TRAPS IN ZIRCONIUM ALLOYS OXIDE LAYERS

Helmar Frank

Department of Solid State Engineering, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University,
Trojanova 13,CZ 120 00 Prague 2, Czech Republic
Phone:+420 224 358 559, fax:+420 221 912 407, e-mail: frank@kml.fjfi.cvut.cz

Summary Oxide films long-time grown on tubes of three types of zirconium alloys in water and in steam were investigated, by analysing I-V characteristics measured at constant voltages with various temperatures. Using theoretical concepts of Rose [3] and of Gould [5], ZryNbSn(Fe) proved to have an exponential distribution of trapping centers below the conduction band edge, wheras Zr1Nb and IMP Zry-4 proved to have single energy trap levels.

1. INTRODUCTION

In continuing our investigation of the conductivity mechanism of thin oxide films grown on tubes of Zr1Nb, ZrNbSn(Fe) and IMPZry-4, used for fuel cladding in light water reactors, which had been grown either at VVER conditions (water at 360°C) [1], or had been oxidized in steam at 400°C, current - temperature measurements had been performed at constant applied voltages. The preparation of the samples, evaporation of Au-contacts, measuring procedures and resulting I-V characteristics are described in the cited paper and will not be repeated here. The aim of this work is the further interpretation of the achieved measuring results to assess the influence of traps. The chemical composition of the samples is in Tab.1

Table 1. Chemical composition (wt%) of zirconium alloys used in the present study

	Nb	Sn	Fe	Cr
Zr1Nb	1	-	-	-
ZrNbSn(Fe)	1	1	0.1	-
IMP Zry-4	-	1.3	0.2	0.1

2. THEORETICAL ASPECTS

The I-V characteristics of high-resistivity semiconductors start at low voltages with a linear part obeying Ohm´s law. At application of higher voltages the current rises faster due to the injection of majority carriers building up a space charge. The current develops a space-charge limited additional part. The measured current values can be fitted to a second order polynomial

$$I = aU^2 + bU + c. \tag{1}$$

The zero current expressed by the constant c can be observed above room temperature as a consequence of temperature-activated liberation of trapped electrons and/or continuing oxidation in air.

The space-charge limited current I_{sc}, i.e. the first term in eq. (1), obeys Child´s law [2]

$$I_{sc} = \frac{9}{8}\varepsilon\varepsilon_0 A\mu U^2 / w^3 = aU^2 , \tag{2}$$

where $\varepsilon\varepsilon_0$ is the relative and vacuum permittivity, respectively, A is the contact area, μ is the mobility of the free carriers, U the constant voltage and w the layer thickness.

The transition from the linear to the square part I_{sc} occurs at the characteristical voltage U_{ch}, when the rising space-charge limited current equals the linear ohmic part $I_o = bU$, i.e.

$$AU^2 = bU, \ or \ U = U_{ch} = b/a . \tag{3}$$

The ohmic current is

$$I_o = U/R = Uen_0\mu w/A . \tag{4}$$

The characteristical voltage U_{ch} , using eqs.(2 and 4), yields

$$U_{ch} = en_0 w^2/\varepsilon\varepsilon_0 . \tag{5}$$

By this expression the concentration n_0 of the free carriers can be obtained,

$$n_0 = U_{ch}\varepsilon\varepsilon_0/ew^2 . \tag{6}$$

This is a simple way to assess the concentration of the free carriers n_0 which, with knowledge of the resistivity ρ measured in the vicinity of the origin, yields also the mobility μ .

An other way to assess the mobility is using eq.(2) directly.

