

# Intercalation of Cu into N-Type Polycrystalline Bi<sub>2</sub>Se<sub>3</sub>

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## Abstract

The intercalation of copper into bismuth selenide (Bi<sub>2</sub>Se<sub>3</sub>) was investigated using aqueous electrochemical methods together with post-annealing. Carrier concentration ranged from the order of 10<sup>18</sup> to 10<sup>20</sup> cm<sup>-3</sup> were obtained. Fourier Transform Infrared (FTIR) Spectroscopy measurements showed that the optical absorption edge of Bi<sub>2</sub>Se<sub>3</sub> changed with the doping level, which was attributed to possible Burstein-Moss effect.

## 1. Introduction

Bismuth selenide (Bi<sub>2</sub>Se<sub>3</sub>) is a narrow-band-gap semiconductor known for its excellent performance as an efficient thermoelectric material. It draws much more attention as a 3-D topological insulator recently. The structure of Bi<sub>2</sub>Se<sub>3</sub> can be considered as layers made up of 5 atom thick (Se-Bi-Se-Bi-Se) covalently bound sheets held together by much weaker van der Waals forces. The existence of van der Waals gap between such covalently bound layers makes the intercalation of copper into the bulk relatively easy. We modulated the carrier density in Bi<sub>2</sub>Se<sub>3</sub> by intercalating copper and observed changes of the optical absorption edge. The calculation of band gap energy with consideration of electron-ion and electron-electron interaction corrections shows strong conduction-band nonparabolicity.

## 2. Methods

Material: N-type polycrystalline Bi<sub>2</sub>Se<sub>3</sub> thin films (~200 nm) grown by Molecular Beam Epitaxy (MBE) technique

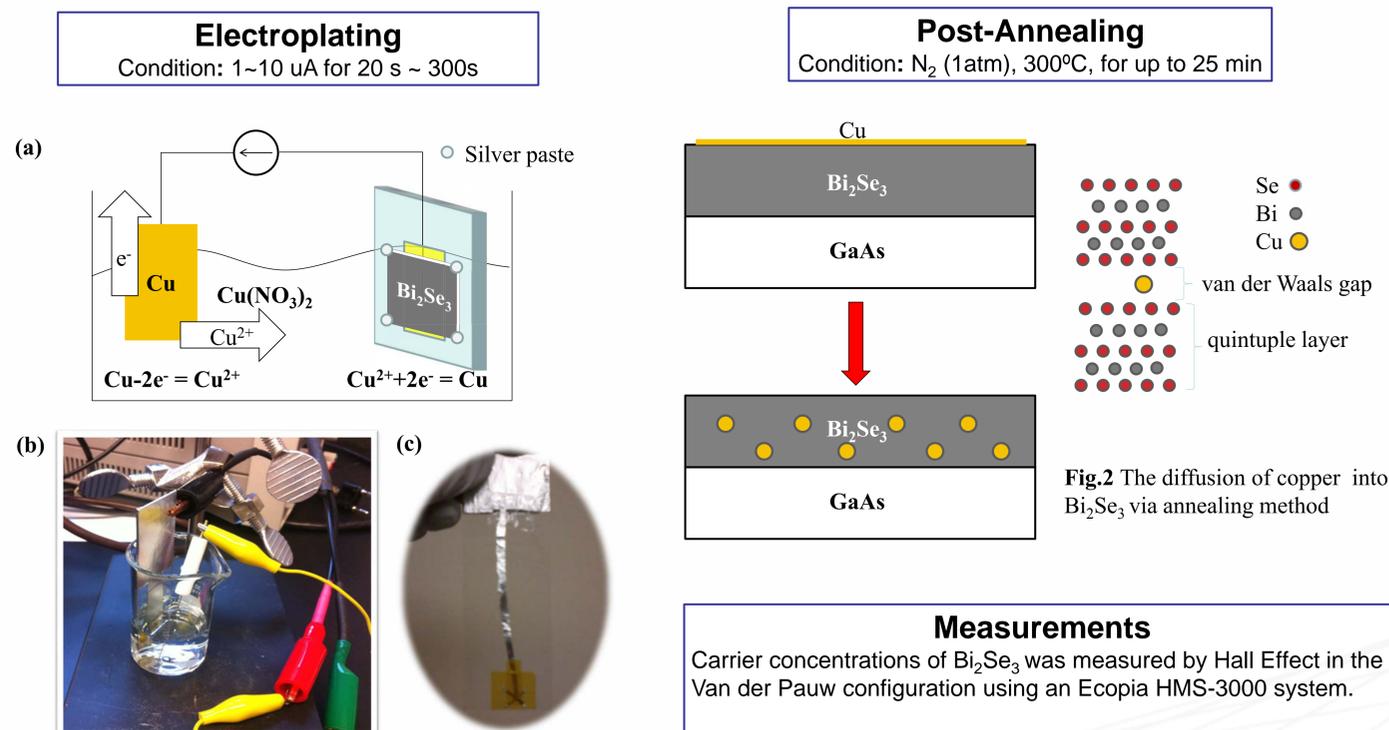


Fig.1 (a) Schematic of electroplating experiment; (b) Picture of the setup; (c) Picture of the cathode

