GROWTH AND MODIFICATIONS OF THERMOELECTRIC PROPERTIES OF ANTIMONY TELLURIDE THIN FILM THROUGH BAND ENGINEERING, CARRIER FILTERING, AND SUBSTRATE EFFECT

ABHISHEK GHOSH

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

Abhishek Ghosh

Department of Physics

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Dedication

This dissertation is dedicated to my parents. Their support, blessings, encouragement, and constant love have sustained me throughout my life.

CERTIFICATE

We are satisfied that the thesis entitled "Growth and modifications of thermoelectric properties of Antimony Telluride thin film through band engineering, carrier filtering and substrate effect" submitted by Mr. Abhishek Ghosh is worthy of consideration for the award of the degree of Doctor of Philosophy and is a record of original and bonafide research work carried out by her under our supervision. The results contained in it have not been submitted in part or full to any other university or institute for the award of any degree/diploma.

Prof. Bodh Raj Mehta
Department of Physics
Indian Institute of Technology Delhi
New Delhi-110016, India

Prof. Rajendra Singh
Department of Physics
Indian Institute of Technology Delhi
New Delhi-110016, India

Date: 10-05-2024

Date: 10-05-2024

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Abstract

Given the escalating global warming resulting from carbon emissions and rising energy expenses, it has become imperative to prioritize the exploration of clean, sustainable, and renewable energy alternatives in today's world. Thermoelectricity is a promising technology that has garnered significant interest from the scientific community which has the potential to produce clean energy by converting waste heat from various sources, including motor vehicles, nuclear plants, and computers, into useful electricity. Enhancing the efficiency of thermoelectric materials is a crucial aspect in realizing the practical application of these materials. While the thermoelectric transport properties of bulk materials have been intensively studied, the understanding of thin film-based nanostructure thermoelectric properties is still incomplete. Therefore, the present thesis work is focused on modulating the thermoelectric performance of one of the prominent TE materials, Sb_2Te_3 thin film, by implementing different mechanisms such as electron filtering, and density of states distortions and so on. The primary work in this direction is achieved by introducing controlled amounts of size-selected Au nanoparticles with a narrow size distribution utilizing an integrated gas phase synthesis approach. The examined nanocomposite exhibits a superior power factor in comparison to other well-established thermoelectric materials, hence providing a strong impetus for further investigation into these compounds. Further, to achieve the desired outcome, a multi-component alloying strategy is adopted, enabling synergistic manipulation of charge carriers and phonon transport by introducing the $AgSbTe_2$ secondary phases in Sb2Te3. The enhanced performance is discussed in terms of energy-dependent charge carrier filtering and band structure engineering, which is corroborated by the first-principal density functional theory-based electronic structure calculation. In addition, a novel approach utilising cross-sectional scanning thermal microscopy (xSThM) is employed to empirically determine thermal conductivity values in both the in-plane and cross-plane configurations. Further, a thorough microscopic analysis is conducted to examine the influence of oxygen on the phonon and charge carrier transport properties of the Sb_2Te_3 thin film. The inclusion of oxygen impurity at the grain boundary in the Sb_2Te_3 matrix has been demonstrated to lead to a substantial increase in the power factor resulting from grain boundary carrier

filtering and modifications in the band structure. Finally, a new strategy based on the utilization of the substrate effect as a means to improve the thermoelectric characteristics of various materials is also proposed. The results highlight the significance of the substrate's contribution to the thermoelectric (TE) transport as the dimensions are reduced. In addition, the film's TE characteristics are closely connected to the properties of the substrate. This approach provides a comprehensive understanding of the substrate effects, encompassing the underlying physics and offering a promising pathway for the utilization of thermoelectric power generation and cooling applications.

Overall, the present thesis addresses the potential TE properties in Sb_2Te_3 compounds by the application of different mechanisms. We believe that the experimental realization of this potential TE material would be very fascinating and would further help in predicting the ZT.

