TRANSIENT AND STEADY-STATE BEHAVIOR OF ELECTRICAL CONTACTS TO PURE AND ALLOYED AMORPHOUS SELENIUM

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We have studied the junction between pure amorphous selenium and a-As$_x$Se$_{1-x}$ and several metals with the aim of determining whether the choice of metal can improve device performance, in particular minimizing the dark current. Samples are in sandwich configuration on glass substrates and consist of 20-50 Om thick a-Se with top electrodes from Cu, Ag, Al, In, and Au. For each of listed metals, current transients after application of bias voltage are measured for up to an hour. As we find, dependencies of current on voltage typically follow power laws (at high fields) and vary from metal to metal. Depending on contact used, the dark currents vary in a range of four orders of magnitude. The current is controlled by injection of hole curriers at the metal/a-Se junction. At the same time, there is no direct connection with the metals work function.

1.Introduction

Despite the large existent literature on the electrical and photoelectronic behavior of amorphous solids [1-5], relatively little attention has been paid to the properties of electrical contacts and the contact interface formed on these materials [6-8]. Exception being the systematic study of Moldavian group performed on some binary and ternary compositions (see review articles [9] and references cited herein). Contacts to amorphous semiconductors do not reveal striking effects: they show no polarity dependence and their resistance is usually negligible compared to that of bulk material. Nevertheless we believe the properties of contacts are important for many transport process, particularly for those of high fields. Moreover, the performance of many amorphous semiconductor devices, e.g. photoreceptors, solar cells, photodetectors etc., is affected by electrical contacts.

Detectors using a-Se as an X-ray photoconductor have illustrated the potential for excellent images as described in a series of articles [10,11]. Recent research at the Sunnybrook Health Science Centre (University of Toronto) by Rowlands and co-workers has shown that an X-ray imaging system based on the X-ray sensitivity of halogenated a-Se:As photoconductor (known as stabilized a-Se) has enormous potential for digital radiographic applications in medical diagnosis [12-14]. Even more, within the last three years, a commercial X-ray medical diagnostic imaging system has been introduced into the market by Philips based on using the X-ray sensitivity of a-Se photoconductive layers. Additionally, several significant patents (e.g., US Philips Corporation, 1995) have been issued to major corporate laboratories that use an a-Se layer vacuum coated onto thin film transistor active matrix arrays and use this plate as an X-ray image detector. Such sensors have been called **direct conversion X-ray image detectors** to emphasize that the X-rays are converted directly to collectable charge carriers in contrast to an intermediate process of converting X-rays to light and then light to charge carriers using photodetectors, the latter systems are phosphor based. Images obtainable from such a devices have been potentially superior to film based radiology and to digital storage.

Amorphous selenium is one of the most important representatives of this large class of non-crystalline materials. Due to its importance as a xerographic photoreceptor, many of the properties of a-Se have been widely studied during seventies, and eighties (Refs [4,5,15-17], to say about few). The majority of the studies have been related to the free surface geometry used in xerography. Essentially much less work has been done on the metal/a-Se junction at high fields. There is now a need to measure and understand the properties of metal to pure a-Se (and a-Se –based alloys) junctions in configurations approximating actual devices such as flat panel X-ray image detectors. In the present article, we have studied the long-term current transients and the I-V relations of the above structures for several metals and try to answer the question to what extent the type of metal can influence the electronic properties of devices with metal/amorphous semiconductor junction.

