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THE INFLUENCE OF INTERFACES ON THE PROPERTIES OF A MODEL DIELECTRIC SYSTEM

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The decisive influence of a highly resistive interface onto a non-ohmic current increase in a model dielectric system is confirmed in the paper. By electron microscopy and an X-ray microanalyser the generation of filaments of increased conductivity in NaCl is shown. Explanation is given by the electronic Schottky mechanism, which elucidates the dependences of d.c. currents on voltage, time, temperature and thickness of samples.

It is shown that a conductive coating of dielectric under the electrodes decreases the risk of prebreakdown states and thus increases the loadability of isolation.

ВЛИЯНИЕ ГРАНИЦ РАЗДЕЛА НА СВОЙСТВА МОДЕЛЬНОЙ ДИЭЛЕКТРИЧЕСКОЙ СИСТЕМЫ

В работе подтверждено существенное влияние высокоомной границы раздела в модельной диэлектрической системе на рост неомического тока. На основе данных электронной микроскопии и рентгеновского микроанализера доказано образование струй повышенной проводимости в NaCl. Интерпретация результатов сделана на основе электронного механизма Шоттки, который позволяет объяснить зависимость постоянных токов от напряжения, времени, температуры и толщины образца.

Показано, что проводящий слой диэлектрика под электродами уменьшает опасность предпробойных состояний, и таким образом увеличивает прочность изоляции.

I. INTRODUCTION

Studying dielectric properties of samples of different materials we cannot avoid the problem of a proper contact between the sample and the electrodes. Some experimental results in literature, where, for example, the current is independent of the sample's thickness or where tan δ shows big extremes, refer to the presence of a decisive influence of the interface between the sample and the electrodes.

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We decided to study this influence of the interface on a model material with a known simple chemical structure for X-ray microprobe analysis, transparent for optical microscopy; the concentration of carriers and the mechanism of electrical conductivity were known.

We compared the properties of the dielectric system with different types of interfaces in a d.c. electrical field following up previous results from superposed d.c. and a.c. voltages [1, 2, 3].

We used samples of $NaCl + 0.05$ mol % $CaCl_2$, where the addition of divalent cations produces cation vacancies, the only charge carriers in the region of low intensities of the electrical field, with temperatures low enough below the crystal's melting point [4].

Pt electrodes were pressed into samples and three types of interfaces were studied: a) sample with a clean, uncoated surface under Pt electrodes; b) sample surface under Pt electrodes coated with graphite; c) sample surfaces under Pt electrodes coated with graphite and an artificial interface in the middle of the sample cleaved parallel to the electrodes.

The highly resistive interlayer arises a) between the NaCl sample and Pt electrodes, c) in the middle of dielectrics. The presence of this interface causes the interfacial polarization, which exhibits a high extreme in $\tan\,\delta = f(T)$ at $T \doteq 250$ °C. In case b) in the absence of the resistive interface, the $\tan\,\delta$ extreme at 250 °C disappears and there remains only the lower one at a temperature $\doteq 68$ °C, unambiguously explained by dipole polarization of complexes: Ca^{2+} — vacancy [5].

Studying the dielectrical systems with interfaces in superposed d.c. and a.c. fields [1, 2] we have seen the differences between a lower and a higher d.c. voltage, though the average intensities did not overlap the value $3 \times 10^5\ Vm^{-1}$. These intensities are low enough so as not to create an electronic increase of carriers concentration in the bulk of the sample. But in systems with an interface the nonhomogeneous distribution of voltage in layers with a different resistivity is important. The highly resistive interlayer binds a greater part of the potential drop and the local intensities in it can reach values necessary to give rise to an electronical part of current by the Frenkel and Schottky effect. The d.c. voltage causes accumulation of carriers from bulk at a highly resistive interlayer and so raises the local field intensity, after a time depending on temperature and voltage. Because of low ion mobility it takes several minutes.

II. EXPERIMENTAL PART, CURRENT MEASUREMENTS

In Fig. 1 three types of interfaces are shown. Sample areas were 1×1 cm, thickness 1 mm. The samples were pressed between Pt electrodes. The interfaces consist of thin air gaps of unequal thickness. The d.c. voltage was obtained from a battery, the d.c. current measured with a Keithley picoampermeter.

