



Semi-Conductors with Mobile Ions Show a New Type of I-V Relations

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Abstract. Semi-conductors with mobile acceptors or donors show a new type of I-V relations. This paper presents experimental results for solid state devices based on copper oxide, found to be Cu_2O , which exhibit these I-V relations. The cells examined are $\text{Cu}|\text{Cu}_2\text{O}|\text{In}$ and $\text{Cu}|\text{Cu}_2\text{O}|\text{Ag}$ and similar ones tested at room temperature. The measured I-V relations are different from those reported for the same type of cells in the past, which were explained to be fixed by a Schottky barrier $\text{Cu}|\text{Cu}_2\text{O}$. We find that the I-V relations relax over a long time which we claim is due to ion redistribution. The new I-V relations can then be explained by assuming that Cu_2O is a mixed-ionic-electronic-conductor and adopting a theory developed by us in the past and modified to be applicable to the relevant defect model here. In this case the contribution of Schottky barriers is insignificant.

Keywords: mixed-ionic-electronic-conductor, MIEC, I-V relations, semi-conductor, Schottky barrier, Cu_2O

1. Introduction

The current voltage relations in a semi-conductor seem to be very well known. This is true also for devices based on the contact between two semiconductors or a conductor and a metal. However, this statement is correct only if the ionic defects in the semiconductor, such as donors and acceptors, are immobile. It is customary to assume that the donors and acceptors, after being introduced into the solid at elevated temperatures, are immobile at room temperature and that any slow diffusion (over a time scale of years) is considered as “aging”. The I-V relations are very different when the acceptors or donors are allowed to move under the applied voltage. The time scale then is that of the measurement, i.e. from a fraction of a second to a few hours. The ionic defect redistribute under the applied voltage which affects the electron and hole distribution, as well. Local neutrality, or quasi local neutrality [1], may take place due to the motion of both electrons/holes and ions. In the region where the concentration of defects

is enhanced the local electronic conductivity may be significantly enhanced while in the depleted regions it may be significantly suppressed. Whether the overall conductivity of the solid is enhanced or suppressed under the applied voltage depends on the details of the defect model.

In order to examine the effect of migration of the ionic defects in a mixed-ionic-electronic-conductor (MIEC) on the I-V relations, we have measured these relations for cells of the type $\text{Metal1}|\text{Cu}_2\text{O}|\text{Metal2}$. Typical measured I-V relations are shown in Figs. 1 and 2, for the cells $\text{Cu}|\text{Cu}_2\text{O}|\text{In}$ and $\text{Cu}|\text{Cu}_2\text{O}|\text{Ag}$, respectively. These results stand in contradiction to those reported for similar cells for many years [2–7] and also in a recent publication [8]. It should be recalled that the $\text{Cu}|\text{Cu}_2\text{O}$ Schottky junction served as the rectifying device before the Si era [2–7] and found interest in solar collector research more recently [9–12]. Typical I-V relations reported in those references are shown qualitatively in Figs. 3 and 4. None show a true Schottky barrier behavior of the form,

$$I = I_0(\exp\{qV/k_B T\} - 1) \quad (1a)$$

using common notation. While an asymmetry is usually reported, the “forwards” branch is, in some cases,

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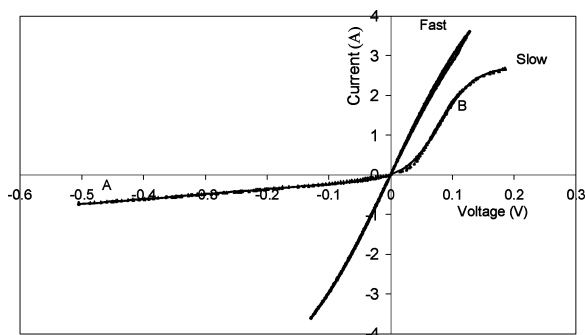


Fig. 1. I-V relations for the cell Cu|Cu₂O|In at room temperature. Voltage defined positive when (+) on Cu. Solid line: Eq. (2b) fitted to “slow” (33 h) results with $n = 2$, $I_0 = 1.3$ A, $V_0 = -0.08$ V, $R = 0.8 \Omega$.

