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ELECTRIC FIELD FORMING AND AGEING PROCESSES IN EVAPORATED SYSTEMS WITH As_2Se_3

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In the article some results are presented due to the electric field forming processes in evaporated layer systems with As_2Se_3. After forming with the electric field $E = 10^7\ Vm^{-1}$, the current decreases by one order and becomes stable. The ageing process, caused by the prolonged treatment with the electric field and accelerated with annealing, changes the U—I characteristics from $I \sim U \exp(kU)$ to $I \sim U^n$, where $n = 4.0$ in the steady state and $n = 2.9$ in the single shot measurements. An explanation of the ageing process is suggested in terms of some redistribution of the space charge in the systems most probably due to the ionic transport.

I. INTRODUCTION

In recent years special attention has been devoted to the investigation of the charge transport in amorphous semiconductors in general, and in chalcogenide glasses in particular. Whereas the theory of the charge transport in amorphous bulk materials has been elaborated to some degree of precision, the theory of the charge transport in layers, and especially in interfaces matel-amorphous substance is still lacking. This is quite understandable as up to know the theory of the surfaces of amorphous substances is a matter of contraversy.

Fritzsche [1] and Jonscher [2] claim, taking into account the theory of the charge transport in crystalline semiconductors, that because of the enormous density of both the shallow and deep traps of the order 10^{24}—$10^{25}\ m^{-3}\ eV^{-1}$, the barrier widths are of the order 10^{-9} m. A barrier of such a thickness is transparent for tunnelling to both the valence and conduction bands, and in the case of the thermally activated hopping via localized states, even for the direct tunnelling between such states. Simmons [3] elaborated a theory where he calculated some interesting properties of contacts of materials with a high density of both the shallow and the deep traps. On the basis of his results, he predicts the thickness of interfaces to be of the order of 10^{-9} m.

In a paper by Fritzsche [4], the impossibility of the building of a blocking or injecting contact with an amorphous semiconductor was limited only to the wide-gap (>3 eV) materials.

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Recently, Krempaský and Červenák [5] elaborated a theory of the U—I characteristics of metal-amorphous semiconductor-metal systems. They found that the region of the electric field, where the contact is current-limiting, gives a linear U—I characteristic, which gives little information on the bulk properties of the amorphous semiconductor. Further they showed the possibility of the forming of the current-controlled negative resistance region, caused by the interface versus the bulk interaction.

We found before experimentally [6] that the Al contact with the work function $\Psi_{Al}=3.4$ eV [7] form the hole-blocking contact with the amorphous chalcogenide As_2Se_3. The ratio of the resistances for the forward and backward biased interface As_2Se_3—Al was found 1/10. The interface region exhibits a linear U—I characteristic, and it holds the potential difference up to $U=1$ V. On the other hand, Au with the work function $\Psi_{Au}=4.8$ eV [7] forms the neutral or slightly hole injecting contact with As_2Se_3.

Nielsen [8] measured the interface of As_2Se_3 and found the energy difference between the vacuum level and the top of the valence band to be 6.2 eV and the energy difference of the top of the valence band and the Fermi level to be 0.9 eV. With the anticipated band bending 0.5 eV in the surface region of the thickness 1.0—1.5×10^{-9} m, the work function may be evaluated to be $\Psi_{As_2Se_3}=6.2-0.9-0.5=4.8$ eV.

In the present article we investigate the forming processes of contact by prolonged treatment with the high electric field. The forming with the electric field was used by Spear and Lanyon [9] on Se samples. Stable and reproducible SCLC characteristics were obtained by them, since a good injecting contact was formed by the electric field treatment. Besides, we present some results of the measurements of the ageing of the metal-As_2Se_3-metal systems, which is supposed to result in the non-homogeneous field distribution in the bulk and interface region, most probably caused by the ionic transport in As_2Se_3 layers.

II. PREPARATION OF THE SAMPLES AND EXPERIMENTAL ARRANGEMENT

The amorphous bulk material As_2Se_3* was flash-evaporated in the vacuum $p\leq10^{-3}$ Pa(10^{-5} torr) on the chemically cleaned substrates of glass and quartz. Before and after the evaporation of As_2Se_3 the semitransparent and massive metal electrodes of either Al or Au were evaporated to form sandwich systems of a thickness of $d\in(0.2;\ 12)$ μm. The thickness of the samples was measured by the Perth-o-meter and optically by the interference microscope MII-4. The composition of the evaporated layers was examined on the microprobe analyser JXA-3A and found to correspond to AS_2Se_{3-x}, where $x\leq0.2$. For the sake of brevity we shall refer in the following to the composition of our layers as As_2Se_3. Samples were found to be homogeneous by means of the IR and optical microscope, except for the small areas of the non-homogenities, covering less than 1 % of the total area.

