Research on Thermal Diodes for Thermal to Electric Conversion

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None

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Introduction

Some years ago we pursued research aimed at demonstrating a solid state analog of a vacuum thermionic converter in which electrons were to boil off of a heated emitter layer, diffuse across a wide solid gap region, and then be collected by a metal contact on the cold side. In the course of this work, we found that the conversion efficiency was very high – much higher than expected, and also much higher than could be accounted for by any solid state thermionic effects. For example, it appeared that the addition of an emitter layer (implemented by simply doping with donors) of thickness one micron, to a near intrinsic bulk thermoelectric semiconductor layer of thickness one millimeter, led to an increase of the efficiency of the bulk layer by factors on the order of 5-8 (in the case of InSb and HgCdTe devices).

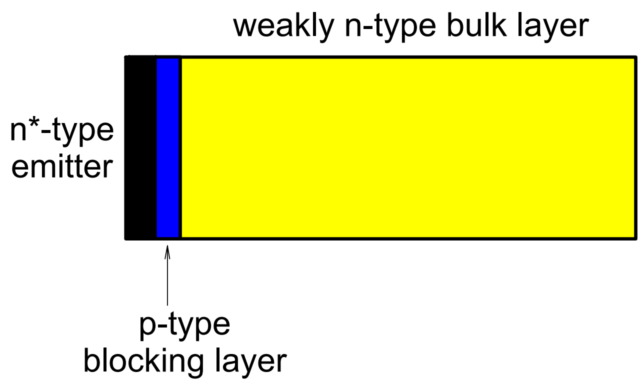

Figure 1: Schematic of an n*pn-type thermal diode.

Our research effort then focused on trying to identify what mechanism was responsible for the new effect. On the experimental side, the enhancement did not have good reproducibility, which indicated that we were missing some important parameter that was not being controlled. On the theoretical side, there was initially no guidance as to how to proceed, since no one had reported such an effect previously, and models found in the literature indicated that no enhancements were expected in the parameter regime we were operating. It seemed to us that we were seeing effects due to nonequilibrium distributions, since our barriers were on a spatial scale commensurate with the scattering length of the high mobility carriers (electrons in these semiconductors). We developed simple barrier models in which the forward current from the emitter into the junction was not balanced (due to thermoelectric effects) by the return current. Such models produced predictions of the short circuit current density which were in reasonably good agreement with the experimental results for devices showing the effect. However, this model was criticized by our colleagues since there seemed to be no way to develop a voltage drop corresponding to experimental observations of the open-circuit voltage enhancement. Any such voltage drop would be shorted out by the high conductivity of the junctions. In response to this, we proposed that a p-type blocking layer could isolate the near-intrinsic solid gap region from the n-type emitter, and thus allow the development of an open-circuit voltage drop. This is illustrated in Figure 1.

Nonlocal transport model

We developed a nonlocal transport model to help analyze this problem. We begin with a time-independent transport equation in the relaxation time approximation, where the band structure is modeled in a reduced Kane model. A formal solution is developed of the form often found in radiation transport problems, except with curved particle trajectories. From the formal solution, we can develop an expression for the electron current density

$$\mathbf{J}(z) = -q\left\langle \mathbf{v} \int d\tau\, e^{-\tau} \left[S_{-}\Theta(k_z) + S_{+}\Theta(-k_z) \right] \right\rangle$$

where τ is the optical depth, where S_+ and S_- are source functions for the electrons in the forward and reverse spatial directions, and where $\Theta(k)$ is unity for positive argument and zero otherwise. The expectation value is taken over all electron momentum vectors at position *z*. In this model, we take the source function to be the Fermi-Dirac distribution function

$$S(z) = \frac{1}{e^{\left[\varepsilon-\varepsilon_F(z)\right]/kT(z)}+1}$$

This model is interesting for a number of reasons. It provides a relatively convenient approximate description of the carrier distribution and associated current density in the case where the distribution need not be close to equilibrium, in terms of an integral (rather from the solution of a transport equation, which is much more complicated). The use of the Fermi-Dirac function for the source function allows us to work with temperatures and Fermi levels in a nonequlibrium problem.

