Utilizing Nanomaterials and the Thermoelectric Effect to Recover Industrial Sources of Heat Waste as Usable Energy

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Over the last 20 years, innovations in technology have made the large-scale extraction of renewable energy considerably more practical. However, power grids in the United States and around the world still heavily rely on thermal sources of energy to generate reliable power that can match consumption rates. The aim of this paper is to investigate a method of increasing the efficiency of existing power structures and manufacturing processes through the application of nanotechnology. While a carbon free energy system is something to strive towards, any research that has the potential to lower carbon emissions is useful and relevant. Nanoelectronics may be able to aid in this reduction effort through the enhanced application of the Thermoelectric Effect, a long-known relation between temperature gradient and electric charge. A successful implementation of this phenomenon would recycle waste heat from existing methods of energy production and manufacturing into usable energy. Engineered semiconducting nanomaterials are currently yielding promising results to this end, although more work is needed before creating a practical large scale energy recycling device. This paper outlines the basic working principles of the Thermoelectric Effect and compiles existing research done on various nanomaterials to gain insight on this exciting approach to lowering emissions.

I. Existing Methods and Infrastructure For Power Generation and Manufacturing

As of 2021 The most common sources of energy powering the United States are still carbon based. Turning resources like coal or peat into useful energy has long since been a problem for engineers to overcome. The basic concept of this

Fig. 1. Common Heat Waste Sources

Industry or Source	Waste Heat Temperature (°C)	Type
Gas turbines	370 - 450	Gas
Steam turbines	200 - 430	Gas
Petrochemical, refinery	150 - 300	Liquid, Gas
Pulp and paper	200 - 400	Liquid, Gas
Aluminium plants	100 - 350	Gas

conversion can be characterized by the steam engine, invented in 1712. Coal or another fuel is burned to heat water which in turn creates high pressure steam that turns a turbine. Three hundred years later, most modern power plants are still based on the same working principle. Engineers have been optimizing the efficiency of these machines for generations, but the highest-level efficiency currently achievable lies between 40% and 50%. The Law of Conservation of energy is mostly responsible for capping work output of generators, but that is not to say there is no room for improvement. The thermomechanical workings of power generation have been long since optimized, but the process continues to unavoidably lose a large portion of energy to heat. This excess heat from any power generation or manufacturing process is called "heat waste." This refers to any unintentionally created heat that cannot be easily converted into work or recycled. It is generally as categorized as being high grade (> 300°C), medium grade (100°C – 299°C) or low grade (< 100°C). About 63% of industrial heat waste output in United States is low grade, but medium and high-grade heat still make up a large portion of waste produced by heavy industries like metal refinement. Existing methods for achieving maximum efficiency at a large scale are difficult to retroactively implement and rely complex mechanisms with high operating temperatures. This presents a large problem when attempting to boost the efficiency of aged infrastructure at a reasonable cost. Engineered thermoelectric nanomaterials may present an affordable energy recycling solution with low complexity and the capability of operating at both high and low temperatures.
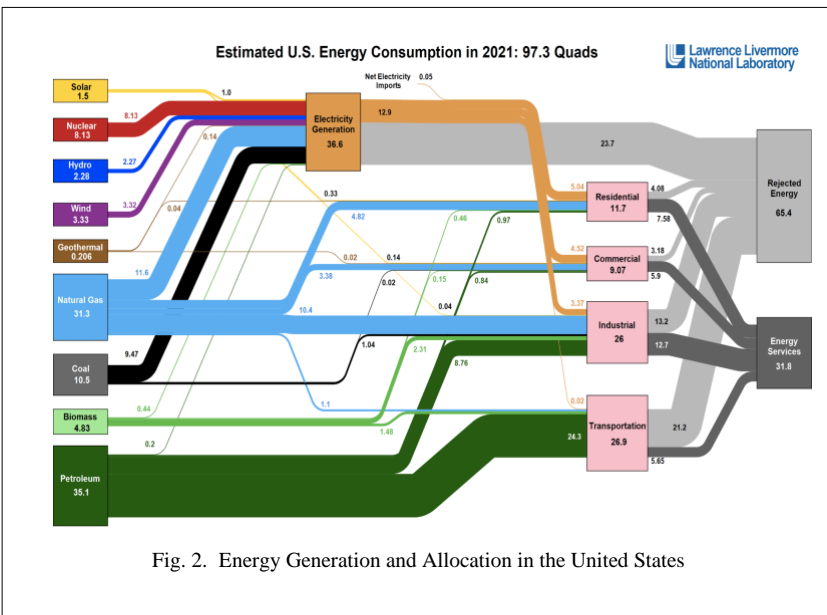

