Thermoelectric effect in quantum wells and hetero-structure

H. L. Kwok
Centre of Advanced Materials & Related Technology and Dept. of ECE, University of Victoria, Canada

Abstract

Thermoelectric effect has attracted much attention recently due to its potential application in cooling and power generation. The related theory (for bulk materials) is not new and the key parameter of interest, i.e., the thermoelectric power TEP or the Seebeck coefficient S can be derived based on charge transport and energy/heat transfer. Over the years, many thermoelectric materials have been identified and exhibited high conversion efficiency. Recent studies on thermoelectric effect in hetero-structures and delta-doped layers have also reported large thermoelectric power and it is of interest to find out if these selectively doped and/or interface layers (sometimes down to 1-2 unit cells) will exhibit the same thermoelectric properties as found in bulk materials. From the perspective of maximizing the thermoelectric power, the question would be whether one ought to favour the use of a quantum well structure or a hetero-structure. This work provides a comparative study on the performance of thermoelectric materials built on these layered structures. Analyses suggest that for a moderately doped surface layer, there is little difference between the 2-dimensional model and the 3-dimensional model. The difference occurs at high doping when a 'metallic' model has to be used. For the quantum wells and the hetero-structure our results indicate that there will be charge migration into the substrate, which may complicate the analyses. In our opinion, this can be the reason for the observed "giant" thermoelectric power found in the TiO_2-$SrTiO_3$ hetero-structure.
Keywords: hetero-structure interface, quantum well, sheet charge density, thermoelectric power, charge migration.

1 Introduction

Thermoelectric effect has been studied for a long time and the physics in bulk materials are well established [1, 2]. Because of its potential importance to power generation and cooling, there is much incentive to look for thermoelectric materials that offer higher figure-of-merit. As far as applications are concerned, the key interest has been to find a material with a large thermoelectric power S; a low thermal conductivity κ, and a large electrical conductivity σ. Most known thermoelectric materials offer limited advantages in one or more aspects of these properties and recently there has been motivation [3–5] to look into materials with novel structures, such as those involving quantum wells and 2-dimensional electron gas layers. In these layered structures, both the charge density and the thermoelectric power are known to be affected by the charge density distribution and careful analyses are needed to better understand how the measured data may be related to the materials properties in the different layers. In this work, we examined the TiO_2-$SrTiO_3$ hetero-structure and the $SrTi_{0.8}Nb_{0.2}O_3$/$SrTiO_3$ multiple quantum well structure and developed analytical equations for the thermoelectric power S based on interface properties. Our observations suggest that for the samples under consideration there is little difference in the computed thermoelectric power S between the 2-dimensional and the 3-dimensional model as long as the charge density distribution is properly accounted for. Based on the data analyzed, there is convincing evidence that a 'metallic' model will better explain the reported data. In the case of the hetero-structure, extensive charge migration into the substrate appears to be the reason for the observed increase in the thermoelectric power.

2 Theory

The calculations of the average carrier density n_{avg} and the average thermoelectric power S_{avg} in inhomogeneous thermoelectric materials have previously been reported [6]. In essence, the average carrier density n_{avg} and the average thermoelectric power S_{avg} can be evaluated using a lumped circuit model consisting of thin thermoelectric layers of different carrier densities. Analytical expressions for instance have been derived even though some of the integrals cannot be expressed in simple form. For an n-type sample in 1-dimension:

$$n_{avg} = 1/t \int_0^t n(x) \, dx \qquad (1a)$$

$$S_{avg} = k/q \left[(B' - 1/(n_{avg}t) \int_0^t n(x) \ln(n(x)) \, dx) \right] \qquad (1b)$$

where t is the sample thickness, $n(x)$ is the charge density, k is the Boltzmann constant, q is the electron charge, and B' is a thermoelectric constant. In principle, Eqn.(1b) may be used to compute S_{avg} with any arbitrary distribution of the charge density provided that the profile is known.