All measurements were carried out in a cryostat [10] with the pressure of the residual gases $p\leq10^{-2}$ Pa (10^{-4} torr). The U—I characteristics in the steady-state were measured using the digital electrometer Keithley 615 for the current measurements, and the digital voltmeter TR 1662 for the voltage measurements. The arrangement for the quasi-steady-state measurements by the single shot pulse method is in Fig. 1, where the single pulses of the voltage $U\in(1$ mV—100 V$)$ were produced by the pulse generator Orion EMG 1117/1 and measured by the digital voltmeter TR 1662. The current through the sample was amplified by the electrometer current amplifier Keithley 615 and fed to the memory type oscilloscope Dynamco 7100.

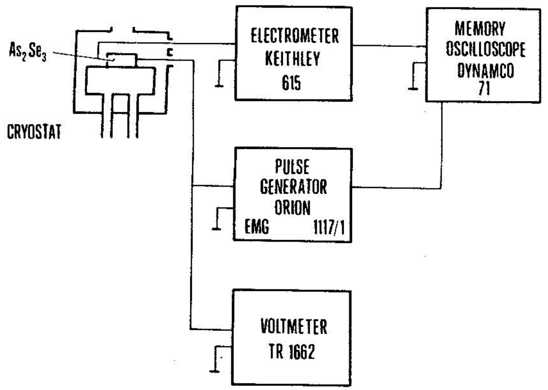

Fig. 1. The block diagram for the U—I characteristics measurement by the single shot pulse method.

III. EXPERIMENTAL RESULTS

The time dependence of the forming process for the sample Au—As_2Se_3—Al is recorded in Fig. 2. Upon the application of the voltage, there are strong fluctuations of the current. After some time, which is different for various samples, the current fluctuatuons disappear and the current becomes reproducible. In Fig. 2, there are two forming processes for both polarities of the applied voltage, indicating that the forming process is changing the properties of the interfaces and not of the bulk material.

In Fig. 3, there are the results of the single shot pulse measured U—I characteristics of the system Au^+—As_2Se_3—Al^- before and after the forming

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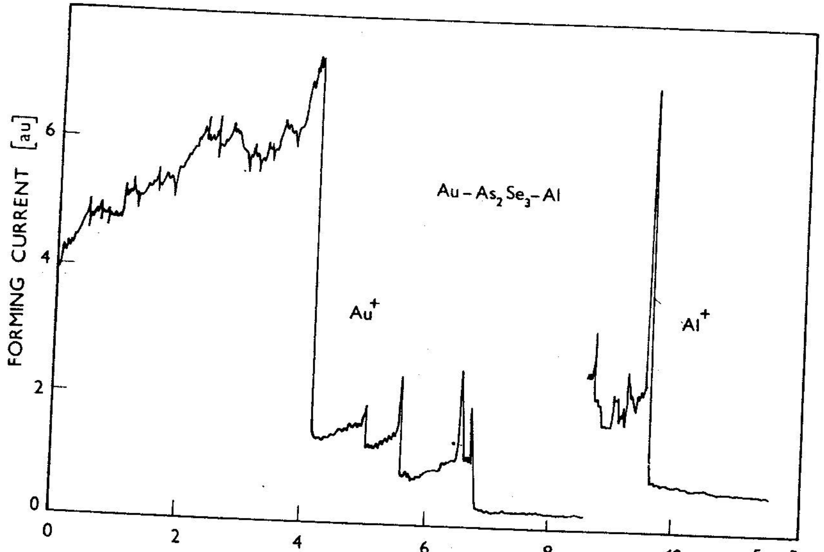

Fig. 2. The time dependence of the forming current for the system Au—As_2Se_3 for both polarities; $T = 300$ K, $E = 10^7$ Vm^{-1}.

process with the electric field $E = 10^7$ Vm^{-1} applied for $t = 20$ min. The U—I characteristic, measured before the forming exhibits a lot of fluctuations, whereas that after the forming is stable and exhibits the dependence $I \sim U \exp(kU)$ or $\sigma \sim \exp(kU)$.