सार

कार्बन उत्सर्जन और बढ़ते ऊर्जा खर्चों के परिणामस्वरूप बढ़ती ग्लोबल वार्मिंग को देखते हुए, आज की दुनिया में स्वच्छ, टिकाऊ और नवीकरणीय ऊर्जा विकल्पों की खोज को प्राथमिकता देना अनिवार्य हो गया है। थर्मोइलेक्ट्रिसिटी एक आशाजनक तकनीक है जिसने वैज्ञानिक समुदाय से महत्वपूर्ण रुचि पैदा की है जिसमें मोटर वाहनों, परमाणु संयंत्रों और कंप्यूटरों सहित विभिन्न स्रोतों से अपशिष्ट गर्मी को उपयोगी बिजली में परिवर्तित करके स्वच्छ ऊर्जा का उत्पादन करने की क्षमता है। इन सामग्रियों के व्यावहारिक अनुप्रयोग को साकार करने के लिए थर्मोइलेक्ट्रिक सामग्रियों की दक्षता बढ़ाना एक महत्वपूर्ण पहलू है। जबकि थोक सामग्रियों के थर्मोइलेक्ट्रिक परिवहन गुणों का गहन अध्ययन किया गया है, पतली फिल्म-आधारित नैनोस्ट्रक्चर थर्मोइलेक्ट्रिक गुणों की समझ अभी भी अधूरी है। इसलिए, वर्तमान थीसिस कार्य प्रमुख TE सामग्रियों में से एक, Sb_2Te_3 पतली फिल्म के थर्मोइलेक्ट्रिक प्रदर्शन को संशोधित करने पर केंद्रित है, जैसे कि इलेक्ट्रॉन फ़िल्टरिंग, और राज्यों के घनत्व विकृतियों आदि को लागू करके। इस दिशा में प्राथमिक कार्य एक एकीकृत गैस चरण संश्लेषण दृष्टिकोण का उपयोग करके संकीर्ण आकार के वितरण के साथ आकार-चयनित एयू नैनोकणों की नियंत्रित मात्रा को पेश करके प्राप्त किया जाता है। जांचा गया नैनोकम्पोजिट अन्य अच्छी तरह से स्थापित थर्मोइलेक्ट्रिक सामग्रियों की तुलना में एक बेहतर शक्ति कारक प्रदर्शित करता है, इसलिए इन यौगिकों में आगे की जांच के लिए एक मजबूत प्रेरणा प्रदान करता है। इसके अलावा, वांछित परिणाम प्राप्त करने के लिए, एक बहु-घटक मिश्रधातु रणनीति अपनाई जाती है, जो Sb_2Te_3 में $AgSbTe_2$ द्वितीयक चरणों को शुरू करके चार्ज वाहक और फोनन परिवहन के सहक्रियात्मक हेरफेर को सक्षम करती है। उन्नत प्रदर्शन की चर्चा ऊर्जा-निर्भर चार्ज वाहक फ़िल्टरिंग और बैंड संरचना इंजीनियरिंग के संदर्भ में की जाती है, जो पहले-प्रमुख घनत्व कार्यात्मक सिद्धांत-आधारित इलेक्ट्रॉनिक संरचना गणना द्वारा पुष्टि की जाती है। इसके अलावा, इन-प्लेन और क्रॉस-प्लेन कॉन्फ़िगरेशन दोनों में थर्मल चालकता मूल्यों को अनुभवजन्य रूप से निर्धारित करने के लिए क्रॉस-सेक्शनल स्कैनिंग थर्मल माइक्रोस्कोपी (xSThM) का उपयोग करने वाला एक नया दृष्टिकोण नियोजित किया जाता है। इसके अलावा, Sb_2Te_3 पतली फिल्म के फोनन और चार्ज वाहक परिवहन गुणों पर ऑक्सीजन के प्रभाव की जांच करने के लिए एक संपूर्ण सूक्ष्म विश्लेषण किया जाता है। Sb_2Te_3 मैट्रिक्स में अनाज सीमा पर ऑक्सीजन अशुद्धता को शामिल करने से अनाज सीमा वाहक फ़िल्टरिंग और बैंड संरचना में संशोधनों के परिणामस्वरूप पावर फैक्टर में पर्याप्त वृद्धि हुई है। अंत में, विभिन्न सामग्रियों की थर्मोइलेक्ट्रिक विशेषताओं में सुधार के साधन के रूप में सब्सट्रेट प्रभाव के उपयोग पर आधारित एक नई रणनीति भी प्रस्तावित है। परिणाम थर्मोइलेक्ट्रिक (टीई) परिवहन में सब्सट्रेट के योगदान के महत्व पर प्रकाश डालते हैं क्योंकि आयाम कम हो जाते हैं। इसके अलावा, फिल्म की टीई विशेषताएँ सब्सट्रेट के गुणों से निकटता से