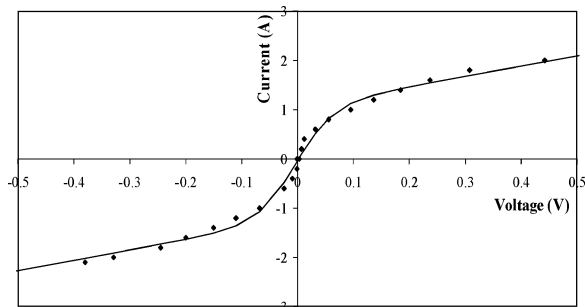


Fig. 2. I-V relations for the cell Cu|Cu₂O|Ag at room temperature. Voltage defined as positive when (+) on Cu. Solid line: Eq. (2b) with $n = 2$, $I_0 = 1$ A, $V_0 = 0.004$ V, $R = 0.38 \Omega$. Due to the small value of V_0 this practically reduces to Eq. (2a).

not exponential in the voltage V and in all cases the “reverse” branch is not exhibiting a limited current. This may be due to a leak in parallel to the barrier the origin of which is not always clear. In some cases it was suggested that metallic precipitates form this parallel path [13, 14]. In a recent publication these “leaking” Schottky I-V relations were observed again and fitted by [8].

$$I = I_0(\exp \{q(V - R_0 I)/k_B\} - 1) + (V - R_0 I)/R \tag{1b}$$

where R_0 is the resistance of the oxide layer (assumed to be independent of the voltage) and R is the leak resistance of the Schottky barrier.

We found that the I-V relations depend on the preparation conditions and one can also recover the “old” I-V

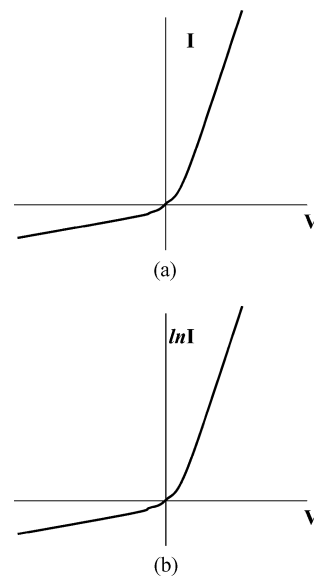


Fig. 3. Two types of I-V relations reported in the past for Cu₂O/Metal contacts. (a): I depends asymptotically linearly on V . (b) I depends exponentially on V for both polarities.

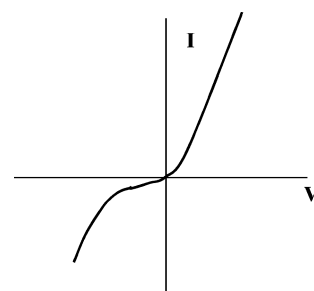


Fig. 4. Types of I-V relations (qualitative representation) reported in the past [2–8] for the Cu₂O/Metal contact exhibiting other I-V characteristics than reported in this work.

relations under certain heat treatment conditions as will be discussed below.

We also observed that the I-V relations change with time. This is indicated in Fig. 1 as “fast” and “slow” (to be explained in detail below). This time dependence was observed for all cells tested, which have thin oxide layers. In Fig. 2 only the “slow” result is shown while the “fast” one is again almost linear. As earlier reported we observed for some cells that the I-V relations changed the nature (i.e. typical curvature) after a breakdown and that they recovered their original nature after a week [15]. We claim that all these variations

with time are due to migration of the ions in the oxide. For bulk samples under dc current for a length of time, morphological changes are observed near the positive and negative electrodes.