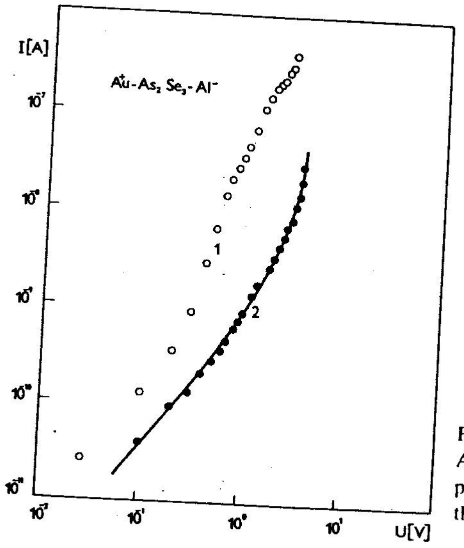

Fig. 3. The U—I characteristics of the system Au^+—As_2Se_3—Al^-, measured by the single shot pulse method for the fresh sample, curve 1; for the formed sample with $E = 10^7$ Vm^{-1} for $t =$ 20 min, curve 2; $T = 300$ K.

The comparison of the steady-state U—I characteristics and the single shot pulse U—I characteristics of the system Au—As_2Se_3—Al for both the polarities of the applied voltage and temperature $T = 300$ K are given in Figs. 4 and 5. The used pulse width is $t = 1$ s. For the polarity Au^+—Al^- in Fig. 4, both the characteristics differ for the voltage $U \leqslant 1$ V, where obviously the $As_2Se_3^+$—Al^- interface is current-limiting. For voltages $U > 1$ V, both curves are identical within the experimental errors, and may be approximated by $I \sim U \exp(kU)$. For the opposite polarity Au^-—Al^+ in Fig. 5, the two characteristics differ substantially, except for the small region of the highest voltages.

It was noted in the course of the measurements that the samples treated for a prolonged period of time by high electric fields exhibit a peculiar, constant and very slow rise of current, which is noticeable especially at higher temperatures. In Fig. 6 there are the single shot U—I characteristics of a fresh Au^+—As_2Se_3—Al^- sample $d = 1.6$ µm, curve 1, and for the same sample annealed for $t = 1$ h on $T = 370$ K,

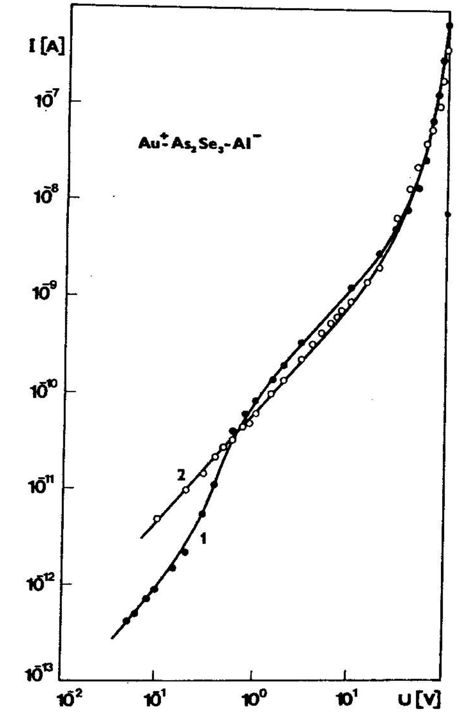

Fig. 4. The U—I characteristics of the system Au^+—As_2Se_3—Al^- measured by the steady-state method, curve 1; measured by the single shot pulse method, curve 2; $T = 300$ K.

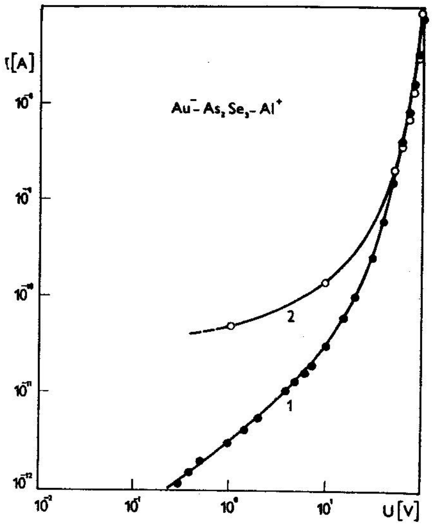

Fig. 5. The U—I characteristics of the system Au^-—As_2Se_3—Al^+ measured by the steady-state method, curve 1; measured by the single shot pulse method, curve 2; $T = 300$ K.