Fig. 2. Energy Generation and Allocation in the United States

II. THE DISCOVERY OF THE THERMOELECTRIC EFFECT AND ITS FIRST APPLICATIONS

The Thermoelectric Effect is a long-known phenomenon first discovered in part by Thomas Seebeck in the early 1820s. Seebeck realized that a temperature gradient generated across two bonded metals creates a measurable flow of current. This process of electricity generated from a heat gradient is known as the Seebeck Effect. His work was later expanded upon by Jean Peltier in the late 1830s. Peltier was able to observe the same effect Seebeck discovered but operating in reverse wherein a temperature gradient across two bonded metals could produce a current. The combination of these two discoveries along with magnetic interactions not relevant to this paper are collectively referred to as the Thermoelectric Effect. Despite being discovered 200 years ago, the practical application of this seemingly trivial phenomenon is still not realized in a practical sense. This can be intuitively and mathematically understood as a problem built into the very nature of an electrical current produced by a difference in temperature. The material required for any useful application must have very low thermal conductivity to maintain a steep temperature gradient while also having very high electrical conductivity to allow for the flow of electrons. Electrical and Thermal conductivity are very closely tied due to the fact that heat carrying particles known as phonons and charge carrying particles known as electrons interact with lattice structures in nearly the same way with regards to conductivity. Metals are good at conducting electricity, but equally good at conducting heat; nonmetals are poor at conducting heat and equally poor at conducting electricity. Engineers use cleverly designed heat sinks to build electrically powered cooling devices without moving parts utilizing the Seebeck Effect, but heat sinks do not come close fulfilling the gradient requirements of a usable Peltier device.

III. CHARACTERIZATION OF THERMOELECTRIC DEVICES

At its core, Thermoelectric Effect is defined by the transfer of energy through a material. To be able to distinctly identify the properties of heat transfer and charge transfer, an accurate model of the atomic interactions between phonons and electrons must be adopted. The crystalline and atomic structure of materials along with their carrier interactions have proven to be the defining characteristics for the efficacy of the Thermoelectric Effect. A high-level mathematical measure of a material's TE merit is cleverly called 'the measure of merit" and is defined by the unitless quantity zT.

$$zT = \frac{\alpha^2 \sigma}{\kappa_t} T \tag{1}$$

This is a temperature dependent measurement based on electrical conductivity, defined in S/m as

$$\sigma = ne\mu$$
- n = Charge Carrier Density (m^{-3})
- e = Elementary Charge (C)
- μ = Charge Carrier Mobility (ms^{-1}) \hfill (2)

along with Thermal conductivity, measured in $Wm^{-1}K^{-1}$ as

$$\kappa_t = \kappa_e + \kappa_l$$
- κ_e = Thermal Conductivity due to electrons
- κ_l = Thermal Conductivity due to *phonons* (Defined by the lattice) \hfill (3)

and Seebeck voltage, or the measure of voltage created by the movement of carriers defined as,