In Fig. 2 the $I(V)$ dependence for different interfaces is shown. The nonlinearity for the arrangement with a highly resistive interface at the electrodes shows a nonohmic character of conductivity. The nonlinear current increase in the arrangement c), takes place at voltages about order higher than at the arrangement a).

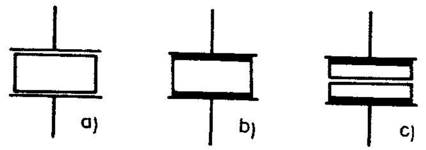

Fig. 1. The three used arrangements: a) resistive interface under electrodes; b) sample with conductive coating; c) interface in middle of sample.

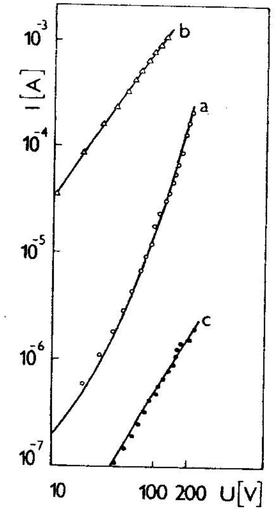

Fig. 2. The current-voltage characteristics in log-log scales. a) ○○○ — sample without conductive coating, resistive interface under electrodes; b) △△△ — sample surfaces adjacent to electrodes coated with graphite; c) ●●● — sample surfaces adjacent to electrodes coated with graphite and sample cleaved parallel to electrodes, resistive interlayer in the middle of sample. $T = 255$ °C, $h = 1.40$ mm.

Measuring the $I(V)$ dependences, the main attention was given to the first part of the nonohmic increase. The voltage used was up to values where the typical signs of the prebreakdown stage in the interlayer appear: strong instability and a marked increase of current with time. The application of higher values of voltages leads to destructive changes of samples.

In Fig. 3 there are the $I(V)$ curves with thickness as a parameter. The current is independent of the thickness at low voltages and depends on it at higher voltages only. D.c. current versus time is shown in Figs. 4 and 5, the initial current decrease changes at higher voltages up to an increase and the gradual formation of

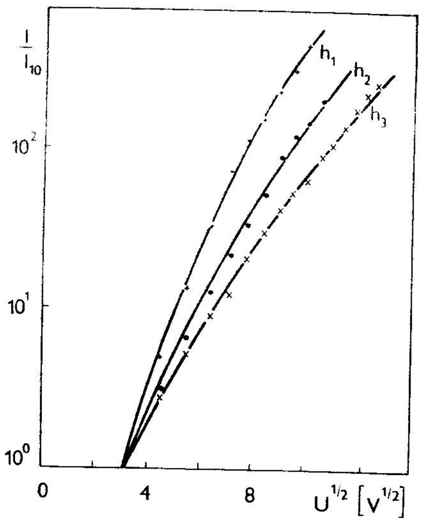

Fig. 3. Thickness dependence of current-voltage curves. $h_1 = 0.38$ mm, $h_2 = 0.88$ mm, $h_3 = 2.20$ mm. $T = 255$ °C.

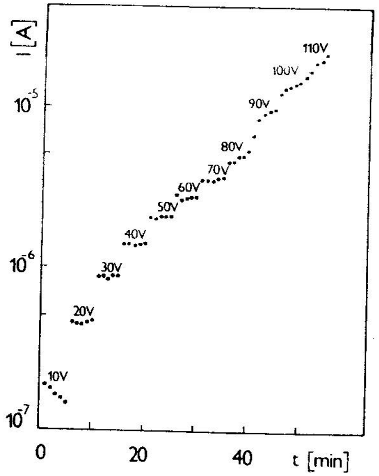

Fig. 4. Current versus time at different voltages. $T = 255$ °C, $h = 1.36$ mm, arrangement a).

instabilities. The transition of $I(t)$ dependence from a decrease to an increase depends on the temperature and the type of interface. In arrangement a) the current increase begins at the temperature of ~250 °C at ~70 V, at the temperature of ~300 °C already at ~20 V. At the same temperatures in arrangement c) the current increase begins always at voltages more than one order higher than in arrangement a).

In Figs. 6 and 7 there are d.c. currents versus time at a cyclic change of voltage. One can observe the monotonic decrease with time and the linearity of the $I(V)$ increase in case of a conductive painted sample, case b), whereas for an unpainted sample an increase of $I(t)$ and a nonlinear increase of $I(V)$ appear after a certain time and voltage.