Such an approach, however, will not be appropriate in the case of a hetero-structure with 'metallic' properties at the interface and complicated by potential

charge migration into the substrate. A more pragmatic approach is to compute S based on the sheet charge density n_S which can be readily measured. To generate a working model, we consider a rectangular sample under longitudinal thermal stress ΔT in the x-direction. The increase in charge flow due to the temperature difference results in a diffusion current density of the form: $J_D = q\ d(n_S D')/dx$, where q is the electron charge, n_S is the density of the charge sheet, D' is the diffusivity, and dx is incremental position. This will be balanced by a current density of the form: $J_T = n_S q\mu E'$, where μ is the charge mobility, and E' is the electric field due to the thermoelectric voltage ΔV_T. As a result, $d(D'n_S)dx$ = - $qE'(D'n_S)/kT$. Since dV_T = - $E'dx + \Delta(E_C - E_F)$ where $\Delta(E_C - E_F)$ is the positional variation of the Fermi level with respect to the energy band (see for example reference [7] p.248), it can be shown that:

$$S = k/q\ [\ln(N_C) - \ln(n_S) + (q' + 1) + p'] \qquad (2)$$

where N_C is the effective density of states (in 2 dimensions), q' is a scattering parameter and p' is a constant. Since $N_C = m^*kT/\pi h'^2$ and p' = 1, eqn.(2) leads to:

$$S' = \ln(m^*k/\pi h'^2) + \ln(T) - \ln(n_S) + (q' +2) \qquad (3)$$

where S' = qS/k, m^* is the density of states effective mass, and h' is the reduced Planck constant. For the TiO_2-$SrTiO_3$ hetero-structure, we assume q' = - 2.83 according to [8].

In 3 dimensions, $N_C = 2(2\pi m^*kT/h^2)^{3/2}$ and p = 3/2 where h is the Planck constant. In this case, we replace n_S by n_S/x_j, where x_j is the "effective" thickness of the charge sheet and this leads to:

$$S' = \ln(2) + 1.5\ \ln(2\pi m_0 k/h^2) + 1.5\ln(T) - \ln(n_S) + \ln(x_j) + (q' + 5/2) \qquad (4)$$

For the quantum well structure made up of $SrTiO_3$/$SrTiNbO_3$/$SrTiO_3$ layers for instance, q' = - 2.11 according to [9].

At high doping, the sample becomes 'metal-like' with the Fermi energy $\varepsilon_F = h'^2(3\pi^2n)^{2/3}/2m^*$. S is then given by:

$$S = (\pi k)^2(1 + r)T/(3q\varepsilon_F) \qquad (5)$$

where r is a scattering parameter normally equal to 2.

3   Results

We first examined the validity of the different models through simulations using eqns.(3), (4) and (5). Assuming a charge sheet of thickness 1 nm [10], we plotted in Fig.1 the computed thermoelectric power S as a function of the charge density. As expected, there was little difference between the 2-dimensional model and the 3-dimensional model at the low charge densities. These models however would not be valid at the higher charge densities when the Fermi statistics broke down. To cover this higher charge density range, we included in the figure the values of

S computed using the 'metallic' model of eqn.(5). When compared to the thermoelectric data taken from $Sr_{1-x}La_xTiO_3$ samples [11], our results clearly indicated that the 'metallic' model was more accurate in the higher charge density range.
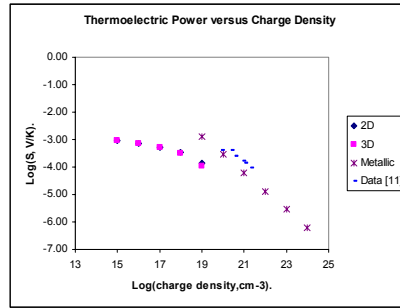