$$\alpha = \frac{\Delta V}{\Delta T} \text{ (V)} \tag{4}$$

zT has mathmatical relationsips that match up with the desired properties descibed earlier with κ_t being in the denominator and σ being in the numerator. It also confirms why semiconductors are used as TE materials as n doped and p doped sections of Silicon enable a controllable and channeled
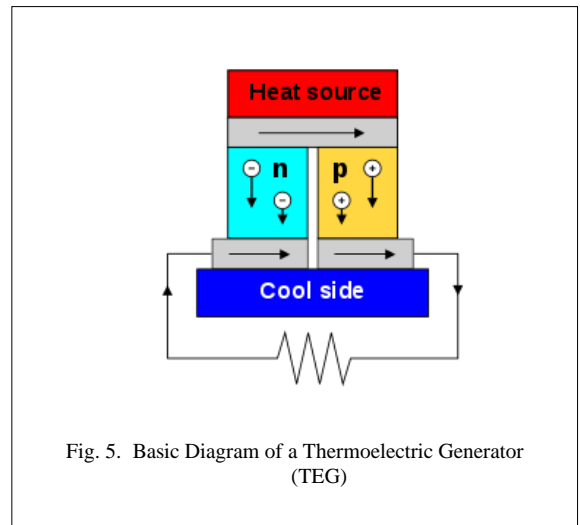

Fig. 5. Basic Diagram of a Thermoelectric Generator (TEG)

charge carrier flow. It is important to also note the Temperature dependancy of zT. Devices have a widely varying zT depending on operating termperatue. This means that T is just as important as the gradient ΛT. In general, TE materials are chosen based on the expected operating temperature of the device, as zT is only maximized over a cetain range of temperatures for a given material. Achieving a zT above 3 at
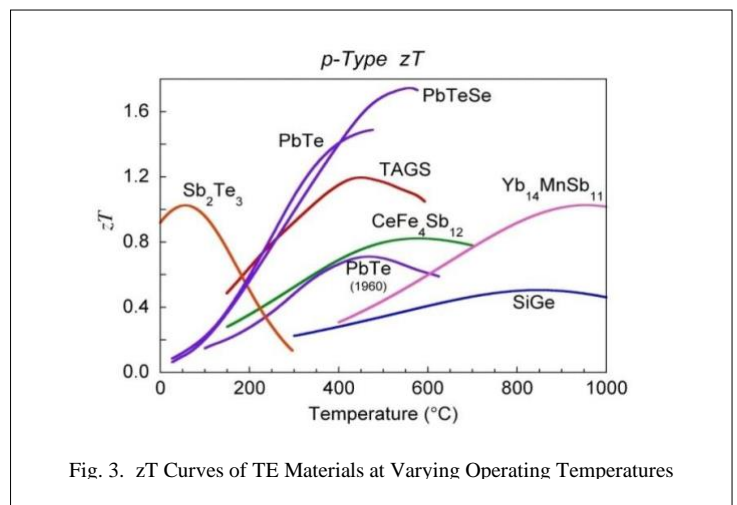

Fig. 3. zT Curves of TE Materials at Varying Operating Temperatures

room temperature is considered to be a possible turning point for the practicallity of TE devices. zT quantifies the general parameters that give a material good TE properties, but fabricating a practical device requires careful consideration of desired function and operating conditions. zT is a dimensionless measurement, and at device level it carries no tangible meaning. In the case of thermal energy recycling, the desired property of the TE material is the efficient conversion of temperature gradient to heat. This is tangibly measured by efficiency. Thankfully, the efficiency of a TE material can be expressed easily with some manipulation of zT.

$$\eta_{max} = (1 - \frac{T_c}{T_h}) \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}}$$

(5)

The efficiency is not linearly proportional to zT and varies heavily with operating temperature. High operating temperatures are a limiting factor in the efficiency of a TE device. TE devices operate with much higher efficiency at higher temperatures. Logic follows that the easiest way to implement an energy harvesting device would be to start with a design for recycling high energy heat waste. Later in this paper, materials optimized for high grade and medium grade heat waste will be explored.
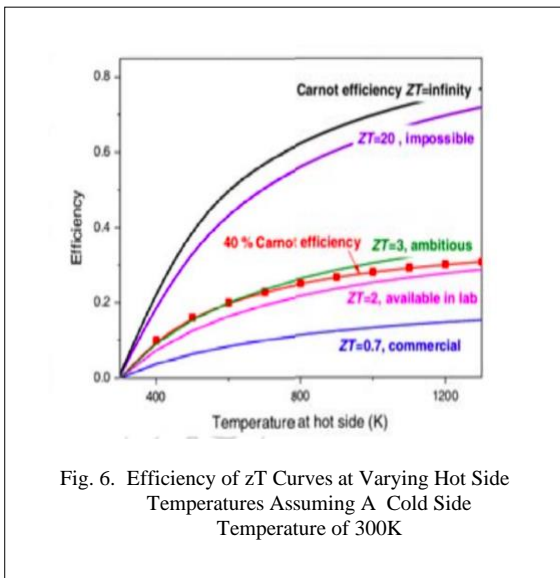

