

## Structural, Optical and Thermal Behavior investigation of 2D Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> in-plane Heterostructures via Aberration Corrected STEM and EELS

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Bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>) and antimony telluride (Sb<sub>2</sub>Te<sub>3</sub>) based low-dimensional materials are considered versatile semiconductors due to their outstanding thermoelectric properties as well as topological insulating properties<sup>[1,2]</sup>. Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> based in-plane heterostructures are synthesized by solvothermal method as a facile and cost-effective technique<sup>[2]</sup>. While surface plasmon resonances (SPRs) in 2D Bi<sub>2</sub>Te<sub>3</sub> nanoplates been shown, little has been done to investigate the effect of alloying elements and heterojunctions in this family of crystals. In-plane heterostructures can act as a potential route to make tunable semiconductor based plasmonic materials<sup>[3,4]</sup>.

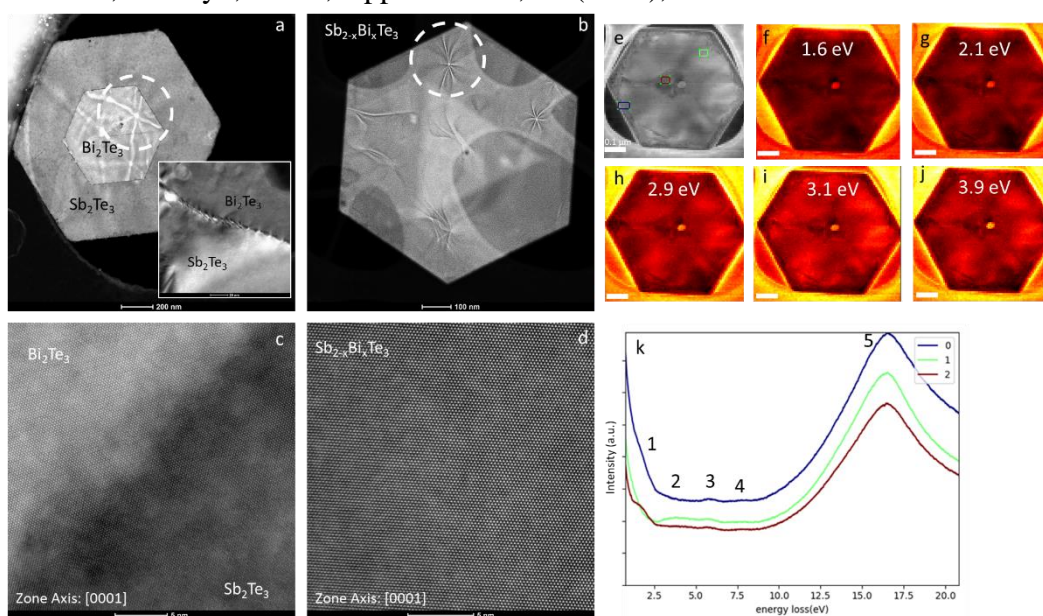
This study utilizes Scanning Transmission Electron Microscopy (STEM) combined with monochromated Electron Energy Loss Spectroscopy (EELS) to investigate both the structural and plasmonic properties in Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> based in-plane heterostructures. Figures 1(a-b) show low-magnification HAADF-STEM images of Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> in-plane heterostructures with a sharp interface and in the form of a fully mixed alloy respectively with strain-induced bend contours in both images. Atomic-scale HAADF-STEM images from both structures along the [0001] direction are presented in Figure 1(c-d) indicating a relatively sharp interface and the fully mixed solid solution alloy. 2D EELS intensity maps of the dielectric photonic mode (<2.5 eV) and surface plasmon modes for Sb<sub>2-x</sub>Bi<sub>x</sub>Te<sub>3</sub> alloy structure on a lacey carbon grid (Figure 1e) are shown in Figure 1f-j. Figure 1k shows Experimental EEL spectrum of marked regions in Figure 1e indicating 5 different peaks corresponding to dielectric photonic mode (peak 1), surface plasmon modes (peaks 2, 3 and 4) and a bulk plasmon mode (peak 5)<sup>[4]</sup>. According to our EELS investigations, a hexagonal Sb<sub>2-x</sub>Bi<sub>x</sub>Te<sub>3</sub> alloy heterostructure can exhibit dielectric photonic and plasmon modes across a wide spectral range, covering the entire visible range (1.6 to 3.2 eV) and ultraviolet (UV) range (>3.2 eV). The surface plasmon resonances observed in the visible range in this semiconducting heterostructure is unique and can provide opportunities in applications such as energy storage.

Furthermore, this study will present the sequential formation and dynamics of thermally induced defects under in-situ TEM heating conditions in the temperature range of RT to 400 °C in vacuum as shown in Figure 2(a-f). The formation and growth of triangular and hexagonal holes start at around 150 °C with no observable morphology change below this temperature and an increased growth rate above 300 °C. Investigating the unique structural, optical and thermal behavior of Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> based alloy and heterojunction nanoplates and understanding the nanoscale optical response variation can provide insight in how to design tunable semiconductor based plasmonic building blocks beyond conventional plasmonic metals. This understanding is crucial for developing next-generation transparent and flexible optoelectronic/plasmonic devices.

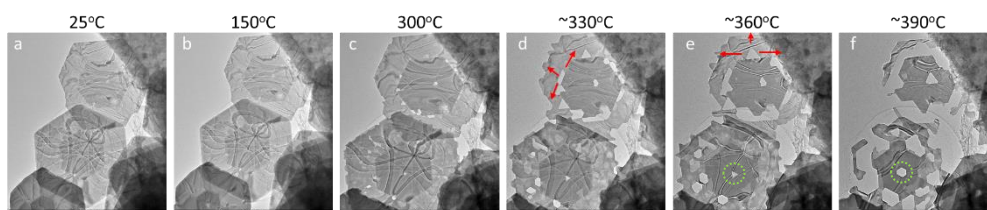
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**Figure 1.** (a) low-mag HAADF-STEM of  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  heterojunction nanoplates (inset shows a high magnification image of the junction indicating the presence of misfit dislocations) (b) low-mag HAADF-STEM of  $\text{Sb}_{2-x}\text{Bi}_x\text{Te}_3$  alloy (c) HAADF-HRSTEM of  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  heterojunction (d) HAADF-HRSTEM of  $\text{Sb}_{2-x}\text{Bi}_x\text{Te}_3$  alloy (e) high-loss spectrum image  $\text{Sb}_{2-x}\text{Bi}_x\text{Te}_3$  alloy (f-j) 2D EELS intensity maps of the photonic mode (<2.5 eV) and surface plasmons at indicated energies (k) low-loss EELS spectrum acquired from marked regions on (e)



**Figure 2.** TEM images of two-dimensional  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  heterojunction nanoplates (a) at RT (b) at 150°C (c) at 300 °C (d) at ~330°C (e) at ~360°C and (f) at ~ 390°C