2.Sample preparation and the experimental procedure

To examine the metal-amorphous chalcogenide contact, simple devices were fabricated in a sandwich-cell configuration on glass substrates, with the chalcogenide alloy as deposited between a top and bottom electrode. In the present study, we used pure amorphous selenium and a-Se alloyed with 2-10 % As. Glassy As_xSe_{1-x} alloy source material was prepared in Nor.Techn.Centre by conventional melt-quenching technology in a similar fashion to that described previously [15,17]. Amorphous Se and As_xSe_{1-x} films with small amounts of As additives were deposited onto glass substrates by conventional vacuum deposition techniques. The glass substrates were previously coated with SnO_2 which forms the bottom electrode. The thickness of pure a-Se and a- As_xSe_{1-x} films ranged from 20 to 50 m. The substrate temperature during the deposition process was 300 K. A semitransparent Au, Ag, Cu, Al, Bi and In electrode was sputtered on the uniform thickness region to complete a sandwich structure: Me/(a-Se)/SnO_2. To limit possible heating of amorphous films, evaporation times were restricted to less than 1 min. The contact area (0.1 cm^2) was defined by the cross-over of the two (bottom and top) electrodes. Prior to any measurement, the samples fabricated in the laboratory were naturally aged in the dark for nearly two weeks to allow their structure and corresponding physical properties to equilibrate.

The measurement technique was similar to that of Wallace for examining contact properties of amorphous films used in Ovshinsky's devices. This apparently simple experiment is complicated by a long-term transient component. After applying the voltage, the current monotonically decays by one to three orders of magnitude in a time range of several hours. In order to be sure that the sample in each experiment is at the same electronic state, we have "resting" the sample (i.e. short-circuiting it in the dark for 10 h) in all cycles. A high input impedance (~ 10^{14} Ohm) electrometer was used to measure the open circuit dc current across the electrodes. For currents of the order of $\approx 10^{-14}$ A, noise from the power supply may obscure the data.

3.Results

Typical time-dependent response of the current in Me:a-Se:SnO_2 (Me indicate top electrode formed by different metals) is illustrated in Fig.1. Some important features are noted here.

First, the character of the time dependence as well as the current level of the traces depend on the material (metal) of electrode biased in this case positively.

Second, for most metals under examination the current magnitude decreases with time after application of bias voltage. Moreover, to reach a steady state more than 1 hour is needed. During this time the initial current decays by from one to four orders of magnitude. At any particular time the magnitude of the current covers nearly five orders depending on the chemical nature of metal chosen.

Finally, in several cases there is hardly to detect any decay of the initial current. We see that this situation prevails for metals such as Al and In.

A typical example of the current-voltage characteristic is shown in Fig.2, plotted in a log-log scale. The procedure consists in taking a cut at this fixed time through the transient for an electrode. Note that most of the metals behaves in a manner similar to that of Fig.2 and exhibit a power law relation I~ V^n where n>1 for higher electric fields. The characteristic apparently flattens at low fields (less than 10^3 V/cm) and the I-V curve is evidently not a simple power law.

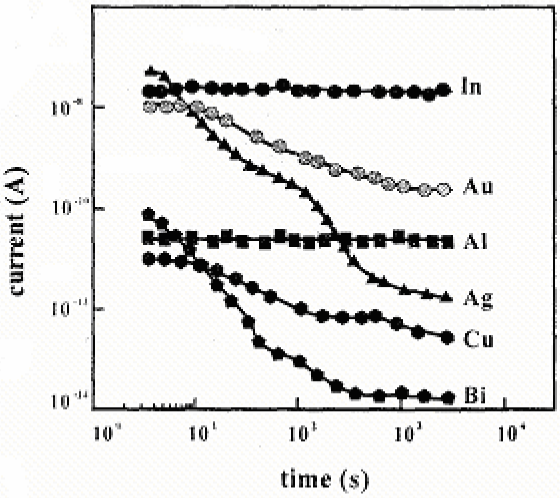

Figure 1. Long-term decay of dc current after application of 40 V bias voltage to Me/a-Se/SnO2 structures.