Fig. 6. Efficiency of zT Curves at Varying Hot Side Temperatures Assuming A Cold Side Temperature of 300K

Fig. 7. Theoretical Applications of TEGs for Varying Grade of Heat Waste

Bismuth Telluride is an example of a low operating temperature TE material with multiple potential applications including powering devices from heat given off by human skin. Optimizing such a device for low temperatures would be more relevant for with biomedical applications than large scale energy extraction. Materials with a higher operating like Tin Oxide are more likely to be used in implementing an energy recycling device.

IV. DESIGNING NANOMATERIALS WITH STRONG THERMOELECTRIC PROPERTIES

To fabricate Nanomaterials with generally strong TE properties, every controllable characteristic of the material must be tuned according to the parameters of zT. This requires defining how the structure and composition of the material relates to electrical conductivity (σ), thermal conductivity (κ) and the Seebeck Coefficient (α). Conductivity κ and σ are already mathematically defined at a small scale based on carrier transport and lattice structure interactions, but an atomic understanding of the Seebeck Coefficient α is considerably more difficult. Understanding the Seebeck Coefficient is especially important since it is the only parameter in zT being squared.

The general formula is given as $\alpha = \Delta V/\Delta T$ (V), which is not very helpful when trying to characterize it at an atomic scale. Defining this voltage generated by the movement of carriers in understandable and controllable terms requires some mathematical dexterity. After solving the Boltzmann Transport equation, the Seebeck coefficient can be given as

$$\alpha = -\frac{k_B}{q} \int \frac{(E-E_F)}{k_B T} \frac{\sigma(E)}{\sigma} dE$$

(6)

While α is now given in terms of familiar terms E_F, q, σ, T and k_B, the equation is no longer very readable. A much more digestible form of this equation is given as Mott's Relation:

$$S(T) = \frac{\pi^2 k_B^2 T}{3q} \left(\frac{1}{N(E)} \frac{dN(E)}{dE} \right)_{E=E_F},$$

(7)

Now it can observed that α is largely defined by the shape of the density of states N(E). A desirable material will have a low density of states since with a sharp slope near the Fermi Level E_F. The relationship between density of states and band structure is visualized in Figure 8 below. The purple line shows N(E) designed with strong TE properties with the yellow region being minimized and the slope at the Fermi Level maximized. The purple valance and conduction bands correspond to TE maximized N(E).

With every term in zT characterized, useful design choices can be made for TE materials. To maximize σ and minimize κ, an ideal TE nanomaterial will have high doping to provide a large number of carriers and a crystalline structure that produces high phonon scattering and low electron scattering. This is usually accomplished by creating very complex lattice structures since this bumps up the phonon