III. ANALYSIS

The nonohmic $I(V)$ increase at values of average intensities 3—4 orders lower than the breakdown fields of material can be explained by local intensities several orders higher in areas of nonideal contact between the sample and the electrodes than the average intensity in the sample. We suppose that the current increase is made possible by the injection of electrons into the highly resistive interlayer by the Schottky mechanism: by lowering the energetic barrier for electron emission from

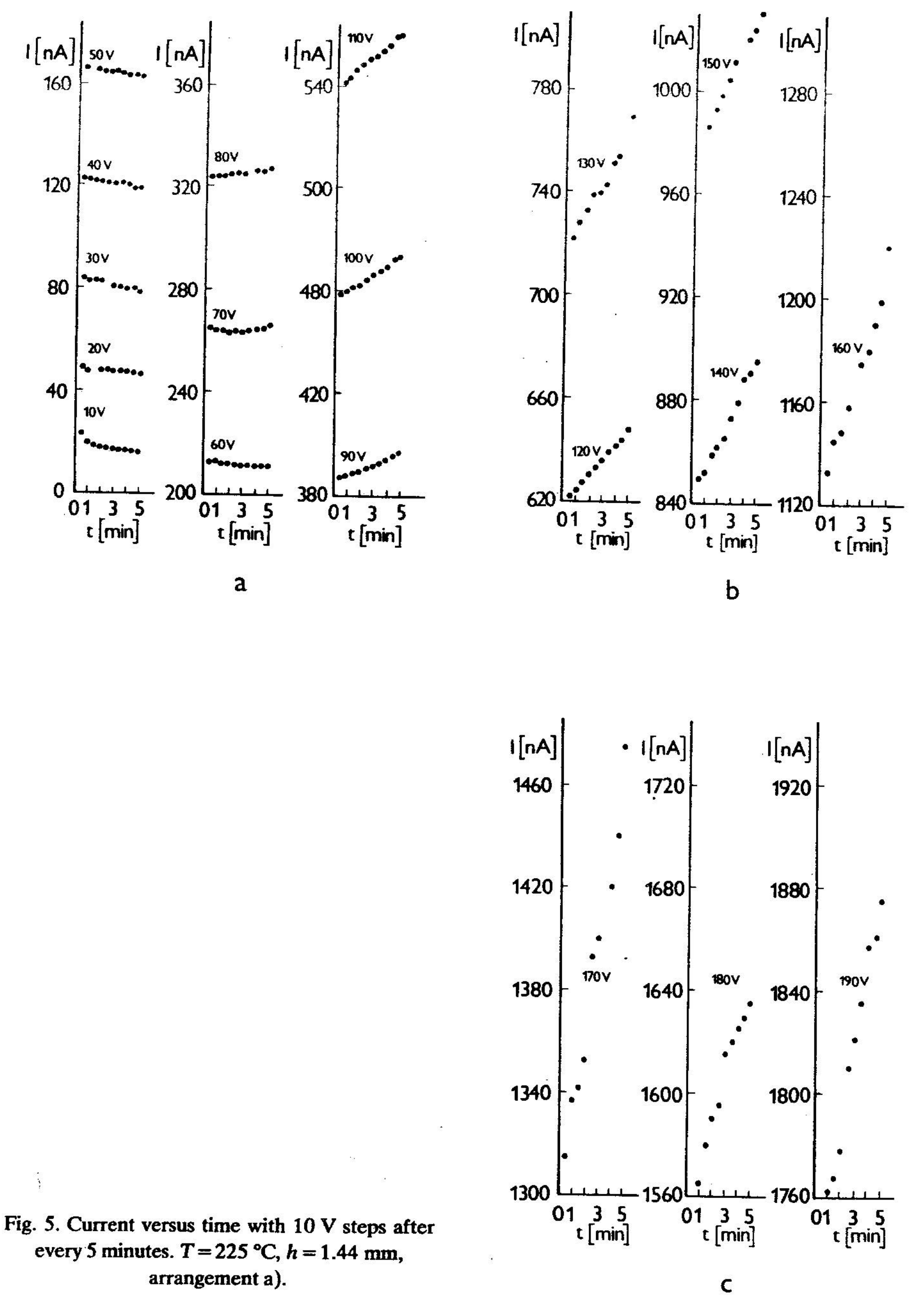

Fig. 5. Current versus time with 10 V steps after every 5 minutes. $T = 225$ °C, $h = 1.44$ mm, arrangement a).

