



Thermoelectric power factor enhancement of AZO/In-AZO quantum well multilayer structures as compared to bulk films

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ABSTRACT

This study investigates and demonstrates the enhancement in thermoelectric power factor for n-type AlZnO/InAlZnO multilayer quantum wells as compared to their counterpart bulk films. A 10–20% improvement is observed for operating temperatures <700 °C. Fabricated structures are composed of 50 periods, with targeted individual layer thicknesses of 10 nm. The best performing multilayer shows an electrical resistivity and Seebeck coefficient of 1000 μV/K and at 700 °C. In addition, a theoretical relationship is derived between the thermoelectric performance and correlating microstructure that demonstrates the deterioration of electronic transport properties at increased interface roughness levels. To determine the microstructure and interface roughness of the films, X-ray and spectroscopy techniques were used. The proposed model is based on how quantum well-width fluctuations caused by increased interface roughness leads to the localization of carriers and thus a decrease in electrical conductivity.

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1. Introduction

Today, most of the energy resources used in industrial processes are discharged as waste heat into the environment. Such exhaust heat accounts for approximately 60% unused energy. Hence, thermoelectric (TE) energy conversion, which converts waste heat into electricity, has received much attention. The conversion efficiency of a thermoelectric material is determined by the dimensionless figure of merit, $ZT = \alpha^2 T / \rho \kappa$, where T is the absolute temperature, α is the Seebeck coefficient, and ρ and κ are the electrical resistivity and thermal conductivity, respectively. However, the three physical parameters comprising Z are all functions of the carrier concentration, n . Taking α and ρ to be directly related, and ρ and κ varying inversely to one another (the Wiedemann–Franz law), the improvement in ZT is not an easy task. Currently available thermoelectric materials have a ZT of less than ~ 1 and the device efficiency of producing electric power rarely exceeds 5%. This performance has limited TE generators to niche applications where requirements for remote operation, reliability, no moving parts, and silent operation have outweighed the more negative aspects of high cost and low conversion efficiency. It is estimated that with a $ZT > 2$ and a temperature difference of 200 K, a 10% heat-to-electric conversion efficiency can be obtained which would make this technology more feasible for mainstream applications [1,2].

Some thermoelectric materials being researched today are nanocomposite alloys of conventionally known TE materials such

as Bi₂Te₃, PbTe and SiGe doped with additional impurities. An example is La-doped PbTe–Ag₂Te nanocomposite which uses the Ag₂Te precipitates to enhance phonon scattering while La-doping allows for carrier concentration control and results in ZT values of >1.5 at 775 K [3]. A secondary set of materials include skutterudites, which use a mechanism of impurity void filling, which have resulted in n-type ZT values of up to 1.7 for CoSb₃ compounds [4]. However, these materials are commonly toxic, low in abundance as natural resources, and thus not environmentally benign. Based on these disadvantages, metal oxides have emerged as an alternate potential candidate for high temperature thermoelectric applications. In addition to their temperature stability and resistance to oxidation, they can also be deposited via a variety of feasible techniques that are easily scalable. However, the main concern is that conventional metal oxide films have exhibited relatively low levels of ZT (~ 0.34 at 1000 °C) due to poor carrier mobility from their ionic structures [5].

The well known and highly investigated p-type superconductor, NaCo₂O₄, was the first metal oxide observed to show promising thermoelectric properties. Upon further research, the layered structure of Ca₃Co₄O₉ has emerged as the leading material candidate with a ZT of 1.2–2.7 at 600 °C [6,7]. This is attributed to the alternate stacking of hexagonal Ca₂CoO₃ layers and rectangular rock salt layers, which results in increased phonon scattering and significantly reduced κ . A second approach is to reduce the ionicity of the metal–oxygen bonds in order to increase the carrier mobility, an example being ZnO-based thermoelectrics. Currently, the most widely studied n-type material is Al-doped ZnO (AZO), which has obtained a ZT value of 0.1 at 1200 °C [8]. More recently, by

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means of co-doping with additional low level impurities (Ga or In), an enhancement of ZT was found. This is either due to an amplification in the phonon scattering at the increased number of interfaces, or the enhancement in the electrical transport properties from raising the density of the states which coincides with the addition of carrier electrons [9,10]. However, ZT values for n-type films remain inferior for practical applications.

The use of lower dimensionality materials has been theoretically proven to be an underlying mechanism in improving the thermoelectric properties of materials, predicting ZT values >3 [11]. Some low dimensional structures include quantum wells (QWs), superlattices, quantum wires, and quantum dots. Within these low-dimensional regimes where quantum effects are dominant, the energy spectra of electrons and phonons can be controlled by altering the size of the structures which allows for the manipulation of the material properties. In theory this regime gives rise to new materials even though the material is made up of the same atomic structure as its parent bulk material. Multilayer QWs also known as superlattices, consist of more than 50 periods with individual layer thicknesses of <20 nm [12]. The first material acts as the active layer while the second material with a larger band gap acts as a barrier for the charge carriers. The band-gap offset thus creates a well that is periodically repeated throughout the multilayer [13]. Fig. 1, is the structural design of our samples which utilize the in-plane transport of heat and current flow (parallel to the substrate), whereas conventional TE-based superlattices highlight the reduction of thermal conductivity via cross-plane transport flow [14]. From the in-plane transport methodology we benefit from (a) enhanced density of states near E_F , which results in an enhanced Seebeck coefficient and (b) an increase in the energy-dependence of the carrier mobility $d\mu(E) = dE$ which results from increasing the scattering time's energy dependence, by preferentially scattering electrons depending on their energy (quantized energy band levels). In addition, by using the in-plane transport structural geometry we can obtain much greater distances between heat source and sink which allows for a lower heat flux, $q_x = \kappa\Delta T/x$, where ΔT is the temperature differential and x is the distance.