scattering while having a less of an effect on electrons. Additionally, the band structure of the material will be tuned to have a partially inverted shape near the band gap.
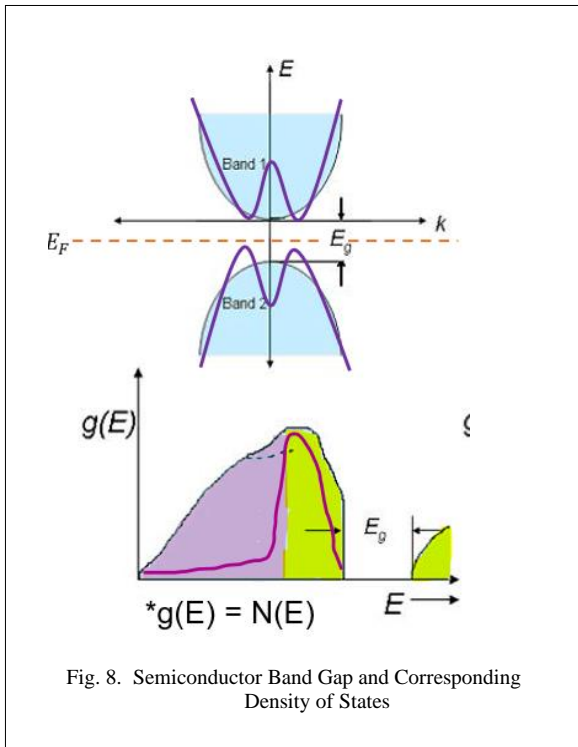

Fig. 8. Semiconductor Band Gap and Corresponding Density of States

V. Zintl-Phase Materials

Zintl-Phase Materials are effective semiconductors being researched for their excellent TE properties. The materials are metal clusters made by combining metals from group 1 and 2 with some another metal, transition metal or alternatively a Lanthanide or Actinide. Zintl Crystal Structure is made up of complex bonds between sub clusters of anions and cations. The result is a volatile structure with a very complex lattice made up of two distinct bond networks. Researchers theorize that the network of polyanions successfully increases phonon scattering and that ionic bond network formed by cations maintains electrical conductivity.
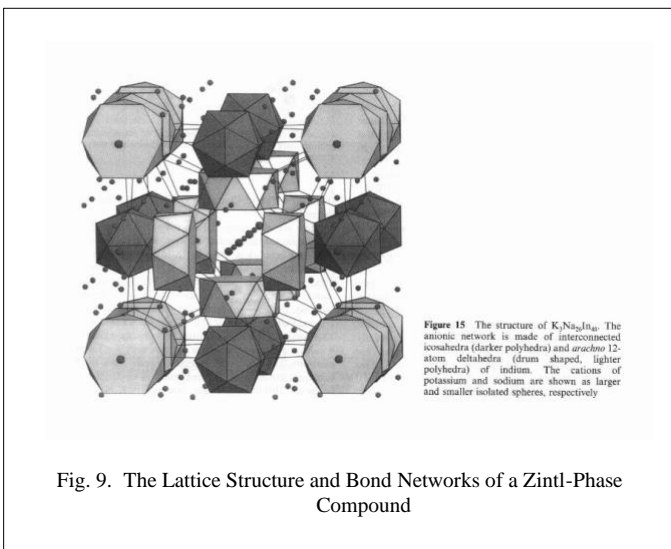
Fig. 9. The Lattice Structure and Bond Networks of a Zintl-Phase Compound

VI. Zintl-Phase Eu_2ZnSb_2 Thermoelectric Characterization (2019)

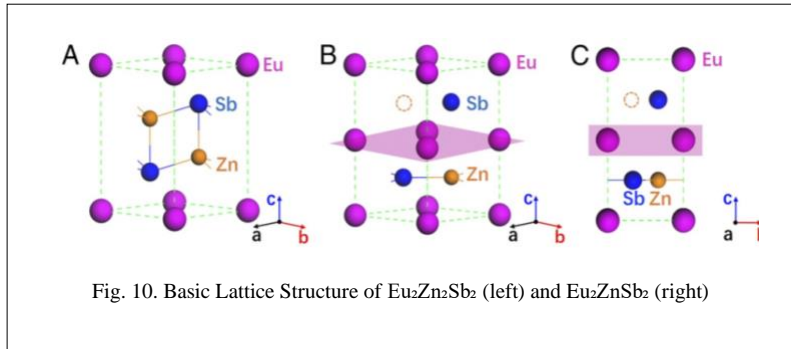Fig. 10. Basic Lattice Structure of $Eu_2Zn_2Sb_2$ (left) and Eu_2ZnSb_2 (right)

