Solar Energy 157 (2017) 657–666

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Wet chemical synthesis of nanostructured semiconductor layers for thin-film solar thermoelectric generator

N.P. Klochko[a], V.R. Kopach[a], I.I. Tyukhov[b,1,*], G.S. Khrypunov[a], V.E. Korsun[a], V.O. Nikitin[a], V.M. Lyubov[a], M.V. Kirichenko[a], O.N. Otchenashko[a], D.O. Zhadan[a], M.O. Maslak[a], A.L. Khrypunova[a]

[a] National Technical University "Kharkiv Polytechnic Institute", 2, Kirpichov st., 61000 Kharkiv, Ukraine
[b] Russian Academy of Sciences, Federal Research Agroengineering Centre, 1st Institutskiy proezd, 5, Moscow 1094282, Russia

ARTICLE INFO

Keywords:
Thin-film solar thermoelectric generator
Bi_2S_3
CuI
PbS

ABSTRACT

The work is devoted to the creation of the nanostructured bismuth sulfide (Bi_2S_3), copper iodide (CuI) and lead sulfide (PbS) semiconductor layers for thin-film solar thermoelectric generator by means of wet chemical synthesis, namely, via Chemical Bath Deposition (CBD) or via Successive Ionic Layer Adsorption and Reaction (SILAR). Ways to overcome the problems of poor adhesion of Bi_2S_3 layers to glass, mica and polyimide substrates and to remove restrictions deal with low thickness limits for Bi_2S_3 and PbS have been shown. Optical properties of the smooth and continuous ~1.0–1.2 μm thick Bi_2S_3, CuI and PbS films researched, which were deposited on the solid glass surfaces and on the flexible mica or polyimide substrates. The obtained films have polycrystalline structures of the corresponding bulk semiconductors with grain sizes of several tens of nanometers. Studies of their temperature dependent resistivities ρ, Seebeck coefficients S and power factors $P = S^2/\rho$ are depicted, which confirmed that the obtained thin-film materials are promising for the solar heat transforming into electricity.

1. Introduction

Thermoelectric generation is a promising approach to convert a temperature gradient, generated by thermal energy, directly into electric energy. As a concept, solar thermoelectric generators (STEGs) have been under constant development since the 19th century and have garnered significant research attention recently (Moraes et al., 2015; Mizoshiri et al., 2012a; Zhu et al., 2015a). The STEGs are based on the thermoelectric electromotive force (emf) commonly called as Seebeck effect and designed by embedding semiconductor materials packaged into an alternating array of positively and negatively doped elements referred to as a thermoelectric module (TEM). Researchers offer various designs of the solar thermoelectric generators. For instance, in some STEG devices (Zhu et al., 2015a) the solar irradiation is initially converted into a thermal energy in a solar absorber, and turn, the thermal energy is converted into electricity using thermoelectric materials. Hybrid solar thermoelectric generator designed by Sundarraj et al. (2017) has the ability to cogenerate heat and electricity. Typically, such hybrid STEG consists of a collector, a heat removal system and a thermoelectric generator (TEG). Another STEG design is a thermal–photovoltaic hybrid solar generator using the thermoelectric modules. In this device, the hybrid module consists of a photovoltaic module, a hot mirror, a near-infrared (NIR) focusing lens and of the TEM. In the STEG operation, near-infrared light, which does not contribute to photovoltaic conversion, is separated from solar light using the hot mirror. When the NIR light is focused onto the hot side of the thermoelectric module by the lens, the voltage is generated by the thermoelectric generator (Mizoshiri et al., 2012b).

Modern research efforts in the field of TEGs are focused on thin-film thermoelectric devices. Thin-film thermoelectric generators are classified into vertical and planar configurations. In vertical configuration, which is similar to that of TEG with massive semiconductor thermoelectric legs, the small thickness of thermoelements impedes the device to establish a large temperature difference between the hot and cold sides. In this context, planar device, in which thin-film n-type and p-type thermoelectric materials, thin-film electrodes and intermediate layers are deposited on the substrates, is better and more convenient. The improvement of the properties of thin-film thermoelectric material has applied a huge potential application in a miniaturization of heat sensors, micropower sources, microcoolers and other thermoelectric