To obtain feasible devices it would be essential to scale-up this technology to large area substrates. For this reason an appropriate deposition technique must be chosen and verified. Molecular beam epitaxy and atomic layer deposition are deposition techniques which provide excellent precision for ultra thin layers thicknesses, but have low throughput due to low growth rates. Out of all the techniques available, RF sputtering provides high quality films at high growth rates, and is relatively easy to scale up to provide feasible large area depositions as needed for alternative energy applications. However, one well known issue coinciding with the high growth rate of RF sputtering is the increased levels of surface roughness. For our device design optimization it is essential to optimize the TE properties of the 10 nm QWs which means we must understand the impact of well-width fluctuations caused by interface roughness (IFR). We have developed a model which correlates the dependence of electrical resistivity to IFR. For the multilayer stacks under investigation the achievable roughness level from deposition becomes extra critical because initial layer roughness will subsequently impact the layer roughness deposited thereafter.

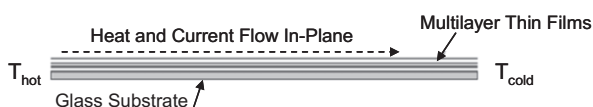


Fig. 1. A representative diagram of our multilayer QW thermoelectric design, using in-plane heat and current transport (Not to scale).

In this work we deposit, characterize, and measure the thermoelectric performances of multilayer QWs consisting of 50 alternating periods of AZO and (In, Al) co-doped ZnO with 2–10 at.% indium. Within this paper we will refer to these samples as InAZO2, InAZO5, InAZO8, and InAZO10 which correspond to 2 at.% In doped $Al_{0.02}ZnO$, 5 at.% In doped $Al_{0.02}ZnO$, 8 at.% In doped $Al_{0.02}ZnO$, and 10 at.% In doped $Al_{0.02}ZnO$ films, respectively. In addition, we will compare thermoelectric performance to previously investigated bulk films of the same materials. Furthermore, we will discuss our newly developed theoretical model relating the electrical resistivity dependence on interface roughness and the subsequent fit to our experimental data obtained via X-ray analysis.

2. Experimental details

Bulk and multilayer films have been deposited using a stainless steel physical vapor deposition reactor equipped with two confocal magnetron sputtering guns. The guns were driven independently by 13.56 MHz rf power supplies. A computer controlled automated system was used to operate the opening and closing of the target shutters in order to control the co-doping process. The targets were commercially sintered 3" disks of Al_2O_3 (2 wt%)-doped ZnO (99.99% purity, Plasmaterials Inc.) and indium (99.95% purity, Plasmaterials, Inc.). Preceding all depositions, the reactor was evacuated using a combination of a mechanical pump and turbomolecular pump to a base pressure of $<5 \times 10^{-7}$ Torr. In order to vary the Indium in film concentration between 2 and 10 at.%, the In target RF power was increased from 10 to 20 W accordingly [14]. Preliminary baseline experiments were performed on AZO to optimize the deposition in terms of high crystallinity, low resistivity, and low root mean squared (RMS) surface roughness. The process parameters are Ar/ O_2 gas ratio of 3, 2 mT operating pressure, 100 W AZO target power, and a 150 °C substrate temperature which is located 40 cm from the target. For comparison purposes all films, both bulk and multilayer films have a total targeted thickness of 1 μ m.

The 50 periods of AZO/InAZO multilayer QW films are deposited with a targeted individual layer thickness of 10 nm, because this will result in quantum well effects (<20 nm). Deposition times varied due to the increased growth rate (1.8–2.7 nm/min) for higher indium RF power (10–20 W) [14]. All films were deposited on 100 m Ω -cm n-type (100) Si wafers as blanket films for characterization purposes. These devices were fabricated by forming 1.5 \times 0.5 cm plateaus of multilayers via reactive ion etching. Chemical selectivity to the Si substrate was not an issue and did not result in any substrate pitting. Devices were then inserted into a custom designed clamp which allows for the Cr/Au electrical contact deposition on the short 0.5 cm ends (Fig. 1) without any subsequent deposition on the top/bottom of the sample. This was done on the samples with multilayer structures as well as just on the substrate, in order to allow for the separation of Seebeck coefficient measurements [15]. This will be explained in further detail in the Section 3.2. In addition, the substrates were cleaned using the standard RCA method, and subsequently dried with N_2 .

3. Results

3.1. Structural and morphological properties

Samples deposited consisted of 50 periods of 10 nm layers with QWs ranging from 0 to 10 at.% indium, resulting in a total thickness of 1 μ m. Phase identification was carried out on a Scintag X-ray diffractometer (XRD) equipped with a Cu K α 1 X-ray source and a horizontal wide-angle four-axis goniometer with stepping motors which allowed for independent or coupled $\theta/2\theta$ axis motion. The multilayer films were initially annealed for 2 h at 900 °C in atmosphere to allow for necessary re-crystallization and then scanned from 20 to 60°. The collected XRD patterns were compared to reference patterns from the standard Joint Committee for Power Diffraction Standards powder diffraction file. For comparison purposes, all sample data has been normalized to its maximum peak intensity.

After normalization, the results obtained are identical to the bulk XRD patterns obtained in a previous investigation of (In, Al) co-doped ZnO bulk films [7]. The XRD pattern in Fig. 2, show that 0 and 2 at.% In films have a sole detectable diffraction peak, which is nearly consistent with that of the (002) standard ZnO crystal plane. Using the Debye–Scherrer formula the grain sizes for the 0 and 2 at.% indium films are 32 ± 2 and 38 ± 2 nm, respectively. This

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