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Properties of solid state devices with mobile ionic defects. Part I: The effects of motion, space charge and contact potential in metal|semiconductor|metal devices

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Abstract

The characteristics of solid state devices based on p-type semiconductors with mobile acceptors are discussed. The devices are basic ones of the form: metal|semiconductor|metal. The metal electrodes are assumed to be chemically inert and to block material exchange. The effect of the contact potentials as well as of the space charge are taken into consideration. The distribution of charge carriers (holes and acceptors) and the I–V relations are evaluated. These results are compared with those of a model in which the acceptors are immobile and with two approximations in which neutrality is assumed either at the boundary or throughout the whole semiconductor. The motion of the acceptors is found, in some cases, to introduce only minor changes in the I–V relations. This finding may be of significance for solid state devices of reduced scale. The I–V relations of samples much thicker than the equilibrium Debye length reduce to the ones obtained assuming local neutrality throughout the sample. The results also depend significantly on the reaction constant between the acceptors and holes to form neutral acceptors.

Keywords: Solid state device; Semiconductor; Mixed ionic electronic conductor; MIEC; I–V relations; Defect distribution

1. Introduction

We discuss solid state devices based on p-type semiconductors with mobile acceptors. Semiconductors that also conduct ions are denoted as mixed-ionic-electronic-conductors (MIECs). MIECs have appeared in solid state devices in the past. For example, Cu|Cu_2O|Pb cells were reported to have rectifying properties by Grondahl and Geiger as early as 1927 [1]. Cu_2O is known [2,3] to conduct copper ions as well as holes. The tarnishing of Cu, which occurs even at room temperature, is an example of such an ionic motion. Cu_2O was reported to show a special type of I–V relations due to such motion [4–7]. In modern solid state devices ionic conduction plays an important role. The doping process involves ionic motion, which takes place at elevated temperatures. The aging process of solid state devices, at room temperature, is a direct result of ionic motion. MIECs also play an important role as electrodes in fuel-cells.

Usually, a poor ionic conductivity can be neglected in large scale solid state devices. However, in nanometric scale devices this ionic conduction may become significant. Such a motion may result in new I–V relations under a slowly varying applied voltage [7]. The small size has two effects. First, the distance that the ions have to move in order to significantly alter their concentration is small. Second, the gradients in the electrochemical potentials are high since the potential differences have a typical value of 0.1–1 V but they appear over a distance which is drastically reduced. The gradient in the ion electrochemical potential is the driving force for the ionic motion.

Although it is relevant to many fields, the full properties of a simple device consisting of an MIEC placed between two electrodes, were never completely evaluated. Only limited solutions were given. Riess et al. gave an explicit analytic solution for MIECs assuming local neutrality (L.N.) for various cases [7–10]. Riess and Tannhauser [11] solved analytically the I–V relations for a van-der Pauw configuration under the approximation of small perturbation. Under the same

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approximation of small perturbations, Jamnik and Maier solved numerically an MIEC model considering the space charge explicitly [12,13]. Meyer et al. [14] solved numerically for an MIEC between two ion blocking electrodes. Being interested in the leakage current in thin films of $Ba_{0.3}Sr_{0.7}TiO_3$, the calculation goes along a different route with respect to the defect model, boundary conditions and length variations.

It is the purpose of this paper to go beyond the local neutrality approximation as well as the small perturbation one and to examine the significance of both space charge and boundary conditions in determining the I–V relations and the defects distribution in a device based on an MIEC. This is the first paper in a series which will discuss the I–V relations in devices based on an MIEC between two electrodes. The, relatively simple, device discussed here contains two metal/semiconductor interfaces and the semiconductor (MIEC) bulk. Thus it contains the key ingredients of a solid state device. In order to be able to cope with the complexity of the equations, the calculations are done numerically using the Chebyshev collocation method.

