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ELECTROLYSIS THROUGH HOMOGENEOUS AND HETEROGENEOUS CONTACTS IN INSULATING SOLIDS

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The basic measurement of the primary state of ionization related to the formation of a non-rectifying contact by the electrolysis of insulating solids under homogeneous and heterogeneous contacts has been carried out. The activation energy involved in the first stage has been found to correlate with the band scheme of energy of contact which is necessary for creating the defect centres towards space charge limited injection.

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1. Introduction

The energy diagram for the injection [1] of electrons into a crystalline insulating solid is understood through the system of heterogeneous metal-insulator contact geometry [2]. The high amount of electrons generated from the metal into the conduction band [1] or to intermediate metastable band into the insulator needs the contact of the type as mentioned. The essential requirement in the first stage of electrolysis [3] is to form an ohmic contact [2,4], i.e., a non-rectifying contact. To activate the process of injection, it is necessary that the ionization [5] be set to form the appropriate contacts. The present paper deals with the mechanism of primary ionization stage with the geometries of homogeneous and heterogeneous metal insulator-metal contacts [2,6,7] and with the comparison of the results, with the aim to evaluate some physical parameters relevant for obtaining the appropriate signature before electrons are injected into the insulating solid.

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2. *Experimental*

Pure NaCl (E-mark powder 99.99%) and impurity doped $NaCl:Ba^{2+}$ (0.006 M%), $NaCl:Mg^{2+}$ (0.001 M%), $NaCl:Al^{3+}$ (0.001 M%) and $NaCl:Cd^{2+}$ (0.001 M%) single crystals were grown in the laboratory by the Czochralski-Kyropolous method, using a microprocessor-controlled furnace and servo-controlled rotation pulling arrangement. Crystals were cleaved along the <100> direction and surface polished. A specimen so prepared was placed between two flat electrodes, one made of brass and the other of platinum. The system was housed in an electrical furnace. The injection experiment was carried out at different temperatures under constant fields of 415 $\mathrm{V\,cm^{-1}}$ or 600 $\mathrm{V\,cm^{-1}}$. In a separate experiment, the injection process was carried out under similar conditions as in the first arrangement with a specimen mounted between a pointed brass cathode and a flat platinum anode. The process was stopped before the onset of the second zone electron injection [8,9]. The measurements were repeated for all specimens. The current was measured with a Bausch and Lomb series 5000 strip-chart recorder.

3. *Results and discussion*

The current growth curves (Figs. 1 and 2) for single and doped crystals indicate the effect of temperature for particular fields of 415 $\mathrm{V\,cm^{-1}}$ and 600 $\mathrm{V\,cm^{-1}}$.