Solutions

To investigate the open-circuit voltage drop, we have developed numerical solutions to the zero-current condition

$$\mathbf{J}(z) = 0$$

where the Fermi level is solved for, given a gradient in temperature and a nonuniform doping profile. Even though this appears to be a straightforward problem, the current is quite nonlinear in the Fermi level, and the associated numerical problem is highly nontrivial. We have applied a brute force method in which small corrections to the Fermi level are optimized to produce the lowest residual repeatedly. It has proven possible to obtain converged solutions, but it takes about a day to do so for a single solution on a 2.5 GHz PC.

We illustrate a smoothed solution for the Fermi level in terms of the effective thermopower (the change in Fermi level per unit change in temperature) in Figure 2. For this calculation we have chosen a symmetric supergaussian electrostatic potential distribution, with an electron concentration of 1.25×10^{18} cm^{-3} away from the barrier, and a hole concentration of 2.44×10^{18} cm^{-3} at the peak of the barrier. The calculation is based on a linear temperature profile that is 300 K at the origin, and with a slope of 10 K per mm around the origin. The thermoelectric result is obtained from an accurate one-dimensional integration over radial k, which can be compared with the equivalent three-dimensional integration obtained from the model. For the effective thermopower from the nonlocal problem, iterations were carried out to reduce the residual under a constraint imposed on the basis functions that the solution be smooth.

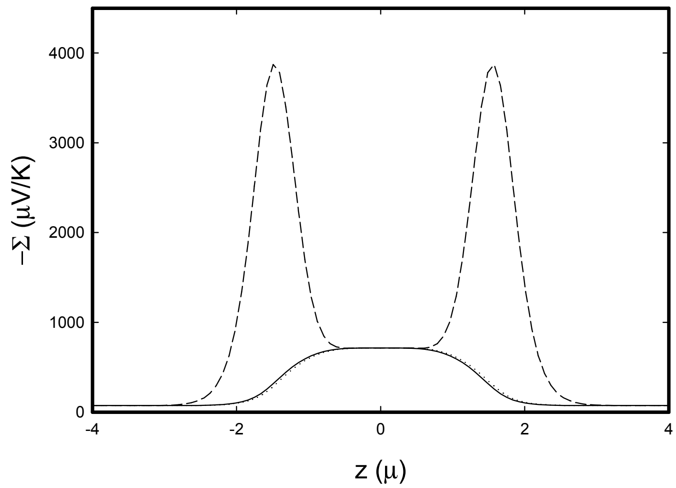

Figure 2: Effective thermopower in the case of a symmetric supergaussian potential distribution. Solid line: thermoelectric response. Dotted line: thermoelectric response evaluated in the model. Dashed line: nonlocal calculation.

One can see that the effective thermopower is symmetric, which is interesting, and may be similar to the lowest-order field correction to the conductivity (Gunn effect) which depends on $|\boldsymbol{E}|^2$. One sees that there is a large enhancement in the effective thermopower correlated with gradients in the doping. Our calculations appear to be the first theoretical prediction of such an enhancement. In essence, the effective thermopower is enhanced by the doping gradient in this calculation by about a factor of 10 over the local thermoelectric value, and by a factor of about 50 over the bulk thermoelectric value. To account for the experimental results, one would require an enhancement in the range of 300-1000.

Similar calculations carried out for problems with stronger doping gradients, and higher spatial resolution show ripples in the solution. An example of this is shown in Figure 3. That such a ripple should be expected in the numerical solution is clear, since the algorithm used is equivalent to a multipoint discretization of a low-order derivative using lots of spatial grid points. We have found that the total jump in Fermi level is relatively insensitive to the precise shape; hence, we can compute meaningful open-circuit voltages even when a ripple is present.