* Corresponding author at: Russian Academy of Sciences, Federal Research Agroengineering Centre, 1st Institutskiy proezd, 5, Moscow 1094282, Russia.
E-mail address: ityukhov@yahoo.com (I.I. Tyukhov).
[1] ISES member.

http://dx.doi.org/10.1016/j.solener.2017.08.060
Received 3 May 2017; Received in revised form 8 August 2017; Accepted 20 August 2017

converters. In addition to small size, the thin-film TEMs constructed with nanostructures have the faster response speed than those of bulk material on account of that can reduce the scattering of the free charge carriers each other, which leads the of the longer average free carrier layer. Moreover, according to Mizoshiri et al. (2012b), thin-film thermoelectric modules present two additional advantages. First, cooling systems such as water chillers are not required because thin-film TEM can be air-cooled. Second, a relatively large voltage is obtained by the integration of a number of serially connected thermoelectric elements made of thin-film p- and n- semiconductors. So, preparing high-performance and low-cost thin film devices has been attracted more and more attention (Lu et al., 2014; Mizoshiri et al., 2012b; Fan et al., 2015; Zhu et al., 2015a; Bulman et al., 2016). For instance, thin-film STEGs proposed in Zhu et al. (2015a) and Zhu et al. (2015b) show much promise in effective use of solar energy as an electric power supply for the microscale devices, including the wireless sensors because of its portability and high integration. In particular, it is proposed to manufacture flexible thin-film thermoelectric generators by a deposition of thin-film n-type and p-type thermoelectric materials, thin-film electrodes and intermediate layers onto a polymer substrate with low thermal conductivity, such as polyimide (Lu et al., 2014; Zhu et al., 2015b; Fan et al., 2015).

Up to now, a low conversion efficiency and fabrication complexities have been identified as the main obstacles to the development of thin-film STEGs (Zhu et al., 2015b). Recently, advances in nanotechnology have opened a door to enhance a figure of merit of thermoelectric materials through nanostructuring due to the increase in Seebeck coefficient. Nanostructuring engineering has been proven an effective way to lower the thermal conductivity with a minimally detrimental impact on to the electrical conductivity, and could hence lead to enhanced efficiency (Ge et al., 2011a; Zhao et al., 2012; Liu et al., 2014). The desirable nanostructures can modify the transport properties of the electrons and phonons in thermoelectric materials and lead to significantly improvements in their figure of merit ZT defined in accordance with Bulman et al. (2016) as:

$$ZT = (S^2/\rho k)T \quad (1)$$

where S, ρ, k and T are the Seebeck coefficient (thermoelectric emf coefficient), electrical resistivity, thermal conductivity and absolute temperature, respectively.

The main advantage in ZT of the nanostructured layers is explained by the interfaces between the nanocrystallites that can scatter phonons more effectively and reduce the thermal conductivity (Johnsen et al., 2011; Zhao et al., 2012; Zhu et al., 2015b).

Currently, the methods available for the fabrication of thin-film thermoelectric devices usually need special equipment and the processes are time consuming such as vacuum evaporation, pulsed laser deposition, molecular beam epitaxy and magnetron sputtering (Mizoshiri et al., 2012b; Zhu et al., 2015b; Fan et al., 2015). Another approach is an inkjet printing using inks that based on previously synthesized nanoparticles of the thermoelectric semiconductor materials (Lu et al., 2014). Compared to the above-mentioned methods, wet chemical synthesis of semiconductor layers, namely Chemical Bath Deposition (CBD) or its modification Successive Ionic Layer Adsorption and Reaction (SILAR), is low cost, affordable and suitable for mass production approach (Ahire et al., 2001; Ubale et al., 2008; Dhere et al., 2010; Desale et al., 2013; Bulakhe et al., 2013; Burungale et al., 2016). The problem of the above methods is that it is commonly possible to obtain only very thin (thickness of a few hundred nanometers) semi-transparent semiconductor films for which quantum confinement is observed due to the small dimensions of their nanocrystallites (Ahire et al., 2001; Valenzuela-Jáuregui et al., 2003; Seghaier et al., 2006; Ubale et al., 2007, 2008; Gao et al., 2011; Desale et al., 2013; Pérez-García et al., 2015). Therefore, we were unable to find in the literature the information about the use of CBD or SILAR for the creation of any thermoelectric films for STEG.