Our interpretation of the I-V relations exhibited in Figs. 1 and 2 is therefore completely different from the previous one assuming a Schottky barrier. The present explanation is based on the I-V relations of a mixed-ionic-electronic-conductor (MIEC). Cu_2O is known to be an MIEC at elevated temperatures (with a dominant hole conduction) [16] and it is assumed that it is an MIEC also at room temperature. Then, under an applied voltage, the ions that serve as mobile acceptors redistribute and so do the holes. This affects the resistance of the Cu_2O layer to hole conduction.

One may suggest that the I-V relations in Figs. 1 and 2 look like those of two Schottky barriers back-to-back. Our key objection to this is that we observe a rate dependence. In the “fast” run the curve is almost linear while in the “slow” one it is quite curved. However, the almost linear “fast” one, shown in Fig. 1, takes three hours to measure and one cannot understand this as due to a lack of response of the holes in a Schottky barrier. It is most likely due to the lack of significant ion motion in the oxide layer. Why are our results different from those reported before is still under investigation. Some possible explanations are discussed below.

2. Experimental

2.1. General

Films of Cu_2O (and CuO) were prepared by thermal oxidation, thermal oxidation through a silver layer, anodic and cathodic oxidation and reactive sputtering. In addition, bulk CuO samples were prepared by a standard ceramic method of pressing and sintering. Cu_2O bulk was obtained from CuO by reduction. We describe in more detail the films obtained by thermal oxidation and the bulk samples.

2.2. Thermal Oxidation

The preparation of $\text{Cu}|\text{Cu}_2\text{O}$ contacts as reported in the literature is done usually by thermal oxidation. A copper plate is heated to above 1041°C in room atmosphere and quenched. A black CuO scale formed during quenching is removed either mechanically or chemically. Afterwards the $\text{Cu}|\text{Cu}_2\text{O}$ pair is annealed at $500\text{--}600^\circ\text{C}$. This results in a new CuO scale on top

of the Cu_2O layer which is then removed [8]. An electrode, such as graphite or lead is then, usually, pressed onto the Cu_2O surface forming the cell $\text{Cu}|\text{Cu}_2\text{O}|\text{M}$, $\text{M} = \text{C}$ or Pb .

The thermal oxidation procedure we used deviated from the previous one in that the annealing and subsequent steps were not preformed. Also in most cases quenching in air only was used after heating a copper foil to over 1041°C . A thick ($\sim 100\ \mu\text{m}$) black CuO layer is obtained which, in many cases, is easily removed. Below it a thin reddish layer of Cu_2O is exposed. X-ray diffraction measurements reveal strong Cu_2O lines, some weak Cu lines (which we assume to be contributed by the copper substrate) and no CuO lines. This means that any CuO , if it is present, forms a thin layer, much thinner than $1\ \mu\text{m}$ and that the Cu_2O film thickness is of the order of $1\ \mu\text{m}$. We denote here layers of the order of $1\ \mu\text{m}$ or less as thin ones. Rapid quenching from $\sim 1041^\circ\text{C}$ was done also by dropping the oxidized copper foil into room temperature water. This resulted in a thick ($\sim 100\ \mu\text{m}$), black oxide, mostly CuO , well adhering to the remaining copper foil which was therefore not used for the present I-V measurements.

We experimented with different ways to do the thermal oxidation with quenching in air resulting in thin oxide layers. However, we observed that there is a simple way to achieve this which yields samples exhibiting the same I-V relations. This is done by heating, using a torch, of the upper surface of a 2 mm thick copper plate, held horizontally. Heating lasts until the upper layer of the copper melts. When the torch is adjusted (fuel vs. oxygen mixture) for the right temperature range only the upper layer of the Cu plate melts. This assures that the temperature of 1041°C is exceeded (as the melting temperature of Cu is 1083°C). (It also controls the local oxygen partial pressure). After the copper is quenched the black scale formed at the outer surface either falls off or is easily removed leaving a reddish Cu_2O on Cu . The thickness is different from sample to sample and not uniform on a scale larger than a few mm. This is due to a non uniform temperature distribution during preparation. This is convenient for research purposes, at this stage, as it provides a range of different conditions. The estimated thickness of Cu_2O is of the order of $1\ \mu\text{m}$ or less. This was determined from X-ray diffraction intensities and by examining cuts using SEM. Intermediate purity (99.9%) and technical grade copper samples were examined. No significant difference was observed in the nature of the I-V relations.