the metal by help of a high electric field. In Fig. 2 it is shown that the nonohmic increase of $I(V)$ begins in case c) at voltages one order higher than in case a). This refers to a more difficult injection of electrons into the interlayer which is not close to the metal electrode. There the injecting "metal" layer can be the sodium accumulated before the interlayer in the middle of the sample. Also the dependence of $I(V)$ on the thickness refers to the Schottky mechanism: at low voltages,

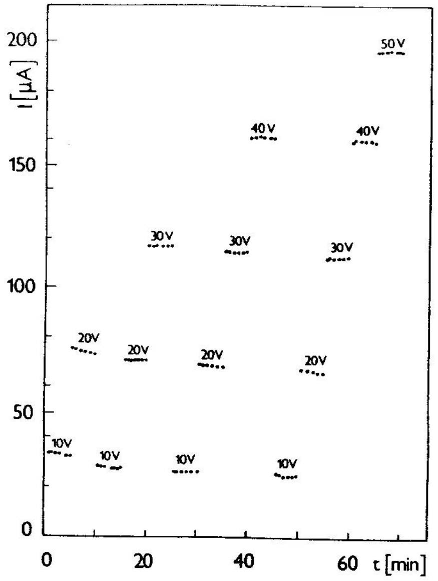

Fig. 6. Current curves at cyclic raised voltage for arrangement b). $T=255$ °C, $h=1.54$ mm.

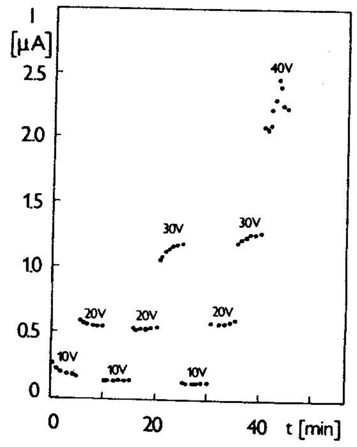

Fig. 7. Current curves at cyclic raised voltage for arrangement a). $T=255$ °C, $h=1.53$ mm.

until the injection begins, all the potential drop is on the highly resistive interlayer and the current is independent of sample thickness because the resistivity of the bulk is relatively negligible. At higher voltages, after the increase of interlayer conductivity by injection of carriers, the conductivity of the system depends on sample thickness. Our curves in Fig. 3 can be compared with [6], where the conductivity mechanism is explained also by Schottky thermoemission. The Frenkel mechanism: the concentration increase in the bulk of the samples caused by an asymmetry of the energy barrier for bonded carriers, created by the field, was rejected with respect to the following: The bulk of the sample has not a sufficient intensity; using electrodes of extremely different sizes, the currents were dependent on the polarity, thus the area near the electrodes is decisive and not the bulk [1].

In Fig. 8 the plotted linear dependences of log (I/T^2) versus $1/T$ correspond to the Richardson–Schottky relation for the density of the thermoemission current (1):

$$I=AT^2\exp\left(-\frac{\Phi_0}{kT}\right)\exp\left(\frac{\beta_s E^{1/2}}{kT}\right) \tag{1}$$

where

$\beta_s=(e^3/4\pi\varepsilon_0\varepsilon_r)^{1/2}$ is the Schottky constant, Φ_0 is the work function of the emitter, E — the local field intensity, k — the Boltzmann constant, T — the temperature, A — the constant for the emitting material.

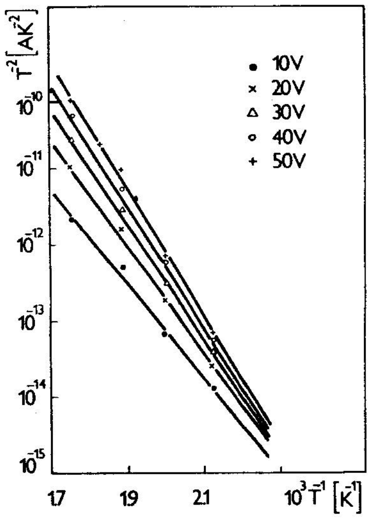

Fig. 8. Current versus temperature for different voltages in log (I/T^2) versus $1/T$. $h=0.9$ mm.

