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Enhanced thermoelectric performance of P-type $Bi_xSb_{2-x}Te_3$ nanowires with pulsed laser assisted electrochemical deposition

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ABSTRACT

Crystalline thermoelectric nanowires with well controlled chemical composition, defects and grain structures are desired for their thermoelectric performance. Here, P-type thermoelectric (TE) nanowires, $Bi_xSb_{2-x}Te_3$, are deposited in anodized aluminum oxide (AAO) templates at room temperature by pulsed laser assisted electrochemical deposition (ECD). Evident differences in the ECD processes resulting from pulse laser irradiation are monitored by cyclic voltammetry (CV) and current–time (I-t) curves, where instant current developments are captured. Variations in the crystal structure due to laser assisted ECD are examined using high-resolution transmission electron microscope (HR-TEM). We find that after laser assisted ECD, nanowires are deposited in the highly oriented crystallographic direction with enhanced crystallinity. Simultaneous enhancements in the electrical conductivity and the Seebeck coefficient are observed for those nanowires treated by laser assisted ECD, while the thermal conductivity remains almost the same. Theoretical calculations based on the Boltzmann transport equations suggest that the reduction of charge carrier concentration by the reduced anti-site defect densities after the laser treatment is responsible for the large enhancement of the Seebeck coefficient for the nanowires. The reduced defect densities also increase the carrier mobility substantially, which results in the enhanced electrical conductivity despite the reduced carrier concentration. This work highlights the beneficial impacts of the laser treatment for the thermoelectric performances of electrochemically grown semiconductor nanowires.

1. Introduction

There has been an explosive demand for energy harvesting devices. Thermoelectric (TE) devices are a viable solid-state technology capable of converting thermal energy into electricity, and vice versa. They have been attracting increased attention due to their great potential applications such as power generation [1,2], solid-state device cooling [3–6], waste heat recovery in vehicles [7], sensor applications [8], and wearable energy harvesting [9]. Performance of a TE material is evaluated by the figure of merit, $ZT = S^2\sigma T/\kappa$, where S, σ, κ, and T are Seebeck co-

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efficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Various approaches have been attempted to achieve high-performance TE materials, including exploiting high-performance bulk crystals, such as "phonon glass electron crystal" [10], introducing nanostructures into bulky materials [11], and reducing the dimension of TE materials [12,13]. Among these different approaches, one-dimensional nanowires are considered to be one of the most attractive pathways to achieve high figure of merit due to modified electronic density of state (increased Seebeck coefficient) and enhanced phonon scattering (reduced thermal conductivity) [14].

Best-performance TE materials at near room temperature are Bi_2Te_3 as *n*-type and $Bi_{0.5}Sb_{1.5}Te_3$ as *p*-type. There are many scalable ways to produce TE nanowires, including solution-based synthesis [15,16], hydrothermal synthesis [17], and electrochemical deposition (ECD) [18]. Even though the first two approaches could yield high-performance products, it is challenging to synthesize *p*-type $Bi_xSb_{2-x}Te_3$ with these techniques partially due to the limited solubility of antimony precursor, i.e. Sb_2O_3 and $SbCl_3$. Instead, template-assisted ECD on anodized aluminum oxide (AAO) templates can be a scalable and tunable method for *p*-type TE materials growth and fabrication. Periodically-distributed channels (pore density of $\sim 10^{10}/cm^2$) provide a large number of oriented nanowires. High chemical stability to organic solvent as well as thermal stability makes AAO template one of the candidates for the standard photolithography. In addition, the moderate thickness ($\sim$60 μm) satisfies the dimensional requirement for the TE device because too thin TE legs are not able to provide enough thermal resistance to keep the sufficient temperature gradient. On the other hand, this electrochemical deposition method, as Kuo et al. experimentally proved, is capable of precise stoichiometry control by manipulating deposition potential [19]. According to the work by Martin-Lopez et al., such changes in stoichiometry induce modulation of carrier concentration [20]. Furthermore, if the aspect ratio between Te and Bi/Sb is controlled properly, the carrier type is also changeable.