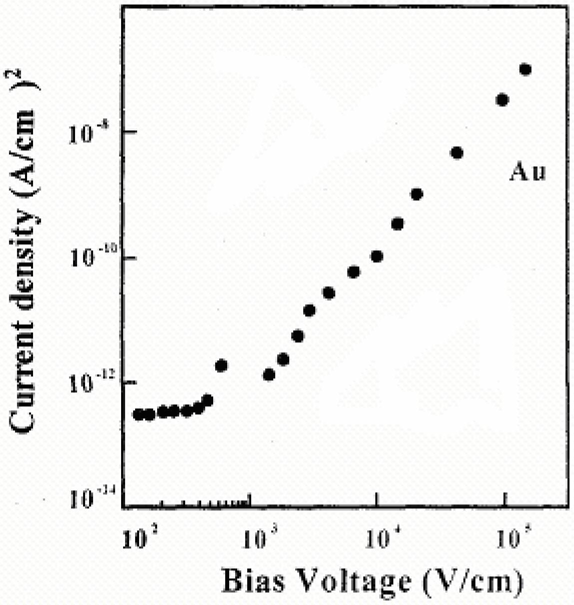

Figure 2. Current versus voltage characteristic for a-$As_{0.02}Se_{0.98}$

Table 1 summarize the electrical behavior of various metal electrodes.

In addition, a series of transients were obtained for the same specimen, but for metal electrode biased negatively. Over the major part the characteristic of Me/a-Se/SnO_2 structure remains essentially the same, confirming that the current is controlled by the bottom electrode to chalcogenide junction.

Table 1. Some electrophysical characteristics estimated for Me/a-Se/SnO_2 structures under positive bias of 200 V

Top contact (Me)	Electron work function Φ, eV	Power low parameter	Ratio of currents I_f/I_{in}
Au	5.1	1.6	$5*10^{-2}$
Ag	4.5	2	1
Bi	4.2	3.7	$2*10^{-3}$
In	4.1	1.2	1
Al	4.2	0.9	1
Cu	4.7	2.7	$3*10^{-2}$

4.Discussion

In this section, we make several remarks on the utility of the results we have partially presented. It can clearly be seen from the transients and I-V relations for various metals that the mentioned look qualitatively different and, as a consequence, any simplified model or theory can explain the data. In order to extract information about the transport properties, we try to consider separately two parts of the above problem: carrier injection across the metal-amorphous selenium junction, and the transport through the bulk of a-Se sample, respectively.

Since both the electron and hole drift are well characterized in prototype amorphous semiconductor a-Se and a-AsxSe1-x, the latter problem seems an easy matter. In the last two decades most of the authors interpret their I-V measurements as a space-charge-limited currents (SCLC). We have emphasized here the importance of drawing a distinction between situation in crystalline and amorphous (Se-based) semiconductors. While contact phenomena in a wide range of crystalline materials appear to be well understood, for amorphous chalcogenides contact phenomena remains a controversial issue. In short, one can not exclude completely a possible influence of SCLC on our data. One would expect space charge region to be formed in amorphous selenides. The presence of extremely slowly decaying currents as a response on applied bias is of favour of such an approach. Next question is closely connected with the space charge region extention, namely with x_0. Further, a charge density

$$\rho(x)=-e^2g(E_F)/U(x)$$

is produced by the band bending potential U(x). From the solution of Poisson's equation

$$d^2U(x)/dx^2=U(x)e^2g(E_F)/_{\varepsilon\varepsilon 0}$$

one can obtain

$$U(x)=U0exp(-x/x0)$$

With the characteristic screening length

$$X_0^2=_{\varepsilon\varepsilon 0}/e^2g(E_F).$$

Note that $g(E_F)$ is the density of gap states at the Fermi level E_F. To account for the short screening length characteristic of amorphous semiconductors, relatively high density of localized states is required. The latter is valid only under condition of negligibly small density of interface states. In practice, space charge accumulation effects are established by time-of-flight (TOF) experiments. Space charge effect influence on photocurrent transients in a-Se is not new (see e.g. Spear,1967). For a very large range of compositions, we observe TOF signal decreasing when the sample is photoexcited without short-circuiting and dark-resting between transits. It seems, however, that SCLC is not of primary importance because there is a strong dependence on the metal used. Additionally, the amount of space charge estimated is not sufficient even in predicted by conventional SCLC theory values.