Contacts for the samples prepared by thermal oxidation of copper in air were made by pressing indium onto the Cu_2O . To press the indium contacts we used a U shape metal clamp with a screw on one side pressing the indium onto the oxide while an insulation is placed between the copper plate and the clamp on the opposite side. Typical I-V relations measured on the thin oxide layers are shown in Fig. 1. It is seen that the results depend on the rate of voltage scan. “fast” and “slow” are not unique and depend on the film thickness and temperature when it is varied in the range 0–50°C. In Fig. 1 “slow” corresponds to a total scan of 33 h and “fast” to 3 h, both done at room temperature. The I-V relations are not symmetric with respect to inverting V and I . However, a shift in V of 75 mV and in I of 1.5 A yields symmetric relations. With area of the sample being 0.25 cm² the current density at 0.1 V is ~ 10 A/cm².

For thick oxide layers the I-V relations exhibited a different form similar to that shown in Fig. 4. The estimated time needed to induce significant changes in the I-V relations is at least 180 days. Indeed a 22 days scan revealed only a small variation of the I-V relations. The current density under ~ 0.1 V is $\sim 10 \mu\text{A/cm}^2$. This low value as compared to a current density of ~ 10 A/cm² is consistent with the much larger thickness of the “thick” samples. However, since the resistivity depends on the stoichiometry [16] an exact, quantitative comparison cannot be made.

2.3. Thermal Oxidation Through a Silver Layer

The sample Cu|Cu₂O|Ag, referred to in Fig. 2, was prepared by diffusion of oxygen, at 300°C, for 60 min. through a 15 μm layer of silver evaporated onto a copper metal plate. In other cases a current of 1 mA was applied to the cell during the oxidation with positive polarity on the copper. We examined also repeated oxidation of a given sample at 300°C for multiple steps of 30 min each. I-V measurements at room temperature were done after each 30 min oxidation step. The oxide layer resistance increased with each step, as one would expect. For the first 4 steps (120 min) the I-V relations look qualitatively as in Fig. 2. We also examined oxidation at higher T (500°C) for different time length (5–120 min). At this temperature oxidation is rapid and thick CuO layers form that peel off readily together with the Ag layer that is meant to serve as an electrical contact.

One can argue that for the samples prepared at 300°C for up to ~ 120 min, in between the silver and the copper, the oxide formed can only be copper, rather than silver oxide. The reason is the larger free energy change for oxidation of copper. Furthermore, a gradient in the oxygen across the silver must exist in order to drive the oxygen diffusion through the silver layer. This decreases the oxygen gradient across the Cu₂O layer formed. The only limitation is that the experiment has to be terminated before a thick Cu₂O layer forms as this significantly reduces the oxidation rate resulting in an enhanced oxygen activity at the oxide/Ag interface. This may yield a CuO layer which develops between the Cu₂O and the silver.

Non destructive examination of the morphology of the oxide layer in the cell Cu|Cu₂O|Ag, is not possible. Electrical conductivity estimates can be misleading. We know from our characterization of Cu₂O that the electrical conductivity of the oxide can vary by a few orders of magnitude depending on the stoichiometry [16]. Yet we tried to determine the thickness of the oxide being formed, in-situ, by calibrating the thickness vs. resistance between the silver layer and the copper. For that we apply a voltage of 10 mV to the Cu/Ag pair and follow the current, while holding the pair Cu/Ag in hot air over an open furnace, operating at 500°C. One would expect that as the oxide is formed the resistance will increase monotonically with the oxide thickness. Preliminary tests show that this works only qualitatively. A problem seems to arise at a loose oxide/metal interface. This is still under investigation.