Eu_2ZnSb_2 is a Zintl-Phase compound tested as TE material in 2019 with ultra-low thermal conductivity. The compound is an improvement on $Eu_2Zn_2Sb_2$ seen in part A of Figure 9. $Eu_2Zn_2Sb_2$ already has very low thermal conductivity, but by adding a layer of Eu diving the lattice and creating a Zn deficiency. The additional layer of Eu in the lattice heightens phonon scattering and the introduction of a Zn deficiency increased the materials electrical conductivity by raising the
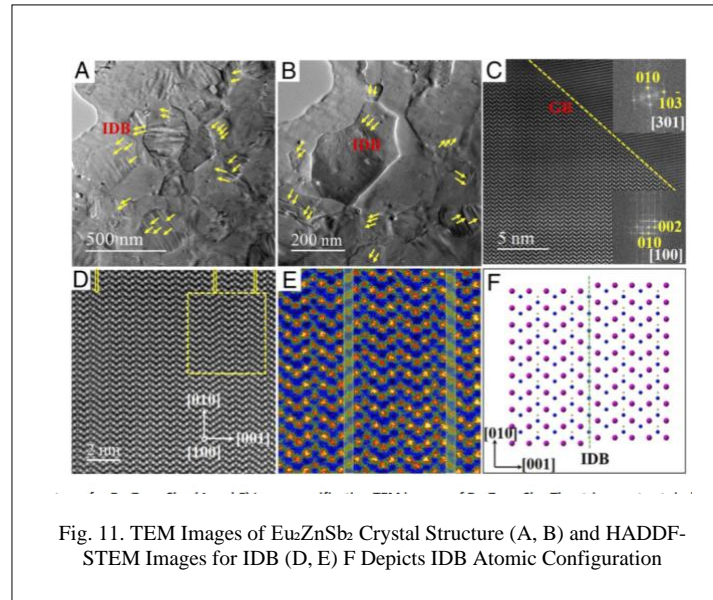

Fig. 11. TEM Images of Eu_2ZnSb_2 Crystal Structure (A, B) and HADDF-STEM Images for IDB (D, E) F Depicts IDB Atomic Configuration

Hall Carrier concentration. The layered nature of the lattice is visible in low magnification TEM images of microstructures. Arrows yellow arrows indicate Inversion Domain Boundaries which researchers considered to play a large part in increasing phonon scattering. This combined with the small size of the boundaries as indicated Figure 10 C yielded ultra-low thermal conductivity. The measured zT of Eu_2ZnSb_2 compared with similar TE materials reveals a strong value of ~1 at high operating temperature of 700 – 800 K, making it a potential candidate for a TEG of high-grade waste. Obviously, the zT needs to be raised higher to justify the fabrication of a full TEG device, but the lattice manipulation achieved by this extremely scalable fabrication process is definite step forward.
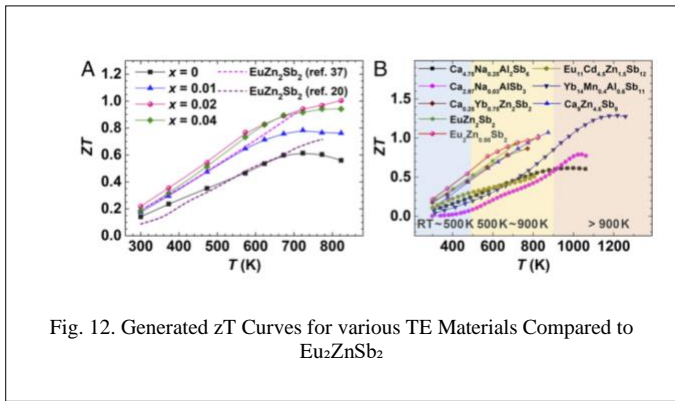
Fig. 12. Generated zT Curves for various TE Materials Compared to Eu_2ZnSb_2