This process, however, has several problems. Firstly, reduction potential for Sb (III) is high, and its large reduction potential deviation from those of Bi (III) and Te (VI) is not easily minimized, resulting in high-rate ECD with poor crystallinity. Thus, controlling growth in nanoscale channel is crucial to produce good-quality nanowires. To address this issue, many efforts have been taken: for example, Li et al. successfully deposited single-crystalline Bi_2Te_3 by employing pulse ECD [21], where low-rate deposition induces nuclei preferably grow in the lamella direction, so-called the 2D growth mode, with high crystal quality [22]. Alternatively, according to our previous work, laser irradiation shows the similar capability to control nucleus growth direction by combining laser energy dose with reduction potential [23]. Even at the high-potential and high-rate deposition condition, localized and instant high-temperature environment in the nanoscale channel caused by laser irradiation induces the small and unstable nucleus growth in lamella direction. Secondly, fabrication and nanowire assembly for accurate TE performance characterization, typically electrical conductivity, Seebeck coefficient, and thermal conductivity measurement, are challenging. In spite of the continuous attempts, the properties measurements for template-assisted grown nanowires, however in most studies, are not comprehensive. Either only electrical properties [24] or thermal properties [25] were characterized, because precise measurements of TE properties require expensive micro-manipulation to place the nanowires on the designed micro-devices [26]. Even though the TE properties were measured properly, the chemically etched-out template loses the possibility for further device fabrication. Thus, avoiding AAO template damage during device fabrication and performance characterization is necessary. Herein, we demonstrate the laser-assisted ECD of *p*-type $Bi_xSb_{2-x}Te_3$ on AAO templates and in-situ fabrication process for TE properties measurement. By integrating laser irradiation into the deposition process, highly oriented nanowires at relatively high reduction potential were observed. Finite element method was used to analyze laser heating mechanism during the growth process. In-situ measurements for TE performance were performed on the fabricated AAO device with/without laser treatment. By characterizing the structural differences and performance changes in the two growth conditions along with theoretical calculations, the impacts of the laser treatment on the thermoelectric performance are discussed in details.

2. Materials and methods

The deposition and fabrication process is presented in Fig. 1. Working electrode preparation was slightly modified from Stacy group's previous work [18]. Typically, an AAO template with the pore diameter of $\sim$100 nm, as shown in Fig. 1(a2) and (a3), and the thickness of $\sim$50 μm was used, on which a 5-nm titanium adhesion layer and 200 nm gold film were deposited by e-beam evaporation (Fig. 1(a1)). This template was used as the working electrode after silver wire was attached by silver paste. Finally, non-AAO part of the electrode was coated with a commercially available nail glue to prevent its exposure to the solution. Pulsed potential ($-$300 mV, 2 s-on/6 s-off) was applied to this working electrode in the electrolyte of Bi^{3+} (2.5 mM), SbO^+ (7.5 mM), $HTeO_2^+$ (9 mM), tartaric acid (0.5 M), and HNO_3 (1 M) to grow *p*-type $Bi_xSb_{2-x}Te_3$ nanowires. During the growth the working electrode was exposed to Q-switched Nd:YAG laser (wavelength 355 nm, pulse width 5 nm) as shown in Fig. 1(b2).

Average deposition rate, calculated by measuring nanowire length in the cross-sectional field emission scanning electron microscope (FESEM) image of the deposited AAO template (Fig. 1(b3)), is $\sim$6 μm/h. As the deposition continues, the growth rate is expected to become faster at the constant reduction potential because the overall electrode resistance decreases since the distance from the tip of nanowire to the template surface is decreasing. Growth lasted until gray flower-like caps were observed on the front surface of working electrode, indicating the overgrowth of nanowires (Fig. 1(c1)). After the deposition, the template was mechanically polished with polishing wheels using polishing paste from coarse ones (6 μm) to fine ones (0.05 μm), removing the overgrown parts, thus eventually exposing more nanowire tips (Fig. 1(d1)), which