2.4. I-V Relations and Breakdown

The I-V measurements reported here were done at room temperature, in air. We assume that the electrodes can be considered to be blocking for ions and the interaction with air is negligible. The applied voltage was limited to below 0.5 V for chemical stability and in order to avoid heating as mentioned below.

When the applied power is too high heating becomes significant, the current increases while the voltage decreases (negative resistance) [15]. Therefore the I-V relations were measured up only to a voltage of ~ 0.5 V and the thin samples measured at room temperature were cooled by a fan. As mentioned before, shortly after the breakdown the I-V relations are different from those shown in Figs. 1 and 2. However, after a week the

I-V relations were found to recover their original shape qualitatively similar to those shown in Fig. 2 [15].

A breakdown, reflected as a sharp increase in current vs. V , but no negative resistance, can have also a different origin. As we discuss below, it is assumed that the electrodes are blocking for material exchange. Under a high applied voltage this assumption may not be valid and an electrochemical reaction can take place at the electrodes. This then results in an enhancement of the measured current. This behavior is not reached within the 0.5 V limit we refer to here.

2.5. Bulk Cu_2O and CuO

With the thin layer samples true four point measurements are not possible. We therefore prepared bulk CuO samples ($10 \times 4 \times 4$ mm) with four Pt + 10%Rh electrodes (0.3 mm diameter) in a row as shown in Fig. 5. Electrodes 1 and 4 are current carrying while the two inner electrodes 2 and 3 are voltage probes. The voltage is defined positive when the larger index electrode is the more positive one. (Thus for $V_1 < V_4$, $V_{14} > 0$). The geometrical coefficients were analyzed by us [17]. The bulk CuO was reduced to Cu_2O at 800°C under 10^{-4} atm $\text{P}(\text{O}_2)$ for 15 h. The I-V relations measured are shown in Fig. 6. V_{23} is roughly proportional to the current. V_{12} and V_{34} are not symmetric with respect to inversion of V and I simultaneously. The relation of I vs. the total voltage $V_{14} = V_{12} + V_{23} + V_{34}$ is qualitatively similar to that shown in Fig. 2. This is more pronounced for I vs. $V_{12} + V_{34}$ with the linear term V_{23} omitted. It is evident that the deviation from linearity occurs in the sections that contains the electrodes. This, however, does not necessarily mean that the deviation is due to the bulk/electrode interface. We claim that this can be due to the region in the bulk near the interface. The measurements started with a time drift at constant current ($\sim 4 \mu\text{A}$) and only then was the current changed. A time dependence is indicated as a hor-

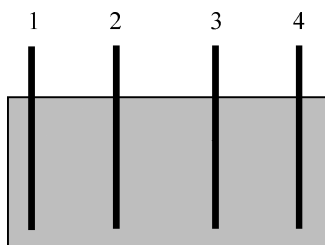
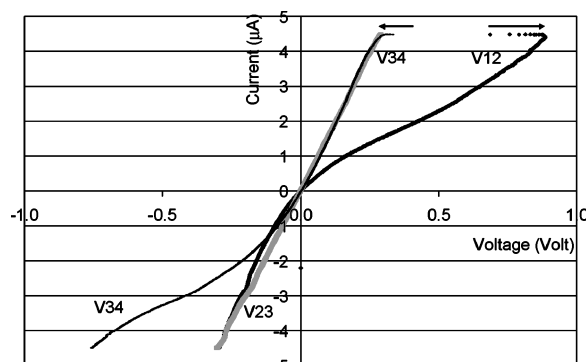
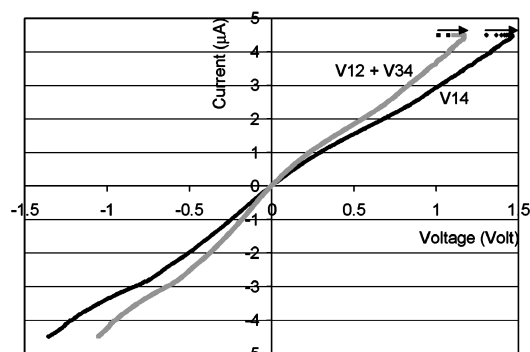


Fig. 5. Four electrode arrangement in a rectangular sample.