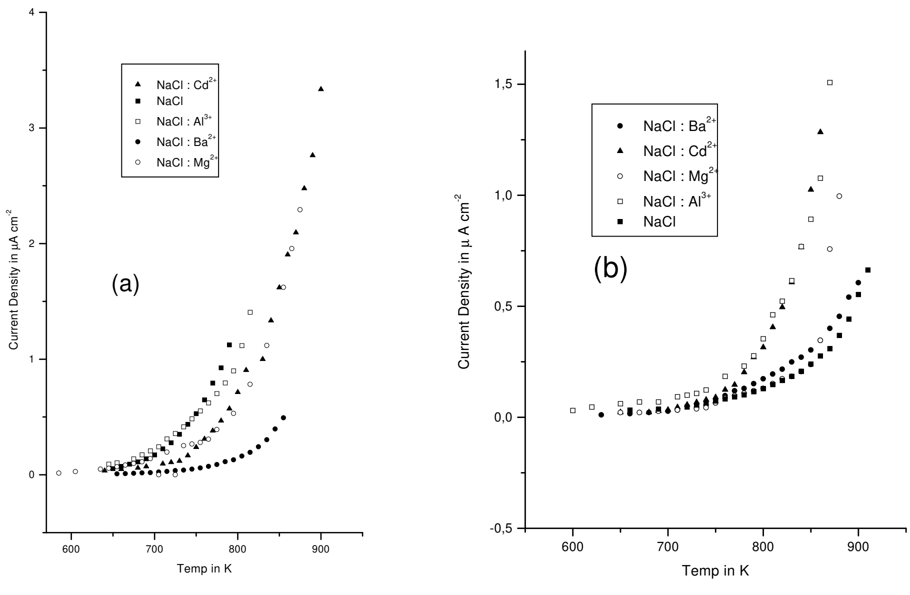

Fig. 1. Current density against temperature for pure NaCl, $NaCl:Ba^{2+}$, $NaCl:Mg^{2+}$, $NaCl:Cd^{2+}$ *and* $NaCl:Al^{3+}$ *at a constant field of a) 415* $\mathrm{Vcm^{-1}}$, *b) 600* $\mathrm{Vcm^{-1}}$ *for homogeneous contacts.*

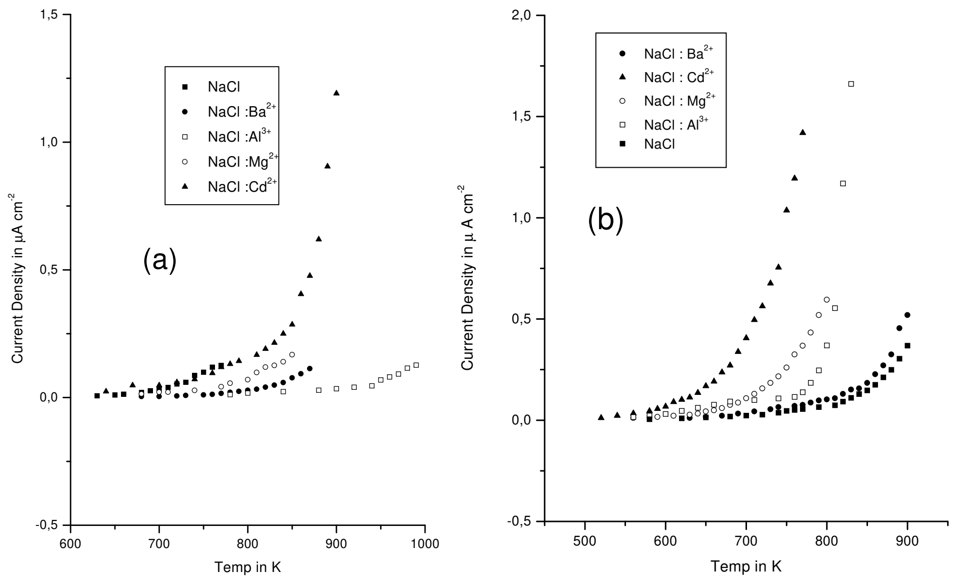

Fig. 2. Current density against temperature for pure NaCl, NaCl : Ba^{2+}, NaCl : Mg^{2+}, NaCl : Cd^{2+} *and* NaCl : Al^{3+} *at a constant field of a) 415* Vcm^{-1}, *b) 600* Vcm^{-1} *for heterogeneous contacts.*

From the theoretical approach [6,10,11], the ionic current density does not depend on the shape of electrodes and is given by

$$J = (e\mu E n_c)\exp(-W_0/kT)\,, \tag{1}$$

where E is the electric field, μ the mobility, n_c the effective density of states of electrons in the conduction band, W_0 the activation energy for ionization, k the Boltzmann constant and T the temperature.

Activation energy [11,12] for ionization has been calculated from $\ln J$ vs. $1/kT$ plot (not shown) for both fields of 415 $\mathrm{V\,cm^{-1}}$ and 600 $\mathrm{V\,cm^{-1}}$. The results for the investigated specimens are shown in Table 1. It is clear from the table that values of W_0 for heterogeneous electrodes are less than those for homogeneous electrodes. These expected results indicate the non-uniformity of fields in the case of the pointed cathode.

So far as the band scheme is concerned, thermodynamical equilibrium demands the Fermi energy to have the same value everywhere in a homogeneous system. If the two systems of particles are brought into contact at a temperature T, the equilibrium will be established and thereby the free energy of the whole system attains a minimum value. The contact geometry can be basically explained on the principle of obtaining Galvani voltage [5] in the case of a metal – insulator and insulator – metal contact.