1.1. Model considered

The following model is considered in this paper:

a) The MIEC is a semiconductor with a large energy band gap. One type of electronic charge carrier (holes) predominates, and the concentration of the minority carriers (electrons) is negligible under all voltage conditions examined.
b) The ionic charges are of one kind (acceptors) and the ions are mobile.
c) The boundary conditions with respect to ions are such that material exchange with the surrounding is blocked. Under the conditions here this means that, in the steady state, the electrodes block the ionic current in the bulk. (See Section 1.2.2). In order to realize this we have in mind inert, metallic electrodes.
d) The concentration of holes at the boundaries, under equilibrium are dictated by the work function of the metal that, under contact, is also imposed on the MIEC outer monolayer. This concentration is, in general, different from the one in the MIEC when not in contact with the metal. The change can be calculated from the difference in the work functions of the metal and the MIEC before they come in contact. We here use the term "contact potential" in a narrow sense, as the difference in the work functions. It thus obtains a fixed value. It is not the more common definition of contact potential which refers to the potential difference over the space charge region in the semiconductor, and changes with current. The general definition coincides under zero current with the present one.
The holes at each boundary between the MIEC and a metallic electrode are assumed to be very close to equilibrium also under current. This means that the concentrations of the holes at the MIEC boundaries (interface monolayers) are pinned (see Section 1.2.2). We shall discuss both symmetric contacts, i.e. equal contact potentials at the two boundaries of the MIEC, starting with two zero contact potentials, as well as asymmetric ones with one finite and one zero contact potential.
e) We further neglect: any density of surface states, the last monolayer ("core" monolayer) which may have different standard chemical potentials, and the image force.
f) A steady state is assumed.
g) The geometry is assumed to be one dimensional.

The exact (numeric) results for the present model are compared with three approximations applied to the same device: a) assuming that the acceptors are immobile. This model is equivalent to that based on a "classical semiconductor", with minority carrier neglected; b) assuming that local neutrality prevails throughout the whole MIEC. This approximation allows neither a space charge in the bulk nor pinning of the hole concentration at the boundaries; c) assuming that local neutrality prevails at the boundaries only. This allows a space charge in the bulk but no pinning of the hole concentration at the boundaries.

The approximation with immobile acceptors yields a trivial solution when both contact potentials vanish. The hole concentration is then uniform and the I–V relations are linear. The I–V relations are not linear when the contact potential does not vanish. In particular when a depletion region in the hole concentration is formed inside the MIEC near the MIEC/electrode interface, a junction is formed at the interface. This junction is of the Schottky type with diffusing holes contributing to the current and the image force being neglected [15,16].

The local neutrality approximation is considered for two purposes. First, by assuming local neutrality *throughout the whole sample* it is possible to calculate analytically an approximate relation between V, the voltage drop across the sample, and I, the current through the sample. Second, it is used to calculate, analytically, the gradient dp/dx in the hole concentration for those regions of the samples in which local neutrality approximately holds (see Eq. (A.3)).

A necessary condition for local neutrality to hold, approximately, throughout the whole MIEC, was shown to be a low voltage [17],

$$0 \leq \beta q V << \frac{4}{3} \ln\left[L/\sqrt{2}\lambda_D\right] \tag{1}$$

where $\beta = 1/k_B T$ with T being the temperature, k_B the Boltzmann constant, q the elementary charge, L the length of the sample (thickness of the layer) and $\lambda_D = \sqrt{\varepsilon/\beta q^2 p_{eq}}$ is the equilibrium Debye length, with ε the dielectric constant and p_{eq} the hole concentration under equilibrium conditions (i.e. $V = J = 0$ where J is the current density) and zero contact potentials (i.e. uniform distribution of the acceptors). In this paper layers are considered to be thin when $L \leq \lambda_D$. For $L \sim 10\lambda_D$ the voltage that is allowed by Eq. (1) is rather low ($V < 3k_B T/q$). Furthermore, for thin layers, with $L < \sqrt{2}\lambda_D$, Eq. (1) has no solution, i.e. the local neutrality approximation cannot be applied to the whole sample. (Neutrality may still hold locally, in part of the sample).

In order to understand the impact of local neutrality on the current density equations we call upon the concept of quasi local neutrality [17]. This means that the difference between the