(a)



(b)

Fig. 6. I-V relation measured on bulk Cu_2O using four electrodes. (a) Current vs. voltage drop on each section V_{12} , V_{23} and V_{34} . (b) Current vs. total voltage drop, $V_{14} = V_{12} + V_{23} + V_{34}$ and vs. $V_{12} + V_{34}$. Arrows: show the initial time evolution at constant current.

izontal line, i.e. a voltage drifting with time for a constant current (drift time 30 min). The curved relations are obtained after significant time elapsed. Therefore, the curved I-V relations are due to ion motion where acceptors depletion occurs close to the negative electrode, as discussed below. The curvature is then not due to a leaking Schottky barrier. It should be noticed that in the positive branch, $V_{14} > 0$ ($V_4 > V_3 > V_2 > V_1$) acceptors are depleted near the negative electrode 1 and accumulate near the positive electrode 4. Thus the hole concentration is enhanced near electrode 4 and the local resistivity drops, while the hole concentration is reduced near electrode 1 and the local resistivity increases. Therefore V_{34} decreases with time for constant current as seen in Fig. 6(a) while V_{12} increases.

Further support for ions motion at room temperature is obtained from lengthy dc measurements (140 h and 10 mA under ~ 2 V) where morphological and

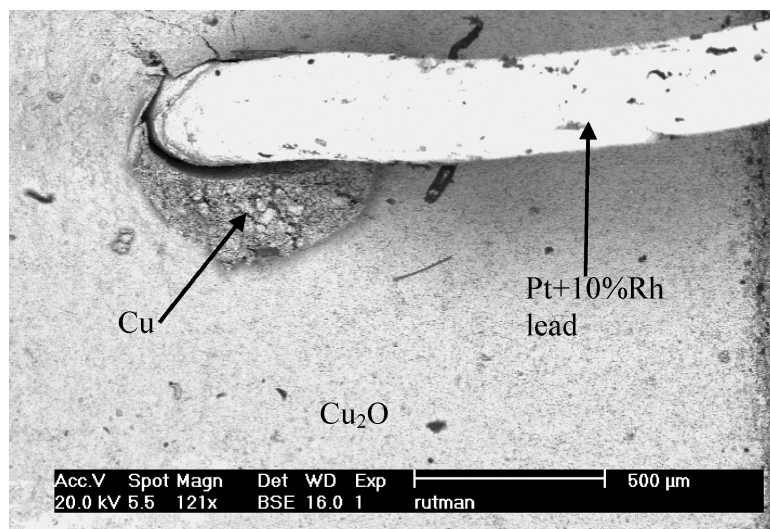


Fig. 7. Accumulation of Cu + Cu₂O near the Pt + 10%Rh negative electrode/lead, inserted into a Cu₂O bulk sample, after applying a current of 10 mA for 140 h, at room temperature.

composition changes are observed near the positive electrode 4 (removal of the oxide material due to arrival of copper vacancies, the composition changes to CuO) and near the negative electrode 1 (pile up of Cu due to removal of copper vacancies, (the pile is mixed with 25 mol% Cu₂O material)), as shown in Fig. 7. This proves that the current is carried in part by ions and not only by holes. We notice that the amount of copper deposited is relative small indicating a small ionic transference number (to be determined quantitatively later). The applied voltage was ~ 2 V higher than that applied to the films (< 0.5 V) and the current density near the wire electrodes significantly higher than in most of the bulk allowing for decomposition of the bulk sample.