TABLE 1. Ionic-conductivity activation energies of pure NaCl, $NaCl:Ba^{2+}$, $NaCl:Mg^{2+}$, $NaCl:Al^{3+}$ *and* $NaCl:Cd^{2+}$ *at constant fields of a) 415* Vcm^{-1} *b) 600* Vcm^{-1}*, for homogeneous and heterogeneous contacts.*

	Activation energy (eV)			
Sample	Homogeneous electrodes		Heterogeneous electrodes	
	Field 415 Vcm^{-1}	Field 600 Vcm^{-1}	Field 415 Vcm^{-1}	Field 600 Vcm^{-1}
Pure NaCl	0.963	0.648	0.928	0.594
$NaCl:Ba^{2+}$	0.966	0.775	0.952	0.630
$NaCl:Mg^{2+}$	0.768	0.772	0.730	0.692
$NaCl:Al^{3+}$	0.774	0.624	0.702	0.535
$NaCl:Cd^{2+}$	0.942	1.033	0.677	0.640

The contact or Volta potential [5] will obviously be equal to the difference of the work functions of the contacting materials as given by

$$|V_c| = \frac{1}{e}|W_1 - W_2|\,. \tag{2}$$

To make it clear, consider in the first step a metal – metal contact. Later this can be modified to the case of a metal – insulator or insulator – metal contact situation by neglecting the temperature dependence of the Fermi energy, with the simplifying assumption that the metals (1 and 2) be at the same temperature T and also that $W_1 < W_2$. When such two metals are brought from infinity to a small mutual distance, an exchange of electrons will set in simply because the thermoionic emission exists at $T > 0$ K. Since $W_1 < W_2$, more electrons will initially cross from metal-1 to metal-2, resulting in an excess of negative carriers on metal-2. As a result, an electric field builts up, causing the formation of a potential difference between the two metals. The potential difference is established at such a value that the net current between the two metals vanishes. It reaches the value V_c of the contact potential in thermodynamic equilibrium. If ξ_1 and ξ_2 are the Fermi energies of metal-1 and metal-2 while in contact and ξ_1' and ξ_2' those before contact, we can write

$$(\xi_1' - \xi_1) + (\xi_2 - \xi_2') = eV_c\,, \tag{3}$$

because of the equipotential behaviour in a metal and because the energies of electrons in metal-1 and metal-2 are reduced by $(\xi_1' - \xi_1)$ and increased by $(\xi_2 - \xi_2')$, respectively. Zero of the energy scale before contact lies below the vacuum potential by an amount of

$$(\xi_1' - W_1) = (\xi_2' - W_2) \quad \text{or} \quad (\xi_1' - \xi_2') = W_2 - W_1\,. \tag{4}$$

The free energy of the total system is given by

$$F = F_1 + F_2 \,.$$

The condition of minimum free energy, $(\delta F)_{T,V,N} = 0$ now reads

$$\delta F = \left.\frac{\delta F_1}{\delta N_1}\right|_{T,V_1} \mathrm{d}N_1 + \left.\frac{\delta F_2}{\delta N_2}\right|_{T,V_2} \mathrm{d}N_2 = 0 \,, \tag{5}$$

where volumes V_1 and V_2 contain N_1 and N_2 particles before contact at temperature T.

With the additional condition

$$N_1 + N_2 = N(constant) \,, \tag{6}$$

Eq. (5) reduces to

$$\left.\frac{\delta F_1}{\delta N_1}\right|_{T,V_1} = \left.\frac{\delta F_2}{\delta N_2}\right|_{T,V_2} = \left.\frac{\delta F}{\delta N}\right|_{T,V}$$

So,

$$\xi_1 = \xi_2 = \xi \,. \tag{7}$$

Equations (3), (4) and (7) yield

$$W_2 - W_1 = eV_c \,. \tag{8}$$

It may be inferred that the band diagrams of the initially separated metals are mutually displaced by eV_c when the contact has been formed. It is a common practice to assume the band scheme of one of the contact materials to be the fixed one ($\xi_1' = \xi_1$), so that scheme for the other material is shifted by the full amount of the contact potential i.e. $\xi_2 - \xi_2' = eV_c$.