Calculating from [1] with the help of the graph from Fig. 8, the activation energy of the conductivity mechanism can be evaluated. The plot of log (I/T^2) versus $1/T$ gives a straight line, the slope of this line, a_n, leads to Φ_0 as follows:

$$\log\frac{I}{T^2}=a_n\frac{1}{T}+b \tag{2}$$

where

$$a_n=-\left(\frac{\Phi_0}{k}-\frac{\beta_s U^{1/2}}{kd^{1/2}}\right)\log e. \tag{3}$$

We consider here only $E=U/d$, where d is the interface thickness; in a more detailed analysis the dependence of the local field intensity on temperature is to be expected.

Let us put the slope of the line as

$$a_n = a_1 U^{1/2} + b_1 \tag{4}$$

where

$$a_1 = \frac{\beta_s}{kd^{1/2}} \log e \tag{5}$$

$$b_1 = -\frac{\Phi_0}{k} \log e, \tag{6}$$

thus

$$\Phi_0 = -\frac{b_1 k}{\log e}. \tag{7}$$

Calculating from (7) we get the value of the energy Φ_0 for the sample without conductive coating as 0.99 eV. The activation energy of conductivity in a dielectric system with a highly resistive interlayer, in arrangement a), calculated from the $\sigma(1/T)$ dependence using (8):

$$W = k \frac{\ln \sigma_1 - \ln \sigma_2}{\frac{1}{T_2} - \frac{1}{T_1}} \tag{8}$$

is also 1 eV. Approximately the same value is given also in paper [7] for the Schottky mechanism.

In case when the highly resistive interlayer is in the middle of the sample, arrangement c), the activation energy is 1.2 eV, which corresponds to a more difficult rise of injection than in case of a resistive interlayer close to the metal electrode.

IV. THE OBSERVATION OF SAMPLE SURFACES BY ELECTRON SCANNING MICROSCOPE AND ELECTRON PROBE X-RAY MICROANALYSER

Fig. 9 gives the picture of the sample after the transition of prebreakdown currents. The dark spots correspond to places with the highest local intensity, where the most intensive injection took place. It gave rise to colour centres which created violet clouds. We assume that the injected electrons filled the traps in the forbidden gap of NaCl (from Ca admixture) and so made the absorption of part of the visible spectrum possible. The energy gap in NaCl is 7 eV, NaCl without impurity levels cannot absorb the visible spectrum with $\lambda = 0.38 \div 0.78$ μm, which corresponds to energies of $1.67 \div 3.26$ eV. The colouring is a consequence of certain impurity levels present in the forbidden gap and is atrributed to the filling of vacancies by injected electrons. Some Na^+ vacancies are present from the Ca^{2+}

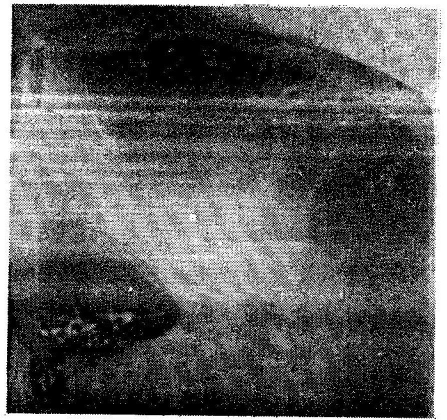

Fig. 9. Violet coloured clouds in areas with the highest local intensity of electrical field where the most intensive injection of electrons occurs. Enlargement 30 ×.

Fig. 10. Filamentary character of over-ohmic current transport in pictures of the sample's vertical cross-section. Diameter of melted channel is about 5 μm. Enlargement 680 ×.

admixture, some are created by local stress and overheating in prebreakdown fields.

Figs. 10—12 show some "dark" places on the sample after the current transition made by the electron scanning microscope: A surface with pits under the negative electrode, with small hills under the positive electrode, the side view at the

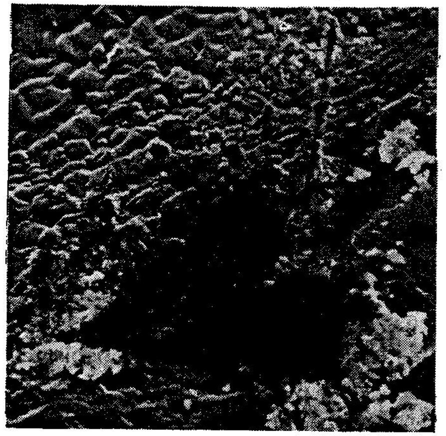

Fig. 11. Sample surface under negative electrode. Enlargement 1320 ×.