Figure 1: A plot of the computed thermoelectric power S as a function of the charge density.
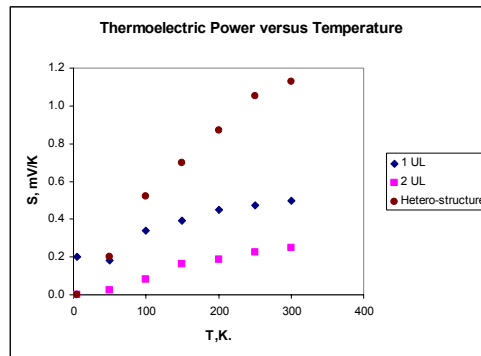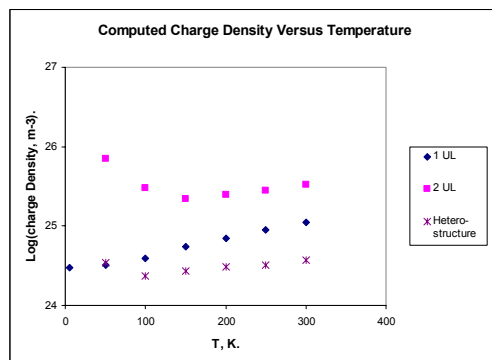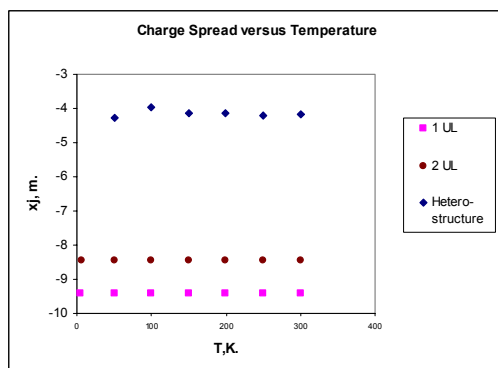

Figure 2: Measured values of S as a function of temperature for the quantum wells and the hetero-structure as reported in [12].

Our next task was to examine the thermoelectric power of quantum wells and hetero-structure as reported in [12]. These quantum wells were sandwiched structures consisting of alternating layers of $SrTi_{0.8}Nb_{0.2}O_3$ and $SrTiO_3$ in the ratio of 1 or 2 ULs (unit layers) of $SrTi_{0.8}Nb_{0.2}O_3$ for every 9 ULs of "intrinsic" $SrTiO_3$. The Sr dopant density was $\sim 2.4 \times 10^{27}$ m^{-3} and the atoms were reported to be fully ionized. For the quantum wells, our initial calculations of the charge density based on the reported values of S had suggested that the expected charge spread x_j ought to cover the entire $SrTiO_3$ (barrier) layers. Assuming this to be the case and the charge densities were essentially uniform in these thin charge layers, we used the values of S in Fig.2 to compute the charge density n as a function of temperature. The results are shown in Fig.3(a). As observed, the extent of charge build up increased with increasing temperature suggesting any

charge migration would be diffusion related. The computation of the charge density and charge spread in the TiO_2-$SrTiO_3$ hetero-structure was more straightforward as the $SrTiO_3$ thickness had been known to be 0.5 mm (and this ought to be much larger than x_j). In addition, the sheet resistivity was also available. Using these data together with the known estimates of the mobility values reported in [9], we computed the sheet charge density (from the sheet resistivity data) as well as the "composite" charge densities (computed from the values of S). The ratio of these values would be the estimated charge spread. The results are shown in Fig.3(b).

(a)

(b)

Figure 3:   Computed values of (a) charge density and (b) charge spread as a function of temperature in the quantum wells and the hetero-structure as a function of temperature.

As observed, there was major charge spread into the neighbouring layers for all of the samples. For the quantum well sample with 2 ULs and the hetero-

structure sample, there was a dip in the charge density between 100K and 200K. We were unsure if this dip could be due to the "phonon drag" effect commonly observed in samples within this temperature range, or possibly charge re-distribution at the lower temperature. In Fig.3b, we showed the charge spread for the hetero-structure at different temperatures (also shown in the figure are the thickness values of 1 UL and 9 ULs). Charge spread in the hetero-structure was rather intriguing as it extended for tens of microns over a broad temperature range. If this observation turned out to be genuine, then the enhancement in the measured thermoelectric power as reported in [12] could well be explained by such charge spread. The actual spatial re-distribution of charge in the hetero-structure would be of significant interest and had been investigated separately [13].

4   Conclusions

In this work, we have found that the thermoelectric power data reported in [11] for highly doped $SrLaTiO_3$ samples can be best explained using an equation (eqn.(5)) applicable to metals. Such a finding encouraged us to use the same equation to analyze the thermoelectric power data in quantum wells and hetero-structure as reported in [12]. Our results suggested that for the quantum well samples, there was charge migration from the quantum wells into the neighbouring (barrier) layers resulting in thermoelectric power higher than the case when charge spread was absent. The extent of charge spread was immense in the hetero-structure which could reach a depth of tens of microns. In our opinion, this might be the reason for the observed "giant" thermoelectric power found in the TiO_2-$SrTiO_3$ hetero-structure reported in [12].

Acknowledgement

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