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Original Article

Thermoelectric Power in wide bandgap Semiconductor ZnO Nanowire

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Abstract *- Nanostructures have a significant promise as potential building blocks for the next generation of thermoelectric devices. While the thermal transport properties of bulk materials have been intensely studied, the understanding of nanostructure thermoelectric properties and their interrelation is still incomplete. In the calculated temperature range, the thermoelectric power (TEP) was linearly dependent on temperature, suggesting the degenerate nature of the ZnO semiconductor nanowire similar to that of the GaN semiconductor nanowire. Observed negative values of TEP indicating that majority charge carriers are electrons in ZnO semiconductor. Linear dependence of TEP with temperature shows that TEP is only due to electron diffusion and not due to the phonon-drag effect. Also observed, the calculated TEP values agree with the experimental results in the overall temperature range 10 – 300 K.*

Keywords *- Thermoelectric power, Seebeck effect, Semiconductor nanowire, ZnO, Mottrelation, Wide bandgap semiconductor.*

I. INTRODUCTION

At present, huge research efforts are dedicated to improving the efficiency of thermoelectric (TE) materials. Nanostructuring is one of the suggested methods to improve their TE performance. However, the morphology of a nanomaterial might play a significant role in its TE properties. Wide bandgap semiconducting nanowires have provided potential candidates for building blocks for short-wavelength optoelectronics, transparent electronics and high-temperature electronics applications [1-3]. Due to the confined geometry of the one-dimensional (1D) nanostructure, however, determination of the carrier concentration by a traditional Hall effect measurement is impossible. Thermoelectric power generation is one of the key technologies for sustainable energy; thermal energy is converted into electric power under a temperature gradient through the Seebeck effect. The dimensionless figure of merit ZT is a parameter used to indicate the thermoelectric performance of materials. ZT is defined as $(S^2\sigma/\kappa)T$, where S, σ, κ, and T denote the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the temperature, respectively. There have been several suggestions to enhance S via an anomalous electronic density of states [4-6] to realise high ZT values, going beyond the conventional 3D free-electron model. For example, Hicks and Dresselhaus theoretically proposed the confinement of carriers to very narrow 2D layers [7]. This is because the density of states for 2D electron gas (2DEG) is quantized into discrete values due to the formation of subbands, and this is expected to dramatically enhance S. Such a low-dimensional confinement effect has been extensively investigated both experimentally [8-10] and theoretically [11-13]; however, whether the 2D density of states directly enhances S in real materials is still elusive. The oxide semiconductor ZnO is an ideal target material for examining the relationship between the 2D density of states and the Seebeck effect. Bulk 3D ZnO has a non-degenerate and simple conduction-band structure [14] with parabolic energy dispersion around the conduction band minimum. When we apply an electric field at the surface of ZnO incorporated into a field-effect transistor (FET), charge carriers are accumulated at the surface, and the gate bias controls the carrier density in the channel. Moreover, by using ionic liquids or electrolytes as gate dielectrics, it is feasible to apply an extremely large electric field at the liquid-solid interface; this leads to a sharp band bending at the surface of the target material and, consequently, to the formation of a high-density 2DEG. In other words, the thickness of the carrier accumulation layer is electrically tunable by the gate electric field, which enables efficient control of the dimensionality of the quantum-confined electron system. Therefore, investigation of ZnO-based FET and bulk ZnO allows a systematic comparison between the 2D and 3D Seebeck effects.

Literature suggests structural manipulation, such as devising nanostructures and monolayers as an effective route to rapid improvement in the performance of thermoelectric materials. For example, nearly 100-times improved efficiency of Si-nanowires has been recorded compared to bulk Silicon [15]. The two-dimensional (2D) structures have

been reported to exhibit significantly improved PF compared to 3D counterparts, provided thickness is smaller than the de Broglie wavelength [16]. There is an experimental investigation on the Seebeck effect of 2D electrons using the electric field effect in ZnO. It is observed that the ion-gain experiment and band calculation demonstrated that the field-induced 2D electrons on an oxide semiconductor ZnO exhibit a higher thermoelectric effect than bulk ZnO [17].

Hence, nanostructuring has been widely practised to enhance the Power Factor and reduce the thermal conductivity to establish high-performance thermoelectric materials. However, besides the high convergence efficiency, energy production via the thermoelectric approach at a large scale requires highly stable, cheap, and non-toxic thermoelectric materials. Being low-cost and environment-friendly, ZnO is likely suitable for large scale energy production. ZnO exhibits considerable PF due to high electrical conductivity and the Seebeck coefficient [18]. However, its high lattice thermal conductivity renders its application for high-performance thermoelectric applications.

Given that nanostructuring significantly reduces the thermal conductivity, single-layered ZnO is expected to demonstrate better thermoelectric performance than its bulk counterpart. The 2D ZnO derived from the polar (0001)-plane of its stable wurtzite structure exhibit a graphene-like structure where the cations and anions are arranged in a hexagonal ring. The graphene-like 2D ZnO has been experimentally grown on Ag(111), and Pd(111) surfaces. However, unlike graphene, 2D ZnO exhibits a considerable energy gap of the magnitude of 2.23–4.0 eV, which is advantageous for applications in semiconductor devices. However, investigations of the thermoelectric response of single-layered ZnO are not reported in the literature to date to our knowledge. This paper studied the thermoelectric power theoretically using the semi-classical Mott relation to compare the existing experimental data for the ZnO nanowire.