VII. Eu_2ZnSb_2 Zintl-Phase Fabrication Method

Synthesizing Zintl-Phase materials is a uniquely straightforward and scalable process compared to other nanomaterials and relies on natural bond formation. Zinc, Europium and Antimony powder are carefully measured according to the stoichiometry of the desired material and placed into a high energy steel ball mill. The powder is pressed into a graphite die and its ready for testing.
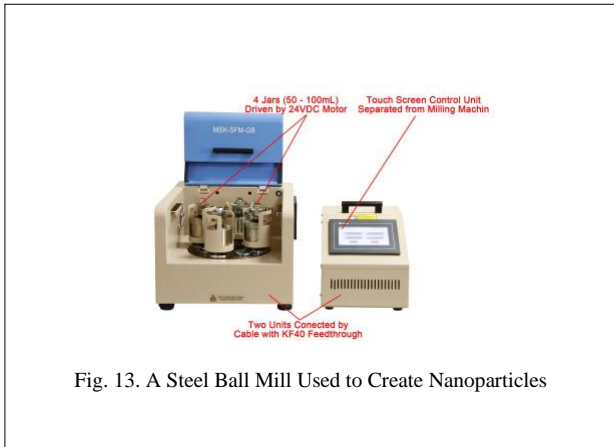

Fig. 13. A Steel Ball Mill Used to Create Nanoparticles

VIII. Thermoelectric Properties of Nanostructure Tin Oxide Thin Films (2018)

Tin Oxide is a low dimensional, wide gap n-type semiconductor tested as TE material by depositing it onto glass and alumina substrates and then doping it with thin films Cu or Fe. For TE characterization SnO_2 on was deposited on porous alumina and glass substrate using the anodizing technique. The anodizing technique is an inexpensive alternative to traditional methods like CVD and sputtering that relies on an electromechanical process to add layers of oxide to the surface of metals. Figure 14 depicts porous oxide deposition onto Al substrate, but the method also works for semiconductors. The films were then doped by depositing thin films of Cu or Fe onto the porous oxide using the dip coating sol-gel technique. This method pairs with the porous oxide deposition and is able to produce a uniform, thin metal film. Lastly, the films were
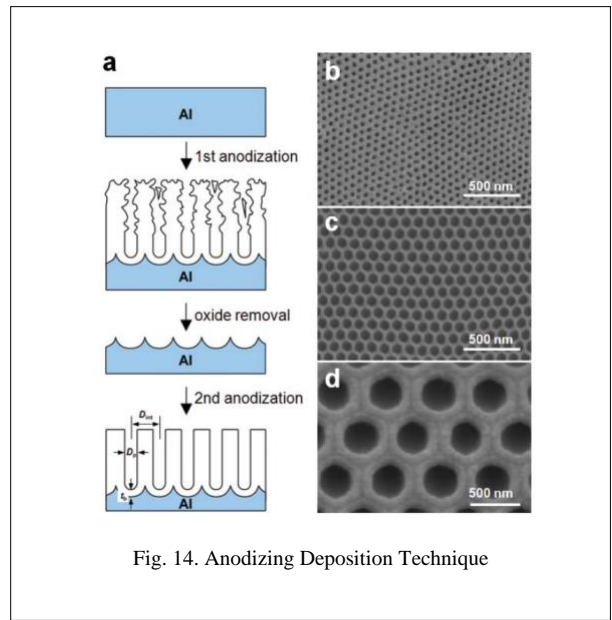

Fig. 14. Anodizing Deposition Technique

sintered at 600°C for 2 hours. The grain size of the prepared films was measured as being in the nano scale using Atomic Force Microscopy seen in Figure 16.
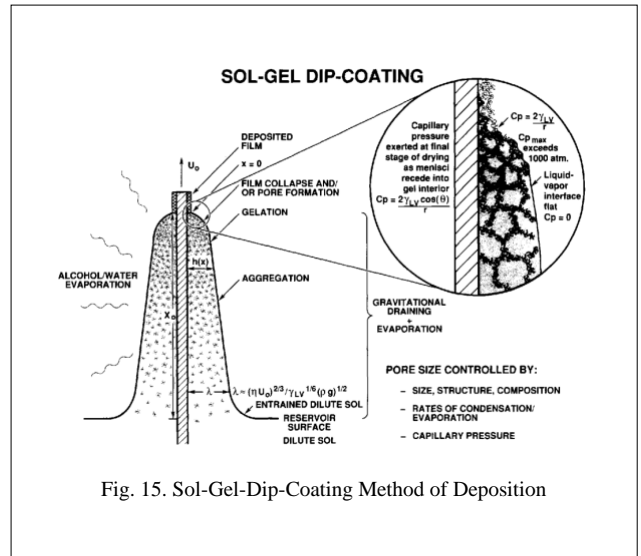

