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# Enhancement of fatigue resistance of Bi-Sb-Te films on flexible substrates by current-assisted thermal annealing

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ABSTRACT

Brittle nature of chalcogenide compounds is a major concern for implementation of bismuth telluride based compound films in flexible thermoelectric devices. In this study we report that the fatigue resistance of Bi-Sb-Te films sputtered on a polyimide substrate is improved by applying a high-density electric current (1–2×10$^3$ A/cm$^2$) through the film during post-deposition thermal treatment. The electrically stressed film was found to suffer less conductivity degradation caused by cyclic stretching than the film thermally annealed at the same temperature. The increase of electrical resistance is well correlated to the enlarging crack width observed in the stretched film. It is proposed that the electromigration-induced Sb-rich precipitates suppress the propagation of microcracks along grain boundaries during cyclic stretching and thus improves the fatigue resistance of the sputtered Bi-Sb-Te films.

## 1. Introduction

A light-weight and long-lasting power supply is constantly demanded for portable consumer electronics. Aside from chemical-based batteries, self-sustained power supply is a highly desired option among various electricity generation/storage technologies [1,2]. One of ideal scenarios for self-sustained power supply would be the direct conversion of environmental or body heat into electrical power. Unfortunately, no known technique except thermoelectric conversion can transform such low-grade heat into electricity. Tertiary bismuth telluride based compounds such as $(Bi,Sb)_2Te_3$ and $Bi_2(Se,Te)_3$ are famous p-type and n-type thermoelectric materials that are suitable for thermal-to-electric conversion at low temperatures [3]. An extensive research effort has been dedicated to the development of micro-generators and biometric sensors by implementing binary or tertiary bismuth telluride films on flexible substrates [4–7]. Nevertheless, the vulnerability of brittle bismuth telluride films during stretching and bending operation remains to be a major issue for flexible thermoelectric devices. Although the fabrication process, structure design and output performance of thin-film thermoelectric devices have been widely researched, the degradation mechanism of bismuth telluride based compound films on a flexible substrate has not been fully understood. The assessment of mechanical operation on the integrity and transport properties of bismuth telluride based thin films becomes essential for flexible thermoelectric devices. In this letter the tertiary $Bi_{0.5}Sb_{1.5}Te_3$ thin film was sputtered on a polyimide substrate to investigated the variation of electrical properties and the formation of microcracks in the Bi-Sb-Te films with cyclic stretching test. A post-deposition treatment for improving the fatigue resistance and electrical conductivity of the sputtered Bi-Sb-Te films is also presented.

## 2. Materials and methods

Bi-Sb-Te thin films were sputtered on a 50 µm-thick polyimide foil (Kapton®, HPP-ST, DuPont) at room temperature using a $Bi_{0.5}Sb_{1.5}Te_3$ alloy target. The deposition was performed at a sputter power of 20 W under an Ar pressure of 5 m torr for 75 min, leading to an approximate 500 nm-thick Bi-Sb-Te films. The specimens were consequently annealed at 270 °C for 5 min in 400 Torr $N_2$ ambient to stabilize their microstructure and physical properties. An electric current of 1.2–1.8×10$^3$ A/cm$^2$ in density was applied through the Bi-Sb-Te film simultaneously during thermal annealing. The thermal and electrical processing parameters were selected based on the consideration of electrical properties and structural integrity of annealed Bi-Sb-Te films, as revealed in a previous publication [8]. A cyclic stretching test was performed on both thermally annealed (TA) and electrically stressed (ES) specimens using a dynamic micro-loading system (BOSE® ElectroForce 3200). The specimens were stretched to a strain of 0.5% at a rate of 5×10$^{-5}$ s$^{-1}$ and relaxed to zero strain repeatedly. A four-point probe stage accompanied with a source-meter (Keithley 2400) was used to measure the electrical resistance of the repeatedly stretched specimen. The microstructure, composition and morphology

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of the stretched specimen were examined by field-emission scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and atomic force microscopy (AFM). The Seebeck coefficients were obtained by using a typical temperature gradient approach [9]. The electrical resistivity, carrier concentration and mobility of the specimens were measured at room temperature under a magnetic field of 0.55 T by a Hall measurement system (ECOPIA HMS-3000).