From these equations, and with a good approximation for the electron concentration Eq. (5), we have

$$\xi_1' - E_{c1}' = \xi_1 - E_{c1} \,, \tag{9}$$

$$\xi_2' - E_{c2}' = \xi_2 - E_{c2} \,, \tag{10}$$

where (E_{c1}', E_{c2}') and (E_{c1}, E_{c2}) are the bottom-energies of the conduction bands of the two metals before and after the contact, respectively. Taking $\xi_1 = \xi_2 = \ldots =$ *const.* and subtracting Eq. (9) from Eq. (10), we obtain,

$$E_{c2} - E_{c1} = (\xi_1' - E_{c1}') - (\xi_1' - E_{c1}') = (\xi_1' - \xi_2') - (E_{c1}' - E_{c2}') \,, \tag{11}$$

$$eV_G = E_{c2} - E_{c1} = eV_c - (E_{c1}' - E_{c2}') \,. \tag{12}$$

The quantity V_G is known as the Galvani voltage which corresponds to the energy difference between the bottoms of the conduction bands of the conducting materials. By adopting $E'_{c1} = E'_{c2}$, Galvani voltage is identical to the contact potential difference under the effect of identical electron affinity of the two metals.

In ionic solids, like alkali halides, the electric current under electrolysis begins to flow by the motion of ions and the ion mobilities are enhanced thermally. Due to the process of electrolysis, the anions reach the cathode and the cations the anode. The ions pile up under the influence of the metal field, and the metal surface potential is raised to such an extent that leads electrons on the negative ions to the Fermi level of the metal anode, or to lower the holes on the positive ions to the Fermi level of the metal cathode so that the charges of both types of ions can be transferred to the metal electrodes.

The activation energy connected to the formation of the contact has a correlation with the Galvani voltage. The Galvani voltage type barrier must be overcome to have an adequate ionization current. Thus the activation energy (W_0) under ionic process is at most equal to eV_c.

The non-uniformity of fields in the case of a pointed cathode is very important for the formation of the ohmic contact. A large supply of carriers from the pointed cathode will be active immediately when the contact is formed. Otherwise, less space charge [6,11] is tantamount to more carriers flowing through the anode thereby attenuating the contact formation energy.

The cessation of this thermodynamical process is consequent upon the formation of an ideal contact and under inhomogeneous geometry of the contact, copious amount of electrons start the process of space charge current necessary for trapping the carriers (general feature of alkali-halide crystals towards the formation of colour centres).

From the results for the activation energy, it is clear that the heterogeneous geometry is effective in deriving the electrons in stage 2 under the influence of the space charge limited (SCL) current and also the basic demand for the continuation of injection. Instead, many point contacts (homogeneous) disturb the geometry on the atomic scale, resulting in the absence of SCL current.

This persistence of ionic current and the absence of the second stage current cause noticeable deviation from the pointed contact geometry along with the exhibition of increase in the value of the activation energy, and are important for the formation of the ohmic contact by yielding disorder in the crystal matrix.

4. Conclusion

The ideal condition of contact is confirmed with a heterogeneous cathode-anode contacting system which is a prerequisite for the electronic current to flow beyond the ionic zone, while under homogeneous contact, there is no evidence for such space-charge limited current injection to follow.

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ELEKTROLIZA KROZ HOMOGENE I NEHOMOGENE SPOJEVE IZOLATORA

Načinili smo osnovna mjerenja početnog stanja ionizacije pri uspostavljanju neispravljačkog spoja nastalog elektrolizom na dodiru istorodnih ili neistorodnih izolatora. Našli smo da je prvotna aktivacijska energija vezana sa shemom pojaseva energijskih vrpci spoja koji su potrebni za stvaranje defektnih središta blizu ograničene injekcije prostornog naboja.