

Oxide Properties of Autoclaved Zircaloy Cladding Tubes Investigated by the Photoelectric Polarization Method

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This report concerns a study which has been conducted for the Swedish Nuclear Power Inspectorate (SKI). The conclusions and viewpoints presented in the report are those of the author and do not necessarily coincide with those of the SKI.

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Summary

Corrosion of zirconium alloys is an important lifetime limiting factor for the nuclear reactor fuel. The corrosion resistance of a metal is highly dependent on the ability of the surface metal oxide to transport electrons and ions, which is related to the stoichiometry of the oxide and the oxide defect concentration.

The Photoelectric Polarization Method (PEP) invented by E. K. Oshe [1] is a structure sensitive method which earlier has been investigated as a possible method to study the defect structure in zirconium oxides [2, 3].

The purpose of the following work is, by using more optimized experimental equipment, to verify if the PEP method is a suitable method to study the defect structure in zirconium oxides and to predict the corrosion resistance for different zirconium alloys.

The conclusions from the experiments are as follows:

- The modifications of the experimental setup by means of a new source of light (deuterium lamp) and a new oscilloscope with an amplifier gave distinct V_{pep} signals.
- The photoresponse is negative for all types of cladding and under all kind of oxidation regimes and hence the oxide is a n-type semiconductor with deficiency of oxygen.
- The method needs to be verified by testing semiconductors with a known defect concentration.

The investigation was financed by ABB Atom AB, Vattenfall Bränsle AB, OKG Aktiebolag, Barsebäck Kraft AB och Statens kärnkraftsinspektion (SKI).

Sammanfattning

Korrosion på zirkoniumlegeringar är en viktig livslängdsbegränsande faktor för kärnbränsle. Korrosionsbeständigheten hos en metall är i hög grad beroende av metalloxidens förmåga att transportera laddningar och atomer. De egenskaper som påverkar denna förmåga är relaterade till oxidstrukturen, oxidens stökiometri och defektkoncentration.

PEP-metoden ("the Photoelectric Polarization Method") är en fotoelektrokemisk metod som skulle kunna användas för att ur korrosionssynpunkt få värdefull information om defektstrukturen i zirkoniumoxider. Metoden har tidigare undersökts dels inledningsvis i ett examensarbete och därefter i ytterligare ett uppdrag [2, 3].

Syftet med följande undersökning är att genom att använda en mer optimerad experimentuppställning verifiera om PEP-metoden är en användbar metod för att studera defektstrukturen i zirkoniumoxider och att kunna förutbestämma korrosionsmotståndet hos olika zirkoniumlegeringar.

Slutsatserna från undersökningen är att

- den förbättrade experimentuppställningen med ny ljuskälla, nytt oscilloskop med förstärkare gav en distinkt signal.
- Fotoresponserna är negativa för alla undersökta legeringar och under alla olika oxidationstillstånd, vilket visar att zirkoniumoxiden är n-typ halvledare med underskott av syre.
- Metoden behöver verifieras genom att undersöka halvledare med en känd defektkoncentration.

Undersökningen har finansierats av ABB Atom AB, Vattenfall Bränsle AB, OKG Aktieförbund, Barsebäck Kraft och Statens kärnkraftsinspektion (SKI).

1 Introduction

Corrosion of zirconium alloys is an important lifetime limiting factor for the nuclear reactor fuel. The corrosion resistance of a metal is highly dependent on the ability of the surface metal oxide to transport electrons and ions, which is related to the stoichiometry of the oxide and the oxide defect concentration.

The Photoelectric Polarization Method (PEP) invented by E. K. Oshe [1] is a structure sensitive method which earlier has been investigated as a possible method to study the defect structure in zirconium oxides [2, 3].

The purpose of the following work is, by using more optimized experimental equipment, to verify if the PEP method is a suitable method to study the defect structure in zirconium oxides and to predict the corrosion resistance for different zirconium alloys.

2 The Photoelectric Polarization Method

This method is classed as a recombination method [1]. In nonstoichiometric oxides containing a large number of defects and impurities, recombination into ground states of nonequilibrium electrons (excited electrons) and holes proceeds exclusively through deep levels of the defects and impurities in the forbidden band of the oxide. Below the method is described according to an article by Oshe [1].

A surface metal oxide acting as a working electrode in contact with an electrolyte is illuminated with ultraviolet pulsating light, see Figure 1. If the energy of the ultraviolet light is greater than the the band gap of the ZrO_2 (>5 eV) the photons will excite the electrons from the valence band to the conducting band. The excitation is a very fast process ($\approx 10^{-12}$ s). Initially, at the start of illumination there are as many excited electrons in the conducting band as holes in the valence band, since there will be holes left in the valence band when the electrons have been excited. Sooner or later the carriers will recombine, most likely via defects. The recombination will initiate a change in the potential.