## 3. Results and discussion

The electrical resistivity of TA and ES specimen prior to cyclic stretching were measured to be 7.8 ± 0.9 mΩ cm and 5.5 ± 0.3 mΩ cm, respectively. The change of normalized resistance ($R/R_0$) against stretching cycles were recorded for TA and ES specimens, respectively, where $R_0$ is the electrical resistance prior to stretching (Fig. 1). Both

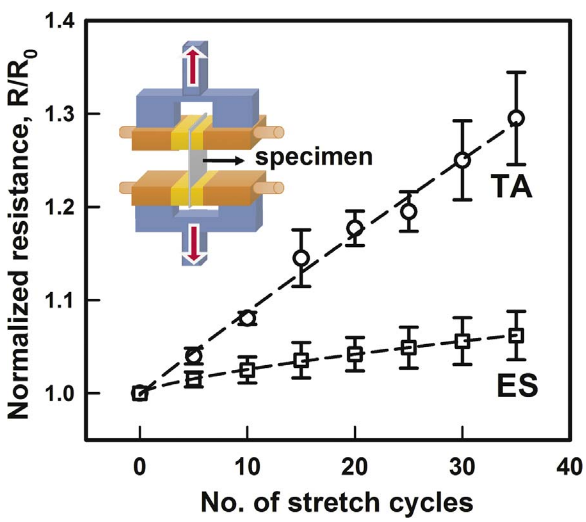


**Fig. 1.** A plot of normalized film resistance versus stretching cycles for the TA and ES specimens. Inset is the schematic of sample stretching stage.

the TA and ES specimens exhibit the rising trend of normalized resistance with the number of stretching cycles, but the ES specimen has a milder rate of increase in resistance than the TA specimen. We note that the electrical resistivity is inversely proportional to the product of carrier concentration and carrier mobility. Since the carrier concentration of the Bi-Sb-Te films studied is approximately in the range of $2.9–3.2\times10^{19}$ $cm^{-3}$ and does not change with stretching operation, the increasing normal resistance must be attributed to the decrease of carrier mobility of the post-stretched films. The carrier concentration of bismuth telluride based compounds is known to depend on the density of lattice defects, such as antisite defects and vacancies [10]. Although a tensile or compressive stress may modulate the generation or annihilation of lattice defects in bismuth telluride based compounds, especially vacancies at Te sites, a gross change of lattice defect concentration would occur only at elevated temperature [11]. For the Bi-Sb-Te films stretched at room temperature, most of lattice defects should be frozen and no marked change in carrier concentration is expected. The argument is also supported by the invariant Seebeck coefficients (~180 μV/K) of the stretched Bi-Sb-Te films, which is usually inversely proportional to carrier concentration. Therefore, the stretch-induced degradation of carrier mobility must be attributed to the change of microstructure or the shift of carrier scattering mechanism of the Bi-Sb-Te films.

Fig. 2A–D shows the planar SEM images of the TA and ES specimens before and after 20 stretching cycles. The post-stretched Bi-Sb-Te films show some microcracks in the direction perpendicular to the stretch direction (Fig. 2B and D), which had not been found in the pre-stretched specimens (Fig. 2A and C). The crack spacing is approximately to be 10 ± 2 μm and does not change significantly with the increase of stretching cycles. However, the post-stretched TA specimen appeared to have wider cracks than the post-stretched TA specimen, as shown in the insets of Fig. 2B and D. Fig. 2E shows the averaged crack width against the stretching cycles for the TA and ES specimens. When the average crack width increased to 103 ± 13 nm in the TA specimen after 30 cycles, it was only 39 ± 13 nm in the ES specimen. Besides the enlarged crack width, the surface morphology in the vicinity of a stretch-induced microcrack at the TA and ES specimen