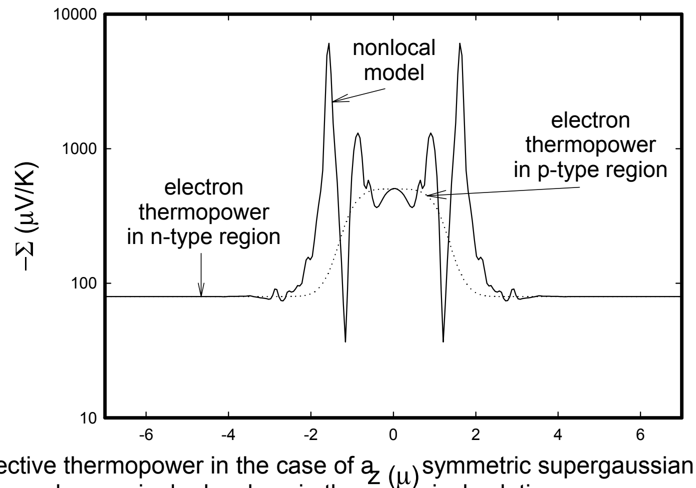

Figure 3: Effective thermopower in the case of a symmetric supergaussian potential distribution, under conditions where a ripple develops in the numerical solution.

The results of such calculations are interesting relative to the experimental results. In the case that the temperature is close to room temperature, the scattering length is long, and the model results for the open-circuit voltage are similar to the values measured experimentally. At higher temperature, the scattering length is much reduced. Models with a moderate gradient scale length show significant reduction in the open-circuit voltage with increasing temperature as shown in Figure 4. Yet the experimental results show that the enhancement increases with increasing temperature. This implies that either the relevant spatial scale is much smaller (which makes it more difficult to achieve a large enhancement of the open-circuit voltage), or else that other physics is involved. From the models that we have analyzed to date, it is our belief that there must be present an enhancement of the thermal gradient in the vicinity of the junctions, which would produce an enhancement of the open-circuit voltage even in the case of moderate junction scale lengths.

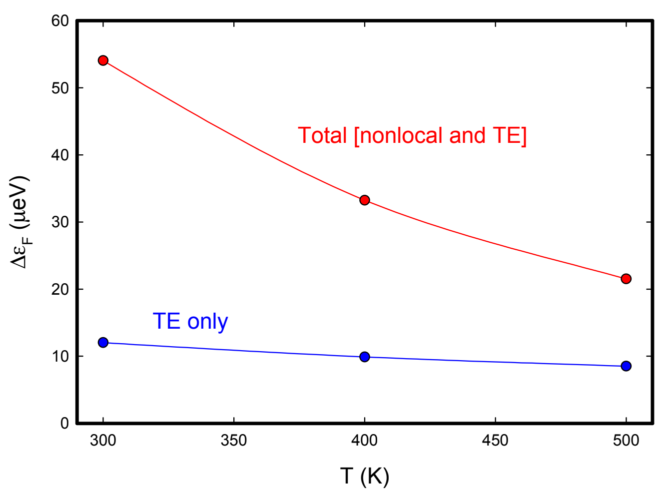

Figure 4: Reduction of nonlocal enhancement as a function of junction temperature for a smoothed triangular electrostatic potential profile (with small thermal gradient) due to a reduction of the scattering length.

Optimization of the barrier layer

Experiments were carried out in which p-type blocking layers were implemented, separating an n-type InGa eutectic emitter region from a weakly n-type bulk InSb. The doping profile is shown in Figure 5. Enhancements of both the open-circuit voltage and short-circuit current were observed. Experiments were done to optimize the barrier in terms of barrier width, and doping concentration. Optima were found in both width and doping concentration. The enhanced efficiency relative to the thermoelectric efficiency of the bulk is shown in Figure 6. One sees that at low concentration, the blocking layer is not strong enough to prevent a shorting out of the open-circuit voltage. At high concentration, the blocking layer inhibits current flow. These effects produce an optimum at a peak acceptor concentration near 7×10^{19} cm^{-3}. This effect is mirrored in the numerical calculations, where the open-circuit voltage is found to increase with increasing acceptor concentration for a model doping concentration in Figure 7. Devices constructed in this way now show reproducible enhancements from device to device.

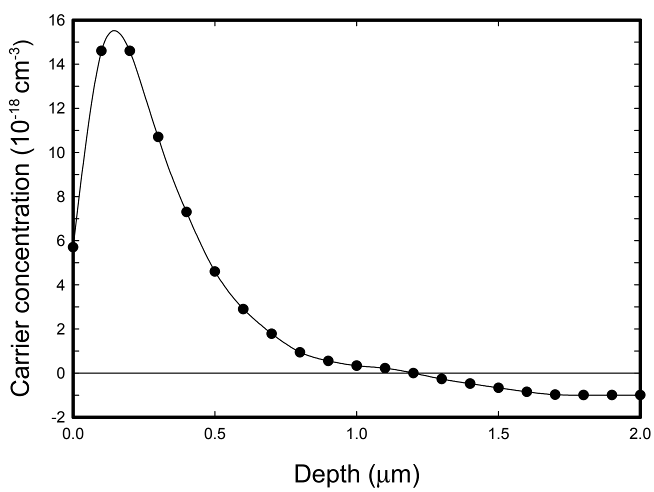

Figure 5: Barrier profile. Plotted is the carrier concentration as acceptor concentration minus donor concentration as a function of distance from the InGa emitter.

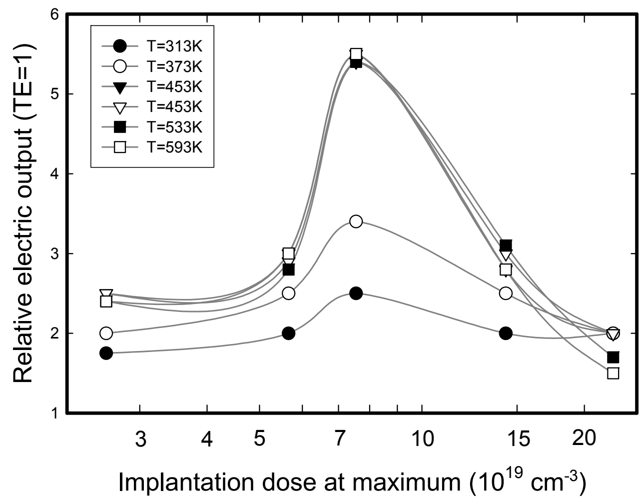

Figure 6: Efficiency relative to thermoelectric performance for InSb thermal diodes as a function of peak barrier hole concentration for the doping profile shown in Figure 5.

Discussion

Enhancements in the efficiency of thermoelectric semiconductors using thermal diode n*pn structures have been demonstrated in InSb, HgCdTe, PbTe, and in other materials as well. Theoretical and experimental studies have provided clarification that a blocking layer is required between the emitter and solid gap regions, and the reproducibility has been greatly improved. The nonlocal current model has been shown to produce significant enhancements of the effective thermopower, and in the case of InSb predictions of the open-circuit voltage enhancement near room temperature appear to be close to the experimental results. At higher temperature, the agreement is not as good, and other effects must be present which have not yet been included in the models. We expect that more sophisticated models will show an enhancement in the thermal gradient. Gang Chen has recently argued that a drop in the electron temperature is expected going from a thin p-type region into an n-type region under conditions where the electrons are not equilibrated with the lattice, due to the reduced heat flow of electrons as minority carriers. We hope to examine this and other modifications of the thermal profile in future work.

References

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