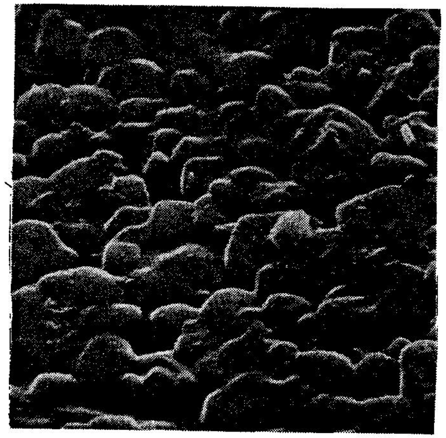

Fig. 12. Sample surface under positive electrode. Enlargement 2920 ×.

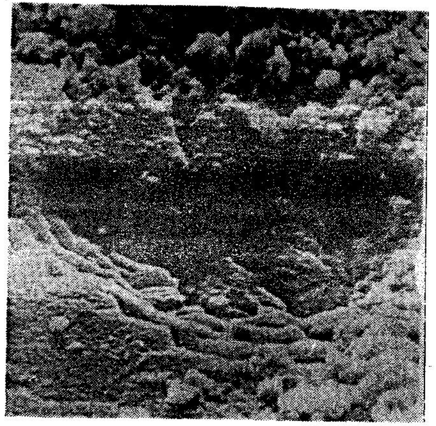

Fig. 13. Surface in the middle of the sample cleaved parallel to electrodes. The hole-beginning of a channel. Enlargement 707 ×.

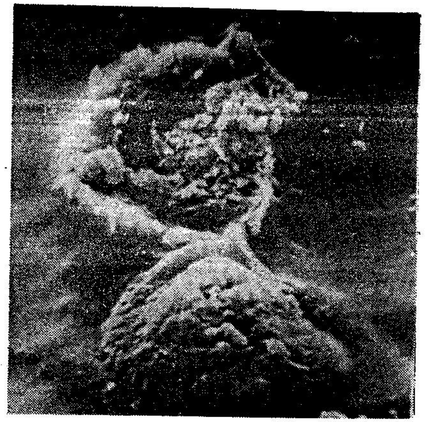

Fig. 14. Surface in the middle of the sample cleaved parallel to electrodes. The hill — the mouth of the channel. Enlargement 1607 ×.

crossection of a crystal, where the filaments are visible. The filaments are created by the transition of high current densities. At a smaller enlargement they look like "trees", similar to those known from the prebreakdown stage of liquid isolants [8].

The paths of an increased conductivity, created by an accidental grouping of defects and by injection, form in the isolant forked channels. They are locally overheated from an extermely increased conductivity. The current instabilities in the overohmic region can also be explained by "filamentary" conductivity. The overmelting of one of the many channels gives always a jump in the current value.

On surfaces of an artificially created interface in the middle of the sample, in arrangement c), we can see similar traces of created channels, Figs. 13 and 14. The injection into this interlayer can issue from a layer of Na metal, from neutralized Na ions accumulated in front of the interface. It is analogical to [9, 10].

Fig. 15 shows a typical photo of the surface by an X-ray microanalyser. Though a topographical picture shows optical non-homogeneity, the display of the present elements before and after the current transport is homogeneous, there are no changes in Na, Ca and Cl concentrations on surfaces and sections of samples. The samples did not contain Pt from electrodes. There were traces of sample material on electrodes in places adjacent to the dark spots on the samples, probably the traces of melted NaCl from overheated filaments, for no chemical element was in a markedly changed concentration in comparison to the bulk of the samples. It indicates that the spots on the sample surface are not caused by ions of one type under the opposite charged electrode, and so the role of electrons in the prebreakdown increase of the current is confirmed.