In the presence of traps with the concentration $N_{t(s)}$ at a single energy level E_s , eq.(2) is changing to

$$I_{sc} = \frac{9}{8}\varepsilon\varepsilon_0 \mu A \frac{N_C}{N_{t(s)}} \exp\left(-\frac{E_s}{kT}\right)\frac{U^2}{w^3} , \tag{7}$$

where N_C is the effective density of states in the conduction band. If the current is measured at a constant voltage as the function of temperature, then plotting $log\ I = f(1/T)$ appears as a straight line with the slope yielding the activation energy E_s of the traps. Measurement of the temperature dependence of the current at various constant voltages yields as much straight lines, which will be parallel, i.e. all having the same slope giving the same activation energy, if there is only one type of traps at a single energy level $E_{t(s)}$. With traps the characteristical voltage changes to U_F

$$U_F = U_{ch}/\theta , \qquad (8)$$

where $\theta = N_C/N_{t(s)} = n/n_t$ is the ratio of free to trapped charge [3] . When the Fermi level E_F rises over the trap level, the traps are flooded and the current rises with a higher power when the voltage exceeds U_F . The concentration of the traps can then be computed using

$$U_F = eN_{t(s)}w^2/\varepsilon\varepsilon_0 \ . \qquad (9)$$

Instead of traps on a single trap level there can be traps distributed exponentially below the conduction band edge. For this case Lampert [4] has shown that the space-charge limited current is given by

$$I = e\mu N_C A\left(\frac{\varepsilon\varepsilon_0}{eP_0kT_t}\right)^l \frac{U^{l+1}}{w^{2l+1}} , \qquad (10)$$

here P_0 is the trap density per unit energy range at the conduction band edge and l is the ratio T_t/T where T_t is a temperature parameter characterizing the exponential trapping distribution

$$P(E) = P_0 \exp(-E/kT_t) , \qquad (11)$$

where $P(E)$ is the trap density per unit energy range at an energy E below the conduction band edge. The total trapping concentration N_t is given by Gould and Rahman [5] as

$$N_t = P_0 \, kT_t \, . \qquad (12)$$

On the basis of the above expressions Gould [6] could show that $\log I$ versus $1/T$ characteristics for a given sample, when extrapolated to negative values of of $1/T$, will intersect at a common point whose coordinates are

$$\log I = \log\left(\frac{e^2\mu w N_C N_t}{A\varepsilon\varepsilon_0}\right) , \ 1/T = -1/T_t \, . \qquad (13)$$

The slopes of the lines are given by

$$\frac{d(\log I)}{d(1/T)} = T_t \log\left(\frac{\varepsilon\varepsilon_0 U}{ew^2N_t}\right) , \qquad (14)$$

which means that the slope is dependent on the measuring voltage. Therefore the lines are not parallel but are converging in the direction of higher temperatures and, extrapolated, will meet at a common intersection point. The intercept on the *log I* axis *(log I_0)* is given by

$$\log I_0 = \log(e\mu N_C U/w) \, . \qquad (15)$$

I_0 represents the current at infinite temperature *(1/T = 0)*, and is a theoretical abstraction, but is given by the constant b in the equation for the line $\log I = a(1/T) + b$ for $1/T = 0$. Using the set of equations (13), (14) and (15), the main parameters μ, N_t *and* T_t may be obtained.

3. RESULTS AND DISCUSSION

The logarithms of the current for different voltages up to 20 V are plotted versus the inverse absolute temperature in Figs.1 and 2 for samples Zr1Nb and Zry-4W, respectively.

In both cases the lines are parallel, with equal slopes, indicating the existence of single trapping levels.

In samples of ZIRLO, on the contrary, the lines of log I = f(1/T) at constant voltages were converging, with a typical example being shown in Fig.3. The slope of these lines decreases with increasing voltage, as is confirmed by Fig.4. In this case the extrapolated lines will meet at an intersection point situated in the negative 1/T domain. The convergence of the straight lines in Fig.3 is evident also in Fig.5, where the straight lines of the logarithm of the current versus applied voltages have a steeper slope at interception with the log I axis (upper line in Fig.5) than at room temperature (lower line in Fig.5).

The intersection point is calculated be solving the equations for the two lines for 35 V:
$\log I_1 = -2.2162\ x + 10.797$, and for 5 V $\log I_2 = -2.3033\ x + 10.076$, respectively, yielding
$x = -8.28$, giving $T_1 = 121$ K. Eq.(15) serves to calculate the mobility μ, assuming the density of states in the conduction band $N_C = 10^{21}\text{cm}^{-3}$, yielding $\mu = 1.9\text{x}10^{-4}\text{cm}^2/\text{Vs}$. This value substituted into eq.(13) serves to calculate the concentration of the traps $N_t = 6\text{x}10^{27}\ \text{cm}^{-3}$.