The change in potential will be recorded and the maximum amplitude of the signal is called V_{pep} which can be described by the following equation [1].

$$V_{pep} = \frac{k_B T}{e} [(E_F - E_{F,p}^*) - (E_{F,n}^* - E_F)] \quad (1)$$

- k_B = Boltzmann constant
- T = temperature
- e = electron charge
- E_F = fermi level without illumination of the ZrO_2
- $E_{F,p}^*$ = fermi hole quasi levels
- $E_{F,n}^*$ = fermi electron quasi levels

The equation reflects the concentration difference of holes (p) and electrons (n) with and without illumination. In nonstoichiometric oxides, the electron concentration differs several magnitudes from the the concentration during illumination. We can assume that

$$\left| \ln \frac{p}{n} \right| \gg \left| \ln \frac{p_0}{n_0} \right| \quad (2)$$

- p = the concentration of holes with illumination
- n = the concentration of electrons with illumination
- p_0 = the concentration of holes without illumination
- n_0 = the concentration of electrons without illumination

Then equation (1) will be approximated as

$$V_{pep} = \frac{k_B T}{e} \ln \frac{p}{n} \quad (3)$$

According to equation (3) V_{pep} is proportional to the logarithm of the ratio of concentrations of nonequilibrium electrons and holes.

The relation between the concentration of carriers and their lifetime will be

$$n = f\tau_n, \quad p = f\tau_p \quad (4)$$

where f is the intensity of light generation of carriers and τ_n and τ_p are the recombination lifetimes of electrons and holes.

In nonstoichiometric defective oxides the recombination of nonequilibrium carriers takes place exclusively through intermediate capture centers, with defects and impurities playing this role. Depending on their nature and charge state, they will act as electron donors or acceptors, N_A , N_D . In real nonstoichiometric oxides, their concentrations will be several orders of magnitude greater than the concentrations of nonequilibrium carriers ordinarily achieved;

$$n, p \ll N_A, N_D \quad (5)$$

N_A = concentration of acceptor defects

N_D = concentration of donator defects

Following, we will consider that the cross section for capture of an electron by an acceptor S_n^A is larger than the cross section for capture of a hole by this same center, and that the cross section for capture of a hole by a donor S_p^D is larger than that for capture of an electron by this same center. In accordance with the condition in equation (5) the change in filling of centers

N_A and N_D by nonequilibrium electrons and holes upon illumination is negligibly small, and we can consider the regime of recombination of nonequilibrium carriers as quasi-stationary. In this case, τ_n and τ_p are independent of each other. For nonstoichiometric oxides, they are substantially different from each other and can be expressed by the following relationships:

$$\tau_n = \frac{1}{N_A S_n^A v} \quad (6)$$

$$\tau_p = \frac{1}{N_D S_p^D v} \quad (7)$$

where v is the thermal velocity of the electron.

In Oshes article [1] it is considered that there is symmetry in the cross section for capture of electrons and holes by acceptors and donors

$$|S_n^A| = |S_p^D|$$

Then, when equations 4, 6 and 7 are taken into account, equation (1) assumes a form expressing the sign and magnitude of the photoresponse directly in terms of the defect structure of the oxide:

$$V_{pep} = \frac{k_B T}{e} \ln \frac{N_A}{N_D} \quad (8)$$

If we assume that the acceptor and donator defects are cation and anion vacancies, then the V_{pep} signal can be related to the oxide stoichiometry:

$$V_{pep} = \frac{k_B T}{e} \ln \frac{V_c^x}{V_a^x} \quad (9)$$

V_c^x = concentration of cation vacancies

V_a^x = concentration of anion vacancies

From equation (9) it follows that the sign of the photoresponse can be used to establish the character of the nonstoichiometry, i.e. to determine whether excess metal or excess oxygen predominates in the nonstoichiometric oxide. It is evident that when $V_{pep}=0$, the oxide corresponds to a defect-free stoichiometric composition.

The magnitude and sign of the photoresponse in volts in this case are determined by processes of carrier recombination, and hence the concentration and nature of defect and impurity. The deviation from stoichiometry (x) can be calculated from equation (9).

$x = \frac{V_c^x}{V_a^x}$ = deviation from stoichiometry, $x=1$ for a defect free stoichiometry

$$V_{pep} = \frac{k_B T}{e} \ln x = \frac{k_B T}{e(\lg e)} \lg x$$

When assuming room temperature the deviation from stoichiometry can be expressed as

$$\log x = 16.5 V_{pep} \quad (10)$$

3 Experiments

3.1 Specimens

The PEP method was applied on five types of SVEA-96/100 cladding, see Table 1. The samples were 15 mm in length and the outer diameter was 9.6 mm.

The chemical analyses of the cladding tubes are given in Table 2. Each alloy was autoclaved at different temperatures and time according to Table 3. The weight gain after autoclaving is also given in Table 3 and in Figure 2.

By using the theoretical density of ZrO_2 (not known to be accurate) when trying to convert the weight gain to oxide thickness, 1 μm thick oxide is about 15 mg/dm^2 oxygen weight gain [4]. If we use this relationship, all oxides tested in this work are less than 1 μm thick.