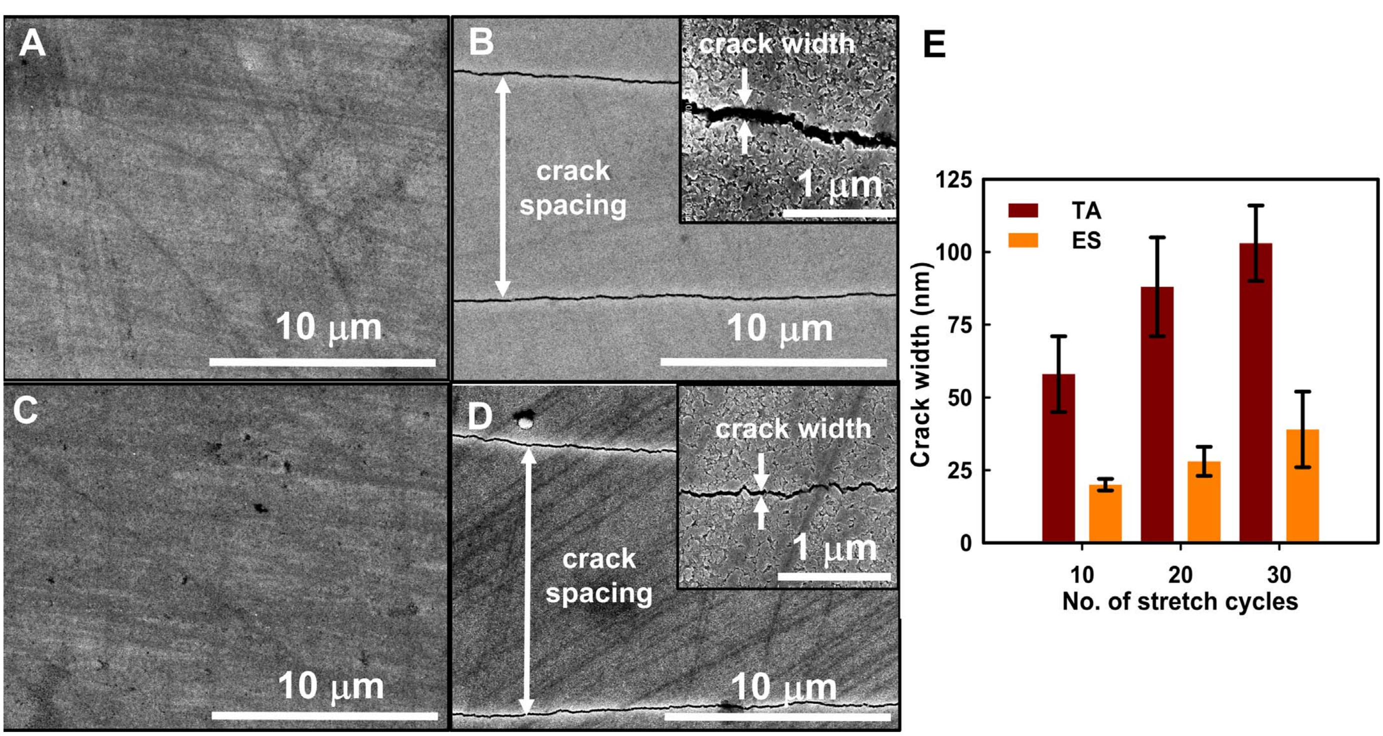


**Fig. 2.** (A)–(D) SEM images of sputtered Bi-Sb-Te films (A) pre-stretched TA, (B) post-stretched TA, (C) pre-stretched ES, (D) post-stretched ES. (E) The averaged crack width in the TA and ES specimens after different stretching cycles.