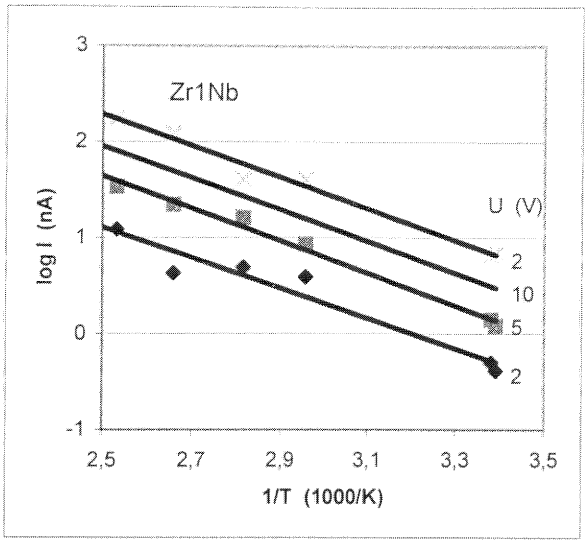


Fig.1 Parallel lines, single trapping level

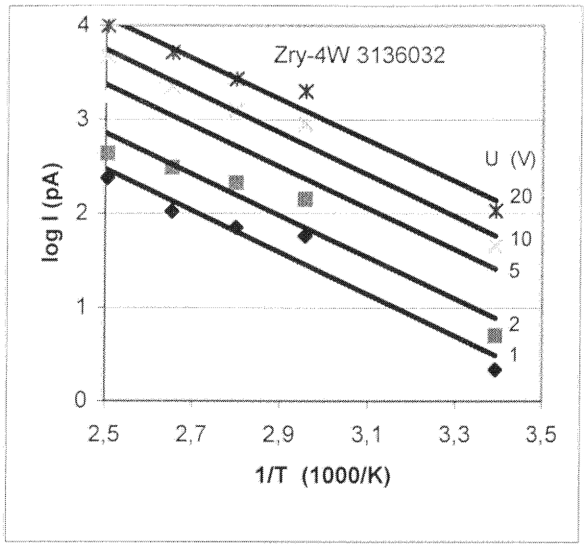


Fig.2 Parallel lines, single trapping level

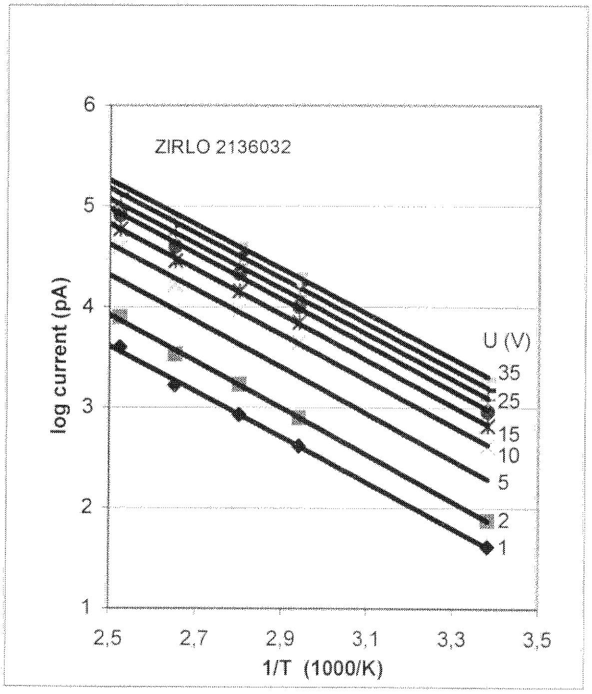
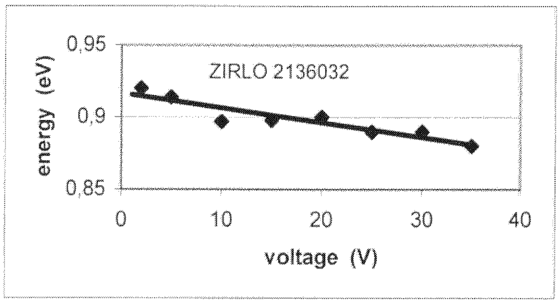