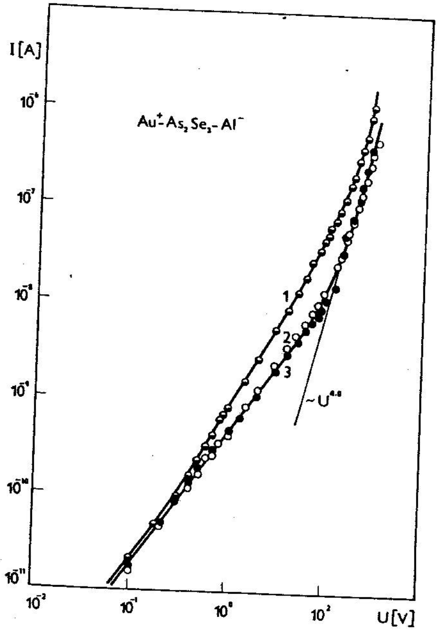

Fig. 6. The *U—I* characteristics of the system Au^{+}—As_2Se_3—Al^{-} $d = 1.6$ μm, $T = 300$ K measured by the single shot pulse method; measured on the fresh sample, curve 1; measured after the annealing for $t = 1$ h on $T = 370$ K, curve 2; the same for $t = 3$ h, $T = 370$ K, curve 3.

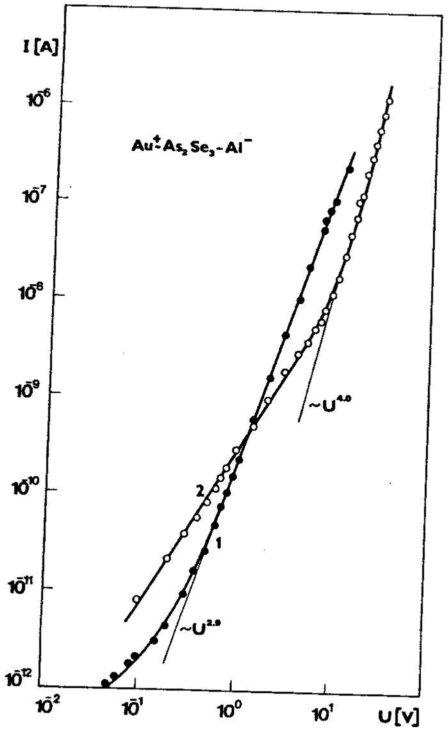

Fig. 7. The characteristics of the annealed system Au^{+}—As_2Se_3—Al^{-} corresponding to Fig. 6, curve 3; measured by the steady-state method, curve 1; and the single shot pulse method, curve 2.

curve 2, and $t = 3$ h, $T = 370$ K, curve 3. It is interesting that whereas the new sample exhibits the dependence $I \sim U \exp(kU)$, the annealed sample gives the steep rise of the type $I \sim U^{4.0}$, which resembles the SCLC dependence with the exponential traps distribution [11]. In Fig. 7, there is the comparison of the steady-state, curve 1, and single shot, curve 2, the *U—I* characteristics of the same sample as in Fig. 6 after the annealing. The character of both curves obeys, starting from a certain voltage, the dependence $I \sim U^{n}$, where for the steady-state dependence $n = 2.9$ and for the single shot dependence $n = 4$. Comparing Figs. 3 and 6 we can see that the prolonged annealing changes the region of the highest voltages from $I \sim U \exp(kU)$ to $I \sim U^{n}$.

We have also tried to establish, whether there is any space charge distribution in the samples. For this purpose we used the SC neutralization experiment, devised in [12]. In principle, this method is based on the application of the single shot decreasing sawtooth voltage, and from the current response we can calculate the SC distribution in the system. In Fig. 8, there are the responses to the pulse of the length $t = 20$ ms, $U = 100$ V for the system Au^{-}—As_2Se_3—Al^{+}; curve 1 is the response of a new sample and is near to the ideal response of an ideal capacitor (the response time of the amplifier $\tau = 3$ ms), resulting in no SC in the bulk of the As_2Se_3. Curve 2 is the response of the annealed sample kept for the period of time $t = 5$ h with the voltage $U = 100$ V of the polarity Au^{+}—Al^{-}. In this case, the neutralization of the negative SC by the holes, injected from the Au contact may occur, and from the measured curve we may establish the distribution of the negative SC formed during the prolonged application of the voltage of the polarity Au^{+}—Al^{-}, as shown in Fig. 8. The negative SC concentration is decreasing from the Al contact towards the Au contact.