ZnO materials have drawn vast attention in the past decades due to their interesting characteristics: non-toxic, abundant resource, cheap and very stable at high temperature (up to 1000 °C). Many researchers have been studying ZnO for thermoelectric applications to improve electrical conductivity and decrease thermal conductivity [19-23]. Due to the solubility limit of the single dopant, simultaneous control of electrical conductivity, Seebeck coefficient and thermal conductivity for a high ZT reach threshold. Therefore, many research groups have been investigating the effects of dual doping on the thermoelectric properties of ZnO. In addition, it is well known that the low-dimensional structure is promising for improving the thermoelectric properties of materials because of their strong quantum confinement effect. Therefore, in this review, we will provide a comprehensive summary of the effect of dopants and nanostructuring on the thermoelectric performance of ZnO materials. ZnO is an n-type semiconductor with a wide direct band gap of ~ 3.2–3.5 eV [24] and a large free-exciton binding energy so that excitonic emission processes can persist at or even above room temperature [25]. ZnO has three different crystal structures: the wurtzite, rock salt, and zincblende structures. However, the most common and stable phase is the wurtzite in ambient conditions. In this paper, we focus on discussing the thermoelectric properties of ZnO with the wurtzite structure having a wideband direct bandgap (~ 3.37 eV) and high exciton binding energy (~ 60 meV). ZnO is a very good material candidate in terms of light-sensing. Still, from the thermal conductivity point of view, it exhibits a poor response, especially in the environmental temperature range. Therefore, another material component with high electrical conductivity is desired as complementary material in the device to enhance the temperature sensitivity.

II. THEORETICAL MODEL

We shall use the well-known Mott formula within parabolic band approximation to estimate the contribution of electrons towards TEP. The low-temperature carrier diffusion TEP is [26]

$$S = - (\pi^2 k_B^2 T/3e) \left| \partial \ln(\sigma(E))/\partial E \right|_{E=EF} \quad (1)$$

Wheres (E) is the energy dependence of conductivity in the relaxation time approximation. In what follows, the mean free path of the carriers is assumed to be independent of temperature, above equation (1) becomes

$$S = - (\pi^2 k_B^2 m^* T / (3\pi^2)^{2/3} \hbar^2 e\, n^{2/3} \quad (2)$$

With constant mean free path and the method point to carrier scattering by impurities being dominant. We must point out that the linear response transport theory based on Fermi liquid description results in an exact expression for the most singular term in terms of damping rate and is valid for correlated electron systems as wide bandgap semiconductors.

In the above equation (2), the right-hand part was derived by assuming energy-independent mobility, where n is the carrier concentration and m^* is the effective mass of the semiconductor material. The above equation (2) is valid for the semiconductor sample studied in this article because the mean free path l_m is much larger than the interatomic distance. That semi-classical approach is appropriate without a quantum correction since $k_F l_m \approx 1$, where k_F is the Fermi wave vector. A similar approximation has already been made in TEP analysis of semi-metallic Bi nanowire [27] and small bandgap semiconductors [28]. We used this approximation in a wide bandgap semiconductor ZnO nanowire and compared it with experimental results.

III. RESULTS AND DISCUSSIONS

We calculated theoretically the thermoelectric power S for the wide bandgap semiconductor ZnO nanowire using the characteristic parameter, $m^* = 0.28m_e$, electron concentration $n = 3.1x10^{24}$ m^{-3}. These calculated data is compared with the experimental results [29], as shown in Figure 1.

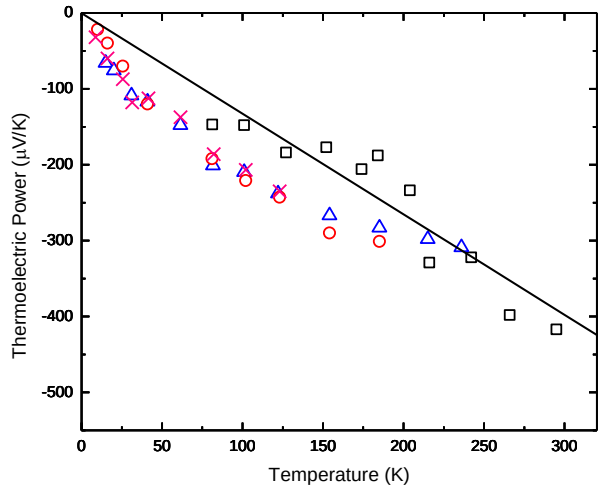

Fig. 1 Comparison of TEP with experimental results [29]. The symbols show experimental data of four different devices, and the line represents our theoretical calculations

The experimental results of ZnO nanowire, which were grown by catalyst-free metallic-organic vapour-phase epitaxy by Lee et al. [29], are shown by different symbols in figure 1. Three different devices are used with different nanowire diameters in the range of 80 – 120 nm, and the fourth one has approximately 1 μm diameter. We agreed with the experimental results in the temperature range 10 – 300 K for different ZnO devices. The measured TEP was about - 400 μV/K at room temperature, varying linearly with temperature. The negative values of TEP indicate that the carrier transport in ZnO nanowire is contributed by electron diffusion, reflecting that the nanowire is an n-type semiconductor. The overall temperature dependence, S directly proportional to T, agrees well with the Mott relation, expected for metal or a heavily doped semiconductor [30]. The major relation in our calculations is that TEP values for the wideband semiconductor increase linearly with temperature. This linear dependence observation suggests no appreciable phonon-drag induced TEP in this nanowire. Thus, TEP can only be described by thermal diffusion of the majority charge carriers.

IV. CONCLUSION

We calculated thermoelectric power TEP using basic semi-classical Mott formula to compare the experimental results of wide bandgap semiconductor ZnO nanowire for various devices and obtained a good agreement in the temperature range 10 – 300K. The measured and calculated TEP increases linearly with temperature, showing that TEP is due to the electron-diffusion process. The negative sign of TEP values indicates that the majority carriers in ZnO are electrons. The calculated value of TEP at room temperature is about - 400 μV/K.

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