Fig.3 ZIRLO 2136032, lines slightly converging



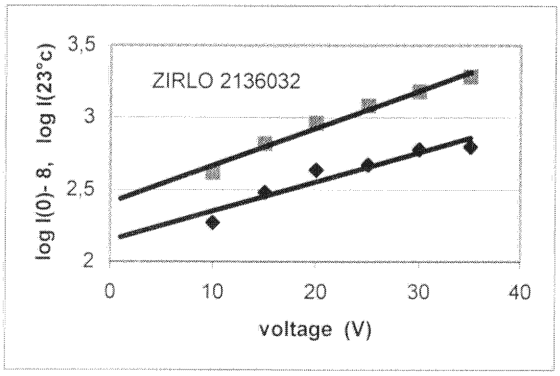


Fig.4 Slopes decreasing with increasing U
Fig.5 Current increasing with voltage

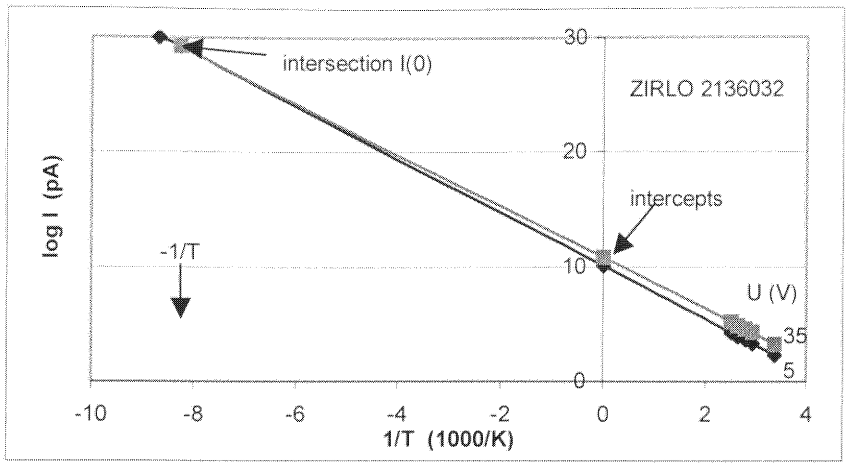


Fig.6 Extrapolation of the straight lines log I = f(1/T) for 5V and 35 V, respectively, yielding the intersection point at –1/T.

As a check on consistency these results were substituted into eq.(14) giving –1.81, and compared with the measured slopes, being –2.3. From a formal point of view this is sufficient, but a concentration of traps of this magnitude is impossible and the mobility is 4 orders of magnitude too high. As can be seen from Fig.5, the accuracy in measurement of T_1 is limited, due to the acute angle of intersection of the straight lines. When inserting the formerly measured mobility 1.1×10^{-9} cm^{-3} into eq.(15), then $N_C = 2.6 \times 10^{21}$cm^{-3}, and
$T_1 = 559$ K, which seems to be more acceptable.