3. Fitting of I-V Relations

The I-V relations shown in Figs. 2 and 6(b) seem to be best fitted by an expression of the form:

$$I = I_0 \tanh\{\beta q V/n\} + V/R \quad (2a)$$

while those shown in Fig. 1 by

$$I = I_0 [\tanh\{\beta q(V + V_0/n)\} - \tanh\{\beta q V_0/n\}] + V/R \quad (2b)$$

where I_0 is a limiting current, q the elementary charge, V the applied voltage, $\beta = 1/k_B T$ with k_B the Boltzmann constant and T the temperature, $n = 2$ or 4 and R a resistance. V_0 is a constant denoted as a “shift” on the V coordinate. We extended a theory developed by us in the past [15, 18]. and derived I-V relations in agreement with Eqs. (2a) and (2b) [19]. The new theory can explain these results if one adopts a certain defect model known for Cu₂O from elevated temperatures [16]. We assume the same defects exist also at room temperature. The difference being that their mobility and concentration are expected to be lower. The defect model comprises, at room temperature:

- (a) Mobile ionic defects: V'_{Cu} with concentration: $[V'_{Cu}] = N$.
- (b) Immobile acceptors O''_i with concentration: $[O''_i] = A/2$.
- (c) Holes with concentration p .

This material is thus a mixed-ionic-electronic-conductor, MIEC. We use the Kröger-Vink notation of point defects [20].

The local neutrality condition is:

$$A + N = p \quad (3)$$

At elevated temperatures no n -type conductivity is observed for Cu₂O and under reducing conditions the

oxide decomposes to Cu without exhibiting a reduced n -type oxide [16]. We believe that this holds also for room temperature because of the large band gap of Cu_2O (2 eV). In other words the p -type conductivity is the dominant electronic conductivity in the oxide even under reducing conditions (before decomposition occurs). It is further assumed that the electrodes used are blocking for material exchange and that this holds also for a copper electrode at room temperature. Since material is transported as ions of one charge value this means also that the electrodes are blocking for ionic current [21].

The I-V relations can be explained, qualitatively, as follows. The applied voltage forces the ions to move. Due to local neutrality the holes follow the changing concentration of the ions (see Eq. (3)). (As long as the gradient in the acceptor concentration is not too high quasi local neutrality can be maintained. For further discussion of the question of quasi local neutrality we refer the reader to ref. [1]). As the electrodes are blocking the transfer of material and ions, the V'_{Cu} ionic defects pile up in the oxide near the positive electrode side and are depleted near the negative electrode side. If there were no fixed acceptors (i.e. $A = 0$) then the resistance of the MIEC would increase with voltage due to the depletion of the ions and holes on one side. This has been shown to lead to I-V relations of the form: [15].

$$I = I_0 \tanh\{\beta q V/4\} \quad (2c)$$

The presence of fixed (immobile) acceptors adds a background constant conduction of holes and thus a parallel current with ohmic I-V relations. The total current is then of the form given in Eq. (2a) with $n = 4$ when the concentration of the immobile ions is low ($A \ll N$) and with $n = 2$ if it is high $A \gg N$. The parameter V_0 appearing in Eq. (2b) reflects the gradient in, $A(x)$, the distribution of the immobile acceptors in the case when $A(x)$ it is not uniform (x is measured perpendicular to the oxide film plane). A gradient in $A(x)$ causes the breaking of the symmetry of the sample with respect to $(+x) \rightarrow (-x)$ and therefore with respect to $(+V) \rightarrow (-V)$ [19].

4. Discussion

It has been shown that the I-V relations measured, in air, at room temperature, on cells of the type

$\text{Cu}|\text{Cu}_2\text{O}|\text{Metal}$ depend on the preparation conditions. For certain preparation conditions the I-V relations look as in Figs. 1 and 2. These can be explained as being fixed by the copper oxide bulk which is a mixed ionic electronic conductor. Under other preparation conditions the I-V relations look quite different, qualitatively as in Figs. 3 or 4. These seem to reflect a Schottky barrier at the bulk metal interface with an ohmic leak in parallel.