Up to this point emphasis has been placed on purely electronic contact-related effects: possible chemical reaction on the interface were ignored. However, it will be seen that in some cases it is difficult or even impossible to avoid chemical reaction or alloying effect. Strong chemical reactions seem to occur at the Ag and Cu contacts. Comparatively thin (200-300 A) metallic electrode gradually disappeared by reacting with the amorphous chalcogenide. Such an effects may be observed even visually: the surface of electrodes become mottle instead of their initially mirror-like reflectance. A steady open circle dc voltage appeared between opposite electrodes. This small voltage is of measurable value (>40 μV) and indicates the chemical reaction process. It is reasonable in the following to consider a simple device structure Me/a-Se/SnO_2, containing alloy region at the interface. The equivalent circuit consists of two branches each of them includes the capacitance C_i and resistance R_i of the bulk region (thickness d_1) and alloy region (thickness d_1), respectively. The following asymptotic values may easily be obtained (in assumption that $C_1 >> C_2$)

$$C_p \sim C_1R_1/(R_1+R_2)^2$$

$$R_p(0) \sim R_1+R_2$$

$$R_p(8) \sim R_2$$

Here (0) and (8) indicates low and high frequencies, while C_p and R_p is the equivalent capacitance and resistance.

This fact is strongly supported by photoemission and electrone microscope studies [14].

For gold contacts diffusion and alloying occurs very slowly. In no case any change in electrical behavior was observed even on a time scale of months following deposition. Further, it is noticeable that when Al was used as a bottom contact, a high contact resistance was evident at low voltages. A commonly know fact that Al oxidized rapidly. Thus, a thin insulating layer was present between the metal and amorphous chalcogenide.

It is apparent that the major mechanism which causes the observed behavior is the current limiting by the injection of holes across the Me/a-Se junction. For all the composition examined here the electron work function is larger (5.3÷6.0 eV) than for each of the metal used as the top electrode. As a result, formation of a Schottky barrier to holes seems to be plausible interpretation.

5.Acknowledgments

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1. N.F.Mott and E.A.Davis Electronic processes in Non-Crystalline materials. 2nd Edn. Oxford: clarendon 1979
2. A.Madan and M.P.Shaw. The Physics and Applications of amorphous semiconductors. 1988 New York: Academic
3. A.Feltz. Inorganic vitreous materials. Berlin, 1987.
4. R.Zingaro, W.Cooper. Selenium, Van Nostrend, New York 1974
5. S.O.Kasap, in: Handbook of imaging materials (Diamond, Ed.) New York (1991).
6. A.Wallace and J.Robertson. Inst. Of phisycs conf. Ser. 22. 1974, p.237-245.
7. Horng-Yhi Wey. Phys.Rev. B 13. 1978, p.3495-3505.
8. M.Alkowitz and H.Seher. Phil. Mag. 35, 1977, p.1585-1608.
9. A.Andriesh, Rev.Roum. Phys. 26, 883 (1984).
10. S.O.Kasap, V.Aiyah, B.Polischuk and A.Baillie. J.Appl. Phys. 83, 1998, p.2879-2887.
11. B.Polischuk, S.O.Kasap, V.Aiyah and M.Alkowitz Can. J. Phys. 69, 1996, 361-369.
12. A.Rowlands and D.Humer. Med. Phys. 18, 1991. 421.
13. W.Zhao and J.A.Rowlands. Med.Phys. 22, 1995, 1595.
14. J.A.Rowlands et al. Radio Graphics 17, 1997, 753.
15. V.I.Mikla, J.Phys.: Cond. Matter. 8, 429 (1996).
16. A.Kikinashi. Appl. Optics, 76, 361, (1996).
17. V.I.Mikla, J. Non-Cryst. Solids, 1999
18. K.Tanaka, J. Non-Cryst. Solids, 198,749 (1996).

ПЕРЕХІДНІ ТА СТАЦІОНАРНІ ХАРАКТЕРИСТИКИ КОНТАКТІВ З АМОРФНИМ СЕЛЕНОМ ТА ЙОГО СПЛАВАМИ

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Представлені результати дослідження поведінки структур Me/a-Se/SnO_2 при прикладанні позитивного зміщення. Для значної кількості металів, що утворюють верхній електрод, визначено електрофізичні характеристики. Розглянуто можливі фізичні процеси, що зумовлюють релаксаційні процеси у досліджуваних структурах.