The leading commercialized TEM materials are mainly tellurium based. Among them, PbTe-based materials are the best for power generation application, although Bi_2Te_3-based materials are renowned for refrigeration near room temperature (Biswas et al., 2012). Note that Bi-Te material thin films are usually applicable for thin-film TEGs because of their excellent figures of merit in near room temperature ranges (Mizoshiri et al., 2012a). For instance, the nanostructured p-type $Bi_{0.5}Sb_{1.5}Te_3$ and n-type $Bi_2Te_{2.7}Se_{0.3}$ thermoelectric films were prepared by Mizoshiri et al. (2012b), Lu et al. (2014), Zhu et al. (2015a) and Zhu et al. (2015b) for the creation of various designs of STEGs, since these materials have high thermoelectric conversion efficiencies at temperatures around 300 °C. However, tellurium is toxic and extremely scarce in the Earth's crust (Yang et al., 2013). Hence it would be desirable to develop alternative materials which involve cheaper and abundant elements (Johnsen et al., 2011; Biswas et al., 2012; Liu et al., 2015). Sulfur is very earth abundant compared to Te and Se (Zhao et al., 2012). As an alternative thermoelectric material, bismuth sulfide (Bi_2S_3) is an important semiconductor with a direct band gap energy 1.3–1.35 eV, although thermoelectric development of Bi_2S_3 is hindered from its high electrical resistivity (Ahire et al., 2001; Ubale et al., 2008; Gao et al., 2011; Ge et al., 2011a; Biswas et al., 2012; Desale et al., 2013; Yang et al., 2013; Du et al., 2015; Liu et al., 2015). Another possibility is PbS, also known as the mineral Galena. According to Zhao et al. (2012), PbS is an ideal candidate for widespread application of environmentally stable and affordable thermoelectric material system, because its high performance can be achieved in both n-type and p-type. A potential advantage of PbS in that it is quite earth abundant and inexpensive, and the Pb is extremely strongly bound, making PbS environmentally safe (Johnsen et al., 2011; Zhao et al., 2012; Parker and Singh, 2014). Furthermore, authors (Johnsen et al., 2011; Zhao et al., 2012; Wang et al., 2013) have predicted great promise of improvement in PbS thermoelectric figure of merit by material engineering such as alloying or nanostructuring. Recently, the large figure of merit and high values of Seebeck coefficients were theoretically predicted and experimentally obtained for a new thermoelectric material copper iodide (CuI) (Nishikawa et al., 2013; Yadav and Sanyal, 2014).

In this paper we present the results of wet chemical synthesis of Bi_2S_3, PbS and CuI films intended for the thermoelectric use at temperatures close to room. Ways to overcome the problems of poor adhesion of Bi_2S_3 layers to glass, mica and polyimide substrates and to remove restrictions deal with low thickness limits in several hundred nanometers for Bi_2S_3 and PbS have been shown. Crystalline structure, optical properties and resistivities ρ of PbS layers obtained by means CBD, and Bi_2S_3 and CuI films have grown with SILAR technique were investigated. Studies of their temperature dependent resistivities ρ, Seebeck coefficients S and power factors $P = S^2/\rho$ have been conducted.

2. Experimental procedures

Wet chemical synthesis of the nanostructured semiconductor layers applicable for thin-film solar thermoelectric generator was fulfilled on hard borosilicate Corning 7059 glass substrates, on soda-lime glass substrates as well as on 0.2 mm thick flexible Muscovite mica sheets or on the Kapton type polyimide 0.15 mm thick substrates. For comparison, the deposition of Bi_2S_3 films was also carried out on SnO_2:F/glass substrates (FTO, TEC 7 Pilkington Company, USA). The thicknesses of the all obtained semiconductor layers were determined gravimetrically in accordance with Ahire et al. (2001) in the approximation that the film densities correspond to those for the bulk materials (6.78 g/cm^3 for Bi_2S_3; 5.67 g/cm^3 for CuI; 7.50 g/cm^3 for PbS).

For the creation of Bi_2S_3 films by SILAR, the carefully cleaned substrates were sequentially dipped into aqueous solution 0.05 M Bi $(NO_3)_3$ at 70 °C for 20 s, then into distilled water for 10 s, then into 0.1 M Na_2S aqueous solution at room temperature for 20 s and again into distilled water for 10 s. Temperature of the distilled water was