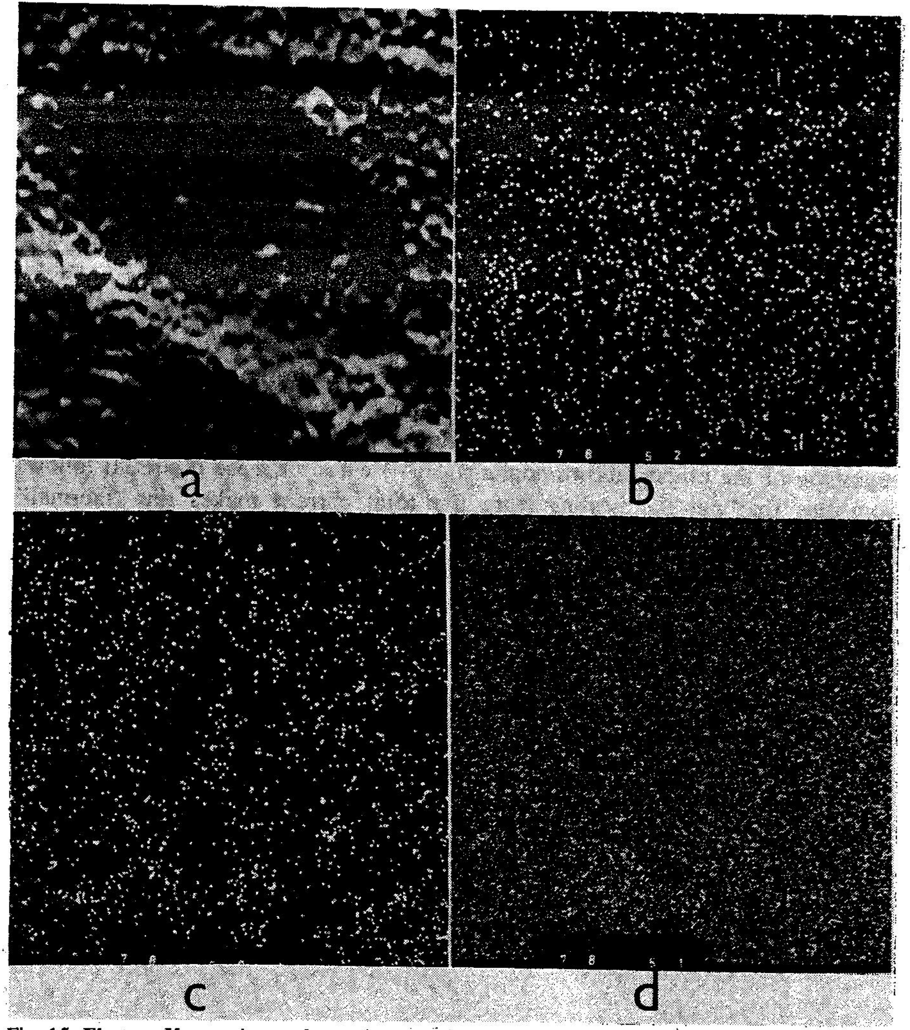

Fig. 15. Electron X-ray microanalyser pictures. a) Topographic; b) Na; c) Ca; d) Cl. Enlargement 180 ×. There were no relative changes in images of elements in spots after over-ohmic currents.

V. CONCLUSION

An analysis of measurements and observations of sample and the electrodes surfaces by electron microscope and X-ray microanalyser have given the following picture of the influence of the interface on the behaviour of the whole dielectric system.

1) The non-ohmic current increase can be explained by the Schottky emission of electrons into a highly resistive interlayer.

2) A characteristic sign of current transition from the ohmic to the nonlinear region of $I(V)$ is the change of the $I(t)$ curve from a decreasing to an increasing one.

3) A typical sign of prebreakdown current, its instability, is a consequence of a filamentary mechanism of locally increased conductivity. Ions accumulated under the interface create: → high local field → electron injection → conductive channel → decrease of potential drop → end of injection → new ions accumulated … and so on. Growing filaments by connecting with one another cause also jumps in the current.

4) A conductive coating of dielectric surface under the electrodes increases several times the values of the flowing currents, but increases also the value of voltages at which the increase of $I(t)$ begins, that is, where the indication of the beginning of the prebreakdown nonlinear $I(V)$ curve increase occurs. It follows from this that not the heating from the total current makes the "thermal" breakdown possible, but that an electronic mechanism is present activated by high local field intensities. The highly resistive and not uniform interface as an origin of conductive channels penetrating through the dielectric, is dangeorus for insulating systems. A better loadability will be obtained by insulators, where an "ideal" electrical contact with metal parts is created by conductive coating.

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