantrasee et al., 2016; Mondarte et al., 2016) due to their natural durability, robustness to the environments in addition with low cost and availability in comparison with conventional TE intermetallic compounds. As ZnO is a wide bandgap material ($E_g = 3.37$ eV) it can be suitable for the creation of *n*-type legs in the semitransparent thin film solar TEGs, if the problem of its sufficiently high resistivity is solved by doping.

However, till now, high cost and complex production technique, such as magnetron sputtering (Loureiro et al., 2014; Fan et al., 2015) and reactive sputtering (Yang et al., 2017; Kneiß et al., 2018) restrict the use of the thermoelectric generators with *p*-CuI and *n*-ZnO thin film thermocouples. To replace the vacuum methods, some solution chemical TE thin film deposition methods are offered (Jiménez-Gonzaílez and Nair, 1995; Khallaf et al., 2009; Tubtimtae and Lee, 2012; Gaspera et al., 2015; Jantrasee et al., 2016; Edinger et al., 2017; Klochko et al., 2017), which have an intrinsic appeal, as they are suitable for large surfaces and suggest low capital expenditure based on simple process equipment. In comparison with other methods, Successive Ionic Layer Adsorption and Reaction (SILAR) is low cost, affordable and suitable for mass production approach. At the same time, SILAR like other aqueous chemical methods has essential drawback, since it typically shows a high defect density, which lowers product performance. Probably therefore, doped and undoped ZnO films obtained via SILAR (Jiménez-Gonzaílez and Nair, 1995; Mondal et al., 2008; Raidou et al., 2014) were not used in the production of semitransparent solar TEGs, and CuI films deposited by this method we reported only recently in Klochko et al. (2017) as nanostructured semiconductor layers for thin-film solar thermoelectric generator.

In this work by means studying the crystal structure, optical, electrical, and thermoelectric properties of the copper iodide, undoped and indium-doped zinc oxide films deposited via SILAR method we have developed and improved SILAR technique to create efficient TE materials that are chip, safe for the environment and can be prepared over large areas. The *p*-CuI and *n*-ZnO:In thin films, which we received on glass substrates, are suitable for the implementation as thermolegs for low cost and available semitransparent planar solar TEG working at near room temperatures at low ΔT through harvesting NIR solar light as an energy source.

2. Experimental procedures

In this study, CuI, ZnO and ZnO:In thin films were synthesized via SILAR method on soda lime glass substrates. Deposition of copper iodide films was carried out similar to that described in Sankapal et al. (2005), Klochko et al. (2017) and Ighodalo et al. (2017) using an aqueous solution containing 0.1 M $CuSO_4$ and 0.1 M $Na_2S_2O_3$ as a cationic precursor, in which a copper (I) thiosulfate complex $Na[Cu(S_2O_3)]$ was formed, according to (Sankapal et al., 2004). The glass substrate was immersed into the cationic precursor for 20 s. A monolayer of copper ions Cu^+ was adsorbed on the surface of the substrate, and other ions were removed by washing the substrate in distilled water for 10 s. For the reaction of the adsorbed Cu^+ with I^- ions, the substrate was then immersed for 20 s into aqueous NaI solution (anionic precursor), which concentration was 0.05, 0.075 or 0.10 M. After that, the loosely coupled particles and ions were removed by washing in distilled water for 10 s. The listed procedure was one SILAR CuI cycle. Such SILAR cycles were repeated 25–40 times. The resulting 100–820 nm thick CuI films were well bonded to the substrates, semitransparent and yellowish in color. The thickness of the CuI film was determined gravimetrically, taking for a calculation the bulk CuI density 5.67 g/cm^3.

SILAR depositions of undoped and indium-doped zinc oxide films,

Table 1
Modes of SILAR deposition and subsequent treatments for some ZnO and ZnO:In films.

Sample	Cation precursor composition				Annealing modes		
	ZnO, mM	KOH, M	$InCl_3$, mM	$Na_3C_6H_5O_7$, mM	Temperature, °C	Atmosphere	Duration, h
ZnO:In	60	2.7	9	3	–	–	–
ZnO:In	60	2.7	9	3	200	Vacuum	1
ZnO:In	120	2.7	9	3	–	–	–
ZnO:In	120	2.7	9	–	200	Vacuum	1
ZnO	120	2.7	–	–	200	Vacuum	1
ZnO:In	185	2.7	9	–	200	Vacuum	1
ZnO	185	2.7	–	–	–	–	–
ZnO:In	620	3.6	9	–	550	Air	2