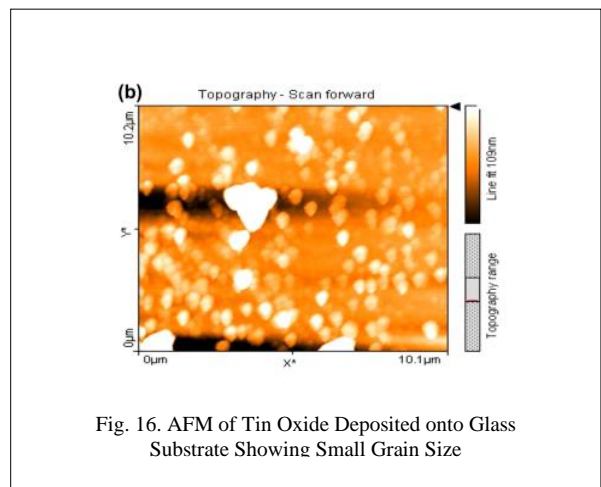Fig. 15. Sol-Gel-Dip-Coating Method of Deposition

Fig. 16. AFM of Tin Oxide Deposited onto Glass Substrate Showing Small Grain Size

Researchers characterized the TE properties by measuring an I-V curve and individual zT parameters with special focus on the Seebeck coefficient.
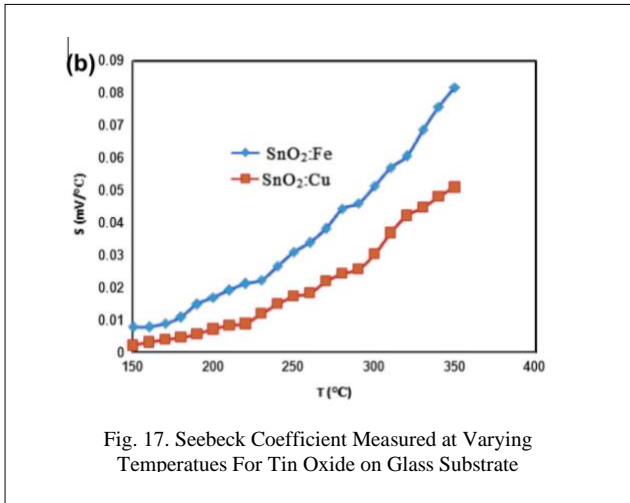

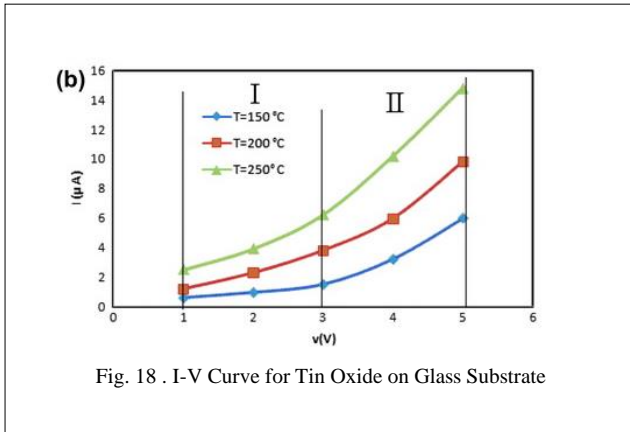Fig. 17. Seebeck Coefficient Measured at Varying Temperatues For Tin Oxide on Glass Substrate

Fig. 18 . I-V Curve for Tin Oxide on Glass Substrate

IX. Copyright Forms

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