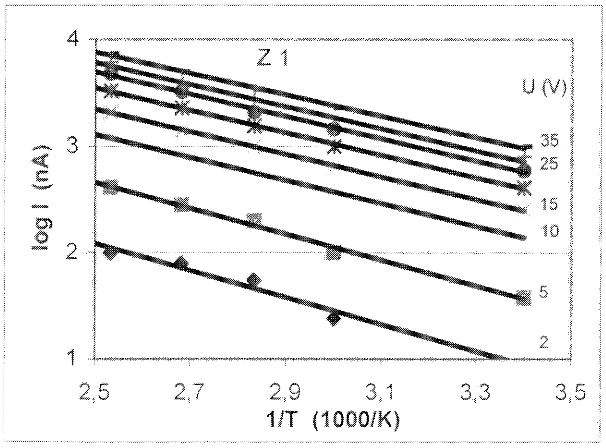


Fig.7 Log I = f(1/T) for U(2 – 35 V), Z1 Normal convergence

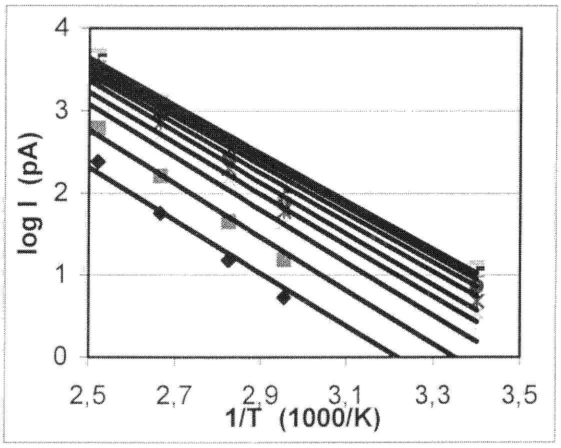


Fig.8 Log I = f(1/T) for U(2 – 40 V), Z2 Large convergence

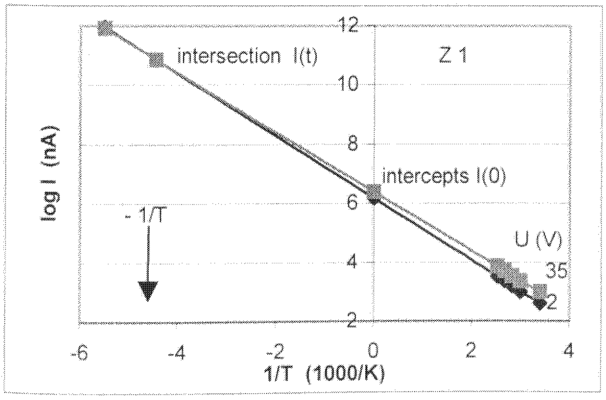


Fig.9 Z1, Intersection at 1/T = -4.45 (225 K)

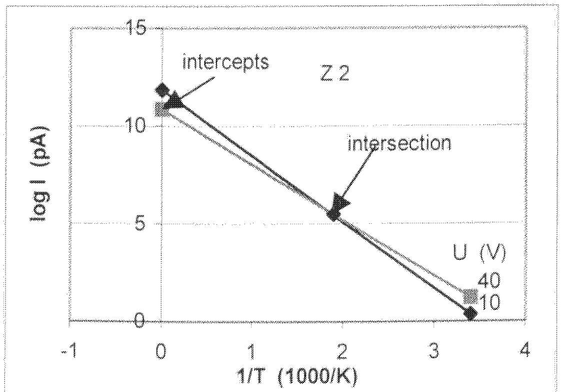


Fig.10 Abnormal intersection at positive 1/T

The behaviour of the other two samples of ZIRLO is depicted in Figs.7 and 8, and their extrapolation in Figs.9 and 10. The intersection point for Z1 gives 225 K, which is in reasonable agreement with Fig.6, but the abnormally high convergence of the lines of Z2 in Fig.8 places the intersection point in Fig.10 into the positive 1/T domain. It should be noted that the straight lines in Figs.7 and 8 are parallel in the linear (ohmic) range at low voltages up to 5 V, and convergent at higher voltages, when the space charge limited current is gaining preponderance. Evaluation of Fig.9 with $T_t = 225$ K and $I_t = 7.24 \times 10^{10}$ nA yields the mobility $\mu = 4.9 \times 10^{-9} cm^2/Vs$, and the trap concentration $1.3 \times 10^{17} cm^{-3}$, which seems reasonable. From Fig.10 only the existence of a high exponentially distributed trap concentration can be derived

4. CONCLUSIONS

Investigation of the temperature dependence of the current at various voltages proved the oxide films of Zr1Nb and IMPZry-4 to have a single trap level situated about 1 eV below the edge of the conduction band. The concentration of the free carriers was about $2 \times 10^{14} cm^{-3}$ and did not depend on the temperature. The exponential temperature dependence of the resistivity was due only to the temperature dependence of the mobility, which was extremely low.

The samples of ZryNbSn(Fe) (ZIRLO), analyzed according to the theory of Lampert [4] and of Gould [5], showed signs of an exponential distribution of trapping centers below the edge of the conduction band, but the accuracy of the measurements did not give sufficiently reliable results because of the high error in assessing the intersection point due to the very sharp angle of the converging straight lines $\log I = f(1/T)_U$

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