**Measurements**  
Carrier concentrations of Bi<sub>2</sub>Se<sub>3</sub> was measured by Hall Effect in the Van der Pauw configuration using an Ecopia HMS-3000 system.  
Optical reflection and transmission data were collected by Fourier Transform Infrared (FTIR) Spectroscopy equipment in ALS at Lawrence Berkeley National Laboratory.

## 3. Results

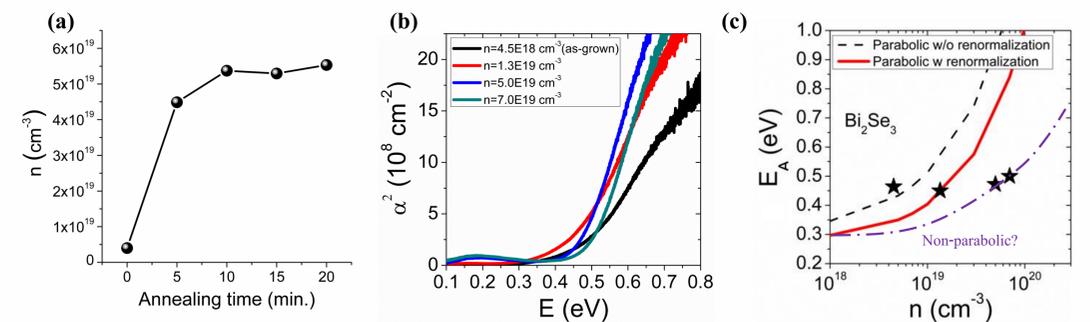


Fig.3 (a) Carrier concentration of Cu-doped Bi<sub>2</sub>Se<sub>3</sub> vs. annealing time; (b) Squared optical absorption coefficient of Bi<sub>2</sub>Se<sub>3</sub> vs. photon energy; (c) Absorption edge vs. carrier concentration comparing theoretical and experimental results

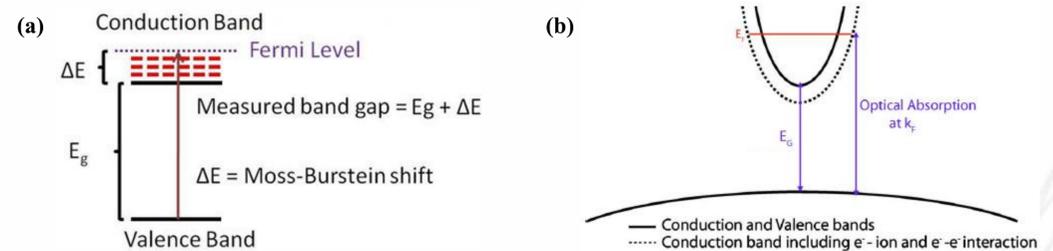


Fig.4 (a) Diagram of Burstein-Moss effect; (b) Conduction band corrected by equation (1).

$$E_A = E_g + \frac{\hbar^2 k^2}{2m_c^*} + \frac{\hbar^2 k^2}{2m_h^*} + \text{nonparabolicity} \quad (1)$$

$$E_{e-e} = -\frac{2e^2 k_F}{\pi \epsilon_S} - \frac{e^2 k_{TF}}{2\epsilon_S} \left[ 1 - \frac{4}{\pi} \arctan \left( \frac{k_F}{k_{TF}} \right) \right] \quad (2)$$

$$E_{e-i} = -\frac{4e^2 \pi n}{\epsilon_S a_B k_{TF}^3} \quad (3)$$

$k$  wave vector  
 $k_F$  Fermi wave vector  
 $k_{TF}$  Thomas Fermi screening parameter  
 $\epsilon_S$  Static dielectric constant  
 $a_B$  Bohr radius

## 4. Summary

- Copper was intercalated into Bi<sub>2</sub>Se<sub>3</sub> successfully by electroplating and post-annealing method
- Carrier concentration increases and stabilizes with annealing time after each electroplating process
- Carrier concentration was modulated by almost two orders of magnitude
- The optical absorption edge changes with carrier concentration, which was explained in the frame work of Burstein-Moss effect

### Reference

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