Table 1: Specimen identification.

Lot no	Material and treatment
99-067	Zr-2P
99-070	Zr-2
99-088	LK-2
99-089	LK-3
99-099	Zr-4

Table 2: Chemical composition of alloys.

Element	Zr-2P	Zr-2	LK-2	LK-3	Zr-4
Sn (%)	1.335	1	1.01	1.385	1.36
Fe (%)	0.17	0.2	0.195	0.18	0.21
Cr (%)	0.1	0.1	0.095	0.105	0.095
Ni (%)	0.05	0.15	0.145	0.05	0.0015
Nb (%)	≤ 20 ppm	≤ 50 ppm	0.002	0.002	0.002
Si (ppm)	70	260	250	80	80
O (%)	0.126	0.1335	0.1415	0.1295	0.1295
N (ppm)	35	≤ 30	≤ 30	35	≤ 30
H (ppm)	11	10.5	9.5	7.5	11
C (ppm)	135	150	150	140	135
Zr	Balance	Balance	Balance	Balance	Balance

Table 3: Weight gain (mg/dm^2) after autoclaving in water.

Tube lot number	Nonoxidized	288°C 20 h	288°C 168 h	360°C 96 h
99-067	-	3.93	7.93	13.78
99-070	-	4.96	8.7	14.28
99-088	-	4.21	8.39	13.63
99-089	-	2.81	6.29	12.23
99-099	-	3.16	6.34	11.97

3.2 Experimental setup

A schematic drawing of the test equipment is given in Figure 1 and some photos of the equipment are given in Figures 3 through 5. The experimental setup consist of:

- Electrochemical cell with optical quartz window and a zirconium tube (specimen) acting as a working electrode (W.E.), a platinum foil served as an encountered electrode for photopotential response (C.E.) and a Kalomel electrode as reference electrode (R.E.)
- Deuterium lamp, *Heraeus D200F*. The emission of wavelengths $<250 \text{ nm}$ ($>5\text{eV}$), is in the same energy interval as the band gap for the semiconductor zirconium dioxide.
- Quartz condenser, $\Phi=50 \text{ mm}$, $f=50 \text{ mm}$, high transmission for wavelengths $<250 \text{ nm}$.
- Chopper, in order to obtain pulsating light.
- Shielding of the cell with Faradays cage, see Figure 4.
- Potentiostat, *Voltalab 21*.
- Amplifier, *Tektronix ADA400A (Differential amplifier)*
- Oscilloscope, *Tektronix TDS 410A*.

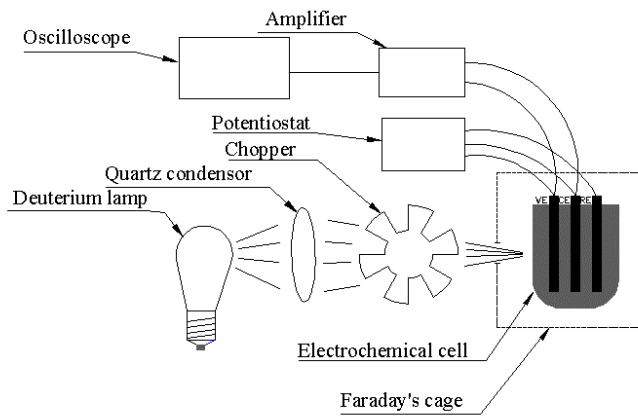


Figure 1: Experimental set-up.

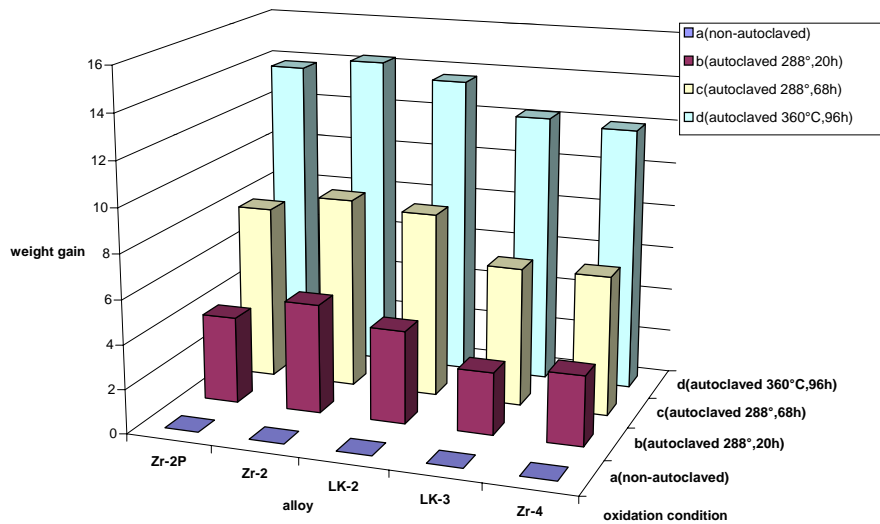


Figure 2: Weight gain as function of alloy and oxidation condition.