The difference between the samples can only be in the morphology (thickness and smoothness) of the oxide layer and in the concentration and distribution of the defects, most probably those of excess oxygen acceptors $A(x)$. $A(x)$ cannot be uniform as near the Cu substrate the concentration of acceptors need to be low while on the other side of the oxide, facing room atmosphere, $A(x)$ is expected to be high. In addition to the deviation from stoichiometry we cannot exclude the possibility that a second phase of CuO is present in small concentrations or as a thin layer that cannot be detected by XRD and other surface physics methods accurate to 0.1% at best. It is at present not possible to examine the distribution in $A(x)$ in a thin layer with thickness of the order of $\sim 1 \mu\text{m}$. The reason is that the value of $A(x)$ (quenched from elevated temperatures) is of the order of 0.1% or less [16].

To understand the new I-V results we suggest the following. Basically the oxide is a MIEC. When prepared as a thin layer the mobile acceptors can diffuse over the small thickness of the oxide within about one hour. This redistribution of the acceptors significantly modifies the hole concentration and thus also the I-V relations. The current, I , is dominated by the hole current. (The motion is under a drift due to an applied voltage thus any diffusion coefficient estimated from the measurements is an upper limit to the true one. An estimate yields $\tilde{D} \sim 10^{-13} \text{ cm}^2/\text{S}$). Any contribution of a Schottky barrier is not observed. This can be explained by assuming that the impedance of the bulk is higher than the impedance of the electrode/ Cu_2O contacts. The significance of the Schottky barrier seems to be dependent on the heat treatment. This suggests that the distribution of defects in the oxide near the contact with the copper plate (except perhaps at the very contact with the metal) is different for different heat treatments resulting in different Schottky barriers characteristics.

The difference in the I-V relations of the cell with the Ag and the In contacts are due to different oxide bulk properties and not metal/oxide contacts. The difference

is in the acceptor concentration and the distribution of the immobile ones. The silver electrode is applied before the heat treatment and oxygen has to diffuse through it. The In electrode is applied after the heat treatment, usually to a Cu₂O layer revealed after a thick CuO scale has been removed.

As a rule, all samples that showed the skewed $\tan h$ behavior of Eq. (2a) or (2b) for “slow” measurements, exhibited almost linear I-V relations when the measurement was “fast”.

5. Conclusion

The I-V relations of devices of the type Cu|Cu₂O|Metal exhibit new I-V relations when the oxide is prepared in a manner different than in the past. We observe a skewed $\tan h$ type I-V dependence, Eq. (2a) or (2b). The $\tan h$ contribution can be explained if the oxide is assumed to be a mixed ionic electronic conductor, MIEC, with mobile acceptors, holes as the dominant electronic charge carriers and electrodes that are blocking for ionic current. The skewness is due to immobile acceptors (with concentration A) assumed also to be present. They introduce additional holes and lead to an ohmic contribution i.e. linear I-V relations. If the distribution of immobile acceptors is not uniform and changes monotonically, the point of symmetry of the skewed $\tan h$ relations is shifted with respect to the origin. The dependence on voltage/current scan rate and the changes in the morphology under lengthy dc current, indicate that ionic motion occurs. We are still working on revealing the exact reason for the difference in our new measured I-V relations shown in Figs. 1 and 2 as compared to others reported in the literature and shown qualitatively in Figs. 3 and 4. We do not think that it is the purity of the copper used as we tried different levels of purity and obtained qualitatively, similar results. We suspect it is dependent on the concentration and distribution of the acceptors in particular the immobile ones. Another possibility being examined is the composition of the oxide whether pure Cu₂O or

contaminated with a small concentration of CuO. We suspect also that it is associated with the thickness of the film which, when thin enough, allows migration of ions within the time of the experiment. In any case the impedance of the metal/oxide contact must be lower than the bulk one.

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