जुड़ी हुई हैं। यह दृष्टिकोण सब्सट्रेट प्रभावों की व्यापक समझ प्रदान करता है, अंतर्निहित भौतिकी को शामिल करता है और थर्मोइलेक्ट्रिक पावर उत्पादन और शीतलन अनुप्रयोगों के उपयोग के लिए एक आशाजनक मार्ग प्रदान करता है।

कुल मिलाकर, वर्तमान थीसिस विभिन्न तंत्रों के अनुप्रयोग द्वारा Sb_2Te_3 यौगिकों में संभावित TE गुणों को संबोधित करती है। हमारा मानना है कि इस संभावित TE सामग्री का प्रयोगात्मक अहसास बहुत आकर्षक होगा और ZT की भविष्यवाणी करने में और मदद करेगा।

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Symbols

ΔT	Temperature difference
S	Seebeck coefficient
σ	Electrical conductivity
ρ	Electrical resistivity
$S^2\sigma$	Power factor
κ	Thermal conductivity
κ_e	Electronic part of thermal conductivity
κ_l	Lattice part of thermal conductivity
k_{xy}	In plane thermal conductivity
k_z	Cross plane thermal conductivity
ZT	Figure of Merit
Π	Peltier coefficient
η	Thermoelectric efficiency
B	Materials parameter
K_{bi}	Bipolar thermal conductivity
m*	Effective mass
E_F	Fermi level
n	Carrier concentration
μ	Electrical mobility
e	Electronic charge
L	Lorentz factor
k_B	Boltzmann constant
μ_w	Weighted mobility
E_g	Band gap

N_V	Band degeneracy
m_b^*	Local density of states
Cv	Specific heat
$\nu(\omega)$	Phonon group velocity
$\nu(\omega)$	Phonon mean free path
R_H	Hall resistance
E^f	Formation energy
V_C	Contact voltage
$R_X(t)$	Interface resistance
V_{nc}	Non-contact voltage
R_p	Probe resistance
a	Probe diameter
P_{max}	Maximum power

Abbreviations

TE	Thermoelectric
RTG	Radioisotope Thermoelectric generator
STEG	Solar TE generators
PV	Photovoltaics
DOS	Density of states
PF	Power Factor
XRD	X-ray diffraction
XRR	X-ray reflectivity
AFM	Atomic force Microscopy
SThM	Scanning thermal microscopy
RF	Radio frequency
DMA	Differential mobility Analyzer
XPS	X-ray photoelectron spectroscopy
FESEM	Field emission scanning electron microscope
HRTEM	High resolution transmission electron microscope
KPFM	Kelvin probe force microscopy
EFM	Electrostatic force microscopy
CFM	Conducting atomic force microscopy
PPMS	Physics property measurement system
RT	Room temperature
NP	Nanoparticle
ESP	Electrostatic precipitator
PBE	Perdew-Burke-Ernzerhof
GGA	generalized gradient approximation

JCPDS	Joint Committee on Powder Diffraction-International Centre for Diffraction Data
BEXP	beam-exit cross-sectional polishing
xSThM	Cross sectional scanning thermal microscopy
GB	Grain boundary
GI	Grain interior
HAADF	High-angle annular dark-field imaging
DFT	Density functional theory
CPD	Contact potential difference
WF	Work function
SAED	Selected area electron diffraction
GI	Grazing incidence