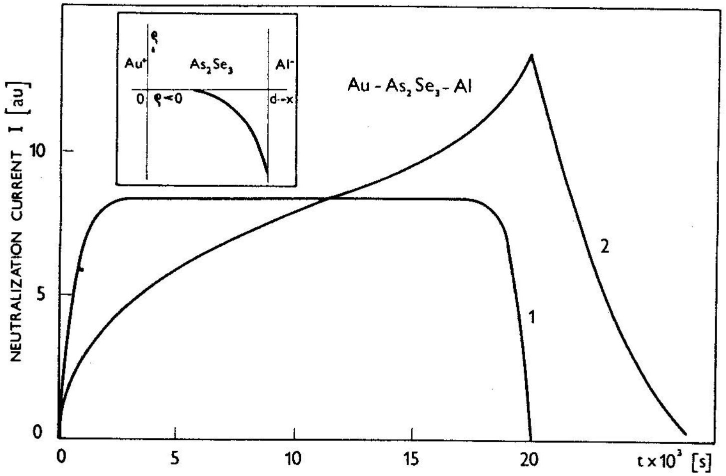

Fig. 8. The time dependence of the neutralization current in the system Au^{-}—As_2Se_3—Al^{+} $T = 300$ K; for the fresh sample, curve 1; and for the sample kept for the time $t = 5$ h with the voltage $U = 100$ V, $d = 7$ μm of the polarity Au^{+}—Al^{-}, curve 2. inset: supposed distribution of the SC as derived from the curve 2.

IV. DISCUSSION

The necessity of the contacts forming for the obtaining of the stable and reproducible measurements was shown by the results of Fig. 3. The principle of the forming process is not quite clear, even if it is widely used in thin film technology. The most probable explanation of the forming processes is the removing of the conductive bridges with some additional SC reorientation in the interface region.

From the results of the single shot measurements with the limited fatigue effects in Fig. 4, it is clear that for the system Au^+—As_2Se_3—Al^-, there is the contact--limited region in the U—I characteristics is for $U \in (0;\ 1)\ V$. For higher voltages the phenomenon is bulk-limited, with little or no influence of the contacts on the resulting U—I characteristics. The conductivity in this region is field dependent, with

$$\sigma = \sigma_0(E=0,\ T)\ \exp\left(\frac{-aeE}{kT}\right),$$

where σ, σ_0 is the conductivity, a is the characteristic length, E is the electric field strength, T is the temperature and e, k are the elementary charge and the Boltzmann constant, respectively.

On the other hand, the system Au^-—As_2Se_3—Al^+ behaves as contact-limited for the whole range of the applied voltages with the exception of the highest voltages. The current through the system may be approximated by [13]

$$j = p(E_{inter})\mu_{bulk}\ (E_{bulk})\ \dot{E}_{bulk}\ ,$$

where $p(E_{inter})$ is the concentration of the free holes in the interface region being the function of the electric field strength on the interface, μ_{bulk} is the mobility of the holes as the function of the electric field strength in the bulk. The regions, where the bulk or interface current-limiting is distinguishable from the shape of the response to the single pulse of voltage. For the contact-limited region of applied voltages, the transient response exhibits big overhoots, resembling the response of the RC differentiating circuit. In the region of the bulk-limited current, the transient response is nearly perfectly rectangular with almost no overshoots.

The ageing process after the annealing at higher temperatures and/or treated with the high electric field has been observed in the bulk samples of As_2Se_3 [14]. In the same paper, the authors calculated the contribution of the ionic current to the total current and found it to be less than 1 %. Generally, it is supposed that ionic currents are negligible in the chalcogenide glasses. This assumption may be correct, but even these small currents can cause strong redistributions of the electric field in the system, because of the charge accumulation due to the lack of the charge neutralization at the contacts. The second source of the ionic current may be the ionic transport of the ions of the metal electrodes. It was found that gold forms both positive and negative ions in As_2Se_3 [15].

The presented results show that the ageing effects may strongly influence the shapes of the U—I characteristics both in the single shot pulse and in the steady-state measurements (Figs. 6 and 7). This may lead to erroneous results as the characteristics of Figs. 6 and 7 resemble the SCLC characteristics of the systems with the exponential trap distribution.

Results of the SC neutralization experiment (Fig. 8) show that the long polarization with the high electric field forms the negative SC in the As_2Se_3 layers. Similar results were obtained in [12] but the origin of the negative SC was considered to be the field-assisted emission of holes from localized states in the region of the positive electrode.

V. CONCLUSIONS

The possibility of the forming of the contacts to the amorphous As_2Se_3 with the high electric field proved to be realizable. The annealing and the treatment with the high electric field causes the ageing effects in the systems with As_2Se_3, resulting in the redistribution of the electric field strength in the systems. The most probable explanation seems to be the ionic transport.

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