Quantum Contributions and Violations of the Classical Law of Mass Action

H. L. GRUBIN^a and T. R. GOVINDAN^b

^aScientific Research Associates, Inc., Glastonbury, Connecticut

^bApplied Research Laboratory, State College, Pennsylvania

The law of mass action refers to the product of concentration of reactants, which for a particular material is a function only of temperature. For non-degenerate semiconductors the law of mass action is represented by the product $NP = N_C N_V \exp(-E_G/k_B T)$. Through solutions to the quantum Liouville equation, it is determined that the law of mass action is generally invalid.

INTRODUCTION

Classically, for a specific material, non-degenerate statistics and equilibrium, the electron density, $N = N_C \exp[-(E_C - E_F)/k_B T]$, and hole density, $P = N_V \exp[-(E_F - E_V)/k_B T]$, yield, a temperature dependent classical law of mass action^{1,2}: $NP = N_C N_V \exp(-E_G/k_B T)$.

Quantum mechanically, it is known, Wigner³, that modifications to the classical density-potential energy relation arise from gradients in charge density, which represent quantum mechanical attractive and repulsive forces. In particular, this relation may be expressed as^{4,5}:

$$(1) \quad N = N_C \exp[-(E_C(\mathbf{x}) - E_F) + (\hbar^2/6m)(1/\sqrt{N})\nabla^2 \sqrt{N}/k_B T]$$

and strong departures from the classical mass action law occur when the density curvature (along with a similar expression for holes) is of the order of: $1/(\nabla^2 \sqrt{N})/\sqrt{N} \approx (6m^2)(E_C(\mathbf{x}) - E_F)$.

Modification of the Law of Mass Action- Approximate and Numerical Aspects

Approximate analyses, via the quantum-corrected hydrodynamic equations (QHD)^{5,6,7,8}, for non-uni-

form electric fields, yields a quantum corrected law of mass action:

$$NP = N_C N_V \exp - \beta \left[E_G + \frac{\partial^2 E_C}{\partial x^2} \left(\frac{\lambda_e^2 - \lambda_h^2}{6} \right) - \left(\frac{\beta}{2} \right) \left(\frac{\partial E_C}{\partial x} \right)^2 (\lambda_e^2 + \lambda_h^2) \right] \quad (2)$$

which with some manipulation can be placed in the form of density curvatures, as in equation (1). Equation (2), consistent with equation (1), demonstrates that departures from the classical relation are determined primarily by the *form*, rather than the magnitude, of the potential energy. In equation (2), the thermal deBroglie wavelengths of electrons, $\lambda_e^2 = \hbar^2/2m_e k_B T$, and holes, $\lambda_h^2 = \hbar^2/2m_h k_B T$ have been introduced. Equation (2) indicates that for a PN junction, where the potential energy varies monotonically and where the sign of the curvature is different at the boundaries of the junction region, there will be differences in the shape of the spatial dependence of the NP product.

Numerical results, showing the violation of the classical mass action law are obtained from the quan-

FIGURE 1 NP product and input conduction band energy. This calculation is performed for a background donor concentration of $10^{24}/\text{m}^3$; the acceptor concentration was zero. The potential undergoes an abrupt change at the 50 nm point

tum Liouville equation, $i\hbar d\rho_{op}(t)/dt = [H, \rho_{op}(t)]$, in the coordinate representation⁹:

$$\begin{aligned} & \left(\frac{\hbar^2}{2m_e}\right)\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x'^2}\right)\rho_e - \\ & (E_C(x) - E_C(x'))\rho_e = 0 \text{ (electrons)} \\ & \left(\frac{\hbar^2}{2m_h}\right)\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial x'^2}\right)\rho_h \\ & + (E_V(x) - E_V(x'))\rho_h = 0 \text{ (holes)} \end{aligned} \quad (3)$$

The solutions to equation (3) are obtained for Boltzmann-like boundary conditions:

$$\begin{aligned} \rho_e(x, x') &= N_C \exp - \\ & [\beta(E_C - E_F) + (x - x')^2/4\lambda_e^2] \text{ (electrons)} \\ \rho_h(x, x') &= N_V \exp - \\ & [\beta(E_F - E_V) + (x - x')^2/4\lambda_h^2] \text{ (holes)} \end{aligned} \quad (4)$$

which for uniform fields solutions are consistent with the classical law of mass action.

Numerical Results: Non-Self Consistent Calculations

We illustrate the departure from the classical law of mass action with *non-self-consistent* solutions to equation (3) for the situation where the conduction

and valence bands are subject to identical changes in potential energy. The parameters chosen for the simulation were taken to maximize the accuracy of the *numerical* calculation. The simulation region was 100nm, and the density matrix was solved on a uniform 1000×1000 grid. The simulations were performed for a band-gap of 1eV, an electron effective mass of 0.067m, and holes with the same effective mass.

Figure 1 displays results for a 400 meV step change in potential energy. According to equation (2) this should lead to an increase in the NP product over the classical result. This is illustrated in figure (1) through solutions to the quantum Liouville equation. Any departure from a constant value of NP represents a violation of the classical law of mass action; and from figure 1, this departure is approximately four orders of magnitude. Since it may be argued that in a PN junction calculation the density gradients are such that it is unlikely that the potential energy will vary over an interval as small as that represented by figure 1, weaker slope calculations were also considered.

Increasing the region over which the potential energy undergoes a 400 meV change results in a shallower slope. The deviation from the classical law of

FIGURE 2 As in figure 1 but with a different potential energy. The NP product is on a linear scale. The peak value of the NP is significantly lower than that of figure 1 (The field is 200 keV/cm.)

FIGURE 3 As in figure 2, with similar slope, but with the beginning and end points extended. The NP product, shown on a linear scale, has a peak value within the interior that is approximately the same as that of figure 2, but extends over a larger region

mass action as indicated by equation (2), is smaller. This is displayed in figure 2 where the potential energy changes value over a region of 20nm.

The change in magnitude of the potential energy is only one contribution to the alteration of the classical law of mass action, and perhaps a weak contribution. The quantum corrected mass action law represented approximately by equation (2) indicates that the shape of the spatial dependence of the potential energy is the determining factor in the departure of the law of mass action from equation (1). As seen in figure 3, keeping the slope of the potential energy fixed, but extending it over a larger region, such that the maximum value of the potential energy increases to 500 meV has the primary effect of extending the region for the departure from the law of mass action. It appears that that magnitude of the departure is relatively unaltered.

CONCLUSIONS

Simple examples using the quantum Liouville equation in the coordinate representation, subject to the imposition of Boltzmann statistics, points to the fact that the law of mass action does not generally apply. The departure will be greatest in those materials having small effective mass. This result clearly has implications for the design of bipolar and heterostructure

bipolar transistors in that the densities expected within specific regions are likely to depart from classical expectations when the critical region is small enough in scale. The consequences of this for design of devices remains to be examined. Self-consistent calculations have also been performed, and for parameters appropriate to GaAs, with results that are consistent with the above discussion¹⁰.

Acknowledgements

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