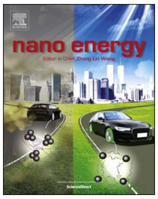
Nano Energy 50 (2018) 256–265

Contents lists available at ScienceDirect

Nano Energy

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



Communication

Photoactive piezoelectric energy harvester driven by antimony sulfoiodide (SbSI): A $A_VB_{VI}C_{VII}$ class ferroelectric-semiconductor compound

Yuvasree Purusothaman[a], Nagamalleswara Rao Alluri[b], Arunkumar Chandrasekhar[a], Sang-Jae Kim[a,*]

[a] *Nanomaterials and System Lab, Department of Mechatronics Engineering, Jeju National University, Republic of Korea*
[b] *Faculty of Applied Energy System, Department of Mechanical Engineering, Jeju National University, Republic of Korea*

ARTICLE INFO

Keywords:
Antimony sulfoiodide (SbSI)
Ferroelectric
Semiconductor
Polymer interfaces
Energy harvester
Piezo-phototronic effect

ABSTRACT

Antimony sulfoiodide (SbSI) has been demonstrated to act as an effective energy harvester due to its ferroelectric-semiconductor characteristics. This has furthered the advancement of futuristic self-powered optoelectronic devices. We studied the feasibility of designing an SbSI-based piezoelectric nanogenerators (PNGs) with polymer matrix interfaces, such as polydimethylsiloxane (PDMS), polyvinylidene fluoride (PVDF) and polymethyl methacrylate (PMMA). SbSI/PMMA composites exhibit promising states with respect to the potential establishment of SbSI/PMMA piezoelectric nanogenerator (S-PNG). Furthermore, as-fabricated S-PNG is highly stable, with an average peak to peak electrical response of ~ 5 V and 150 nA. The employment of SbSI overcomes the limitations of PNGs made of insulator materials, enabling the generation of dual harvesters. The piezo-phototronic properties of SbSI/PMMA composite and single SbSI micro rod (SMR) were extensively investigated. These harvesters incorporate both mechanical and optical sources, thereby providing broad opportunities for the expansion of piezoelectronic material systems.

1. Introduction

Piezoelectric-semiconducting materials have attracted wide attention [1,2] due to the insulating nature of available energy materials such as PZT [3], Ba(Zr, Ti)O_3 [4], $SrTiO_3$ [5], (K, Na)NbO_3 [6], (Bi, Nd)Ti_3O_{12} [7] quartz [8], and polymers like polyvinylidene fluoride (PVDF) [9] and PVDF-TrFE [10], as this restricts their potential applications to hybrid energy harvesters, human interfaces, robotics, smart sensors and self-powered optoelectronic systems [11,12]. Since the first demonstration of nanogenerator with ZnO [13], there has been increasing research interests in extracting coupling effects from materials by combining piezoelectric and semiconducting properties towards the realization of piezotronic and piezo-phototronic devices [14]. Eventually, GaN [15], CdS [16], ZnS [17], and InN [18], which is part of the wurtzite family, have been intensively investigated by researchers looking to develop devices with strong piezoelectric properties coupled with semiconducting characteristics. Recently, there have been interesting reports of the generation of piezoelectric potentials on layered semiconducting metal chalcogenide materials, such as GaSe [19] and MoS_2 [20]. Reasonable performance is achieved by embedding optically active material (perovskite, $CH_3NH_3PbI_3$) into piezoelectric polymers such as PVDF, paving the way for the development of hybrid energy harvesters [21]. However, despite the efforts made thus far, there is still plenty of room to further explore semiconducting materials with piezoelectric properties [22]. The ternary V-VI-VII semiconductor group element antimony sulfoiodide (SbSI) is among the materials of greatest interest for potential energy harvesting. SbSI has many interesting characteristics, being a ferroelectric, n-type semiconductor with an indirect bandgap of 1.8–1.9 eV, pyroelectric co-efficient of ~ 6×10^{-2} $Cm^{-2}k^{-1}$ and piezoelectric co-efficient of ~ 1×10^{-9} C/N (d_{33}), along with the highest known curie temperature of ~ 22 °C [23,24]. Its physical properties have led to its role in the development of photoconductive, piezoelectric, pyroelectric and optical devices. Several publications reporting the efficiency of SbSI for thermal imaging, nonlinear optics, and photosensors are particularly noteworthy [25,26]. However, there have not been any reports on extensively exploring the suitability of SbSI as a candidate for energy harvesting applications.

In this work, we present the first report on the development of PNGs using $A_VB_{VI}C_{VII}$ group SbSI, and demonstrate it as an emerging material for use in energy harvesting. We synthesized SbSI rods using a simple yet cost-effective and low-temperature solid state reaction (SSR) technique. We conducted a detailed investigation to optimize the reaction parameters with respect to the reaction temperature (S_T; 250 °C, 350 °C)

---

* Corresponding author.
E-mail address: kimsangj@jejunu.ac.kr (S.-J. Kim).

https://doi.org/10.1016/j.nanoen.2018.05.058
Received 21 March 2018; Received in revised form 10 May 2018; Accepted 22 May 2018

and time (1, 15, 24 h). Our analysis of the hysteresis loop reveals SbSI as a potential mechanical energy harvesting candidate with a remnant polarization, P_r, of ~ 0.35 μC/cm^2. We determined the orientations of the dipole moments with respect to poling time (P_t ~ 15, 30, 60, 120, 180 min), and found them to exhibit an enhanced P_r of ~ 1 μC/cm^2. We further investigated a possible means of developing planar SbSI based piezoelectric nanogenerator (S-PNG) modules with widely preferred polymer matrices, such as polydimethylsiloxane (PDMS), (Polyvinylidene fluoride) PVDF and polymethyl methacrylate (PMMA). We found that an S-PNG based on an SbSI/PMMA composite serve to be the prime device configuration capable of generating a stable piezoelectrical performance of ~ 5 V and ~ 150 nA under a linear mechanical force (F) of 2 N. The influence of photoactive semiconducting properties in S-PNG and single SbSI micro rod (SMR-PNG) is demonstrated with realization of piezo-phototronic effect. The generality of the reported findings indicates that SbSI has great potential for future lead-free energy harvesting applications. By means of its multifunctional properties (ferroelectric-semiconductor-photoactive), SbSI will aid researchers in contributing to the development of hybridized self-powered devices based on multisource energy harvesting.

2. Results and discussion

The SSR SbSI synthesis method has been studied in detail, and is shown schematically in Fig. 1. The X-ray diffraction (XRD) peak pattern shows that we achieved the desired SbSI product with a S_T of 250 °C. The spectrum in Fig. 1c confirms that we obtained highly crystalline, well oriented orthorhombic phases of SbSI at 250 °C [25]. All of the peaks perfectly match the space group of *Pnma* (ICSD reference pattern: 98–004-0159). The fact that no additional peaks were observed confirms the absence of possible byproducts or impurities, such as SbI_3 and Sb_2S_3/SbS_3. Meanwhile, iodine (I_2) decomposes at elevated processing temperatures (350 °C), gradually causing the formation of impure crystalline phases, as shown in Fig. S1 [27]. The predominant peaks at (121), (310), (330), (200) indicate that, in comparison to bulk crystal, the sizes of the SbSI crystals were reduced by SSR-assisted synthesis [25]. We further hypothesized that prolonged soaking times (S_t: 15 and 24 h) would reduce the quality of the crystals, but the desired SbSI crystal phases formed (Fig. S2). Thus, we consider the reaction at 250 °C/1 h to be the favorable processing condition for obtaining well crystallized SbSI via the SSR method. Besides, it endorses the longer ribbon-like molecular chain arrangements in as-synthesized SbSI along its (001) plane axis which reasons the formation of SbSI in long rod-like homogeneous structures with diameter ~ 1–2 μm and length ~ 20–50 μm, respectively (FESEM image, Fig. 2a). The rods are oriented in a zigzag manner, and appear to be highly malleable. This is conventionally believed to provide a stability, enabling the material to withstand high mechanical force when utilized as an energy harvesting material. Further, we conducted energy dispersive spectrometry (EDS) analysis to identify the elemental composition, as shown in Fig. S3. The percentages of each type of atom are approximately equal, in the range of 32.77 (Sb): 33.30 (S): 33.93 (I), which proves the accuracy of the elemental ratios in the obtained product. SbSI exhibits lattice vibrational modes of less than 400 cm^{-1} that can be categorized into a low frequency range (LFR, < 100 cm^{-1}) and a high frequency range (HFR, > 100 cm^{-1}) [28]. Fig. 2b shows the Raman active modes of the

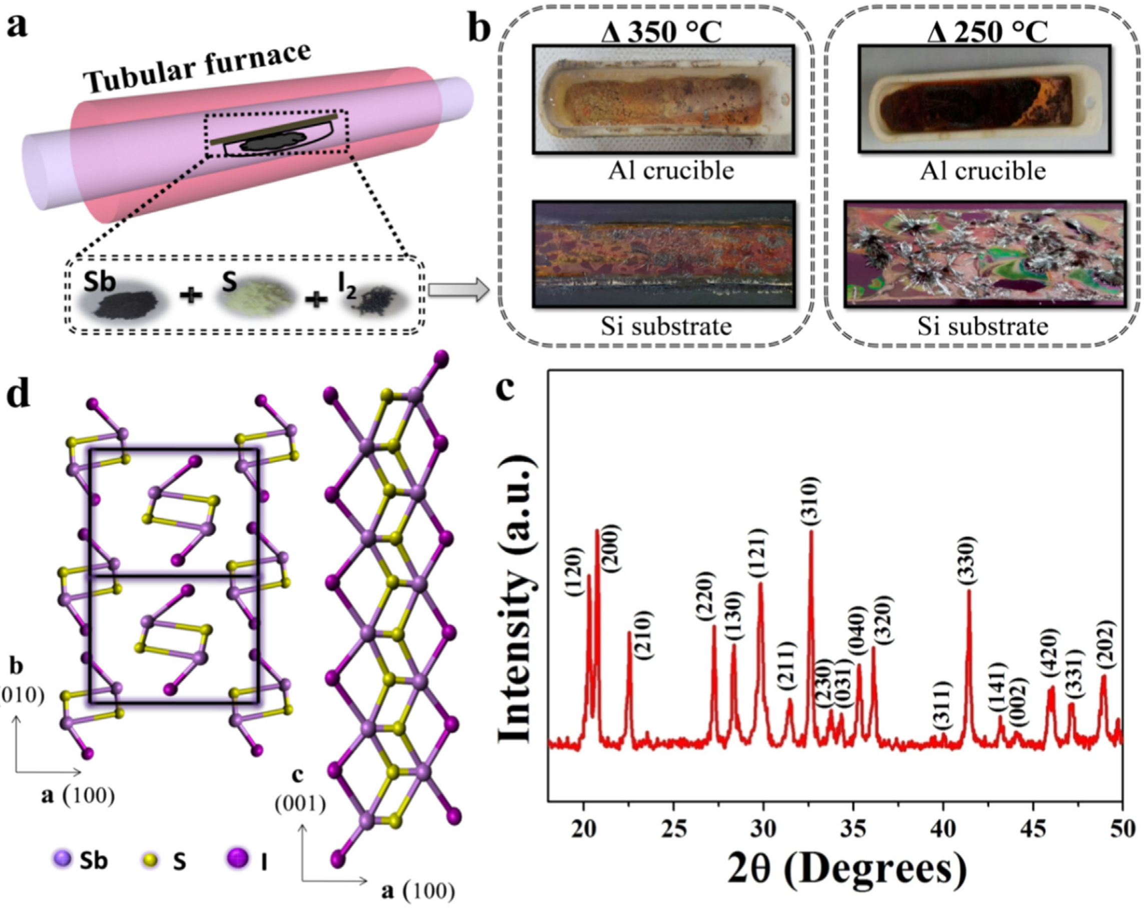


Fig. 1. **(a)** Schematic illustration of the synthesis of antimony sulfoiodide (SbSI) via the solid state reaction (SSR) technique, **(b)** Formation of SbSI powder in aluminum (Al) crucible and deposited SbSI microwire on p-Si substrate, **(c)** X-ray diffraction (XRD) spectrum of as-synthesized SbSI powder at 250 °C, and **(d)** Atomic arrangements of SbSI along the (010) and (001) axes, forming the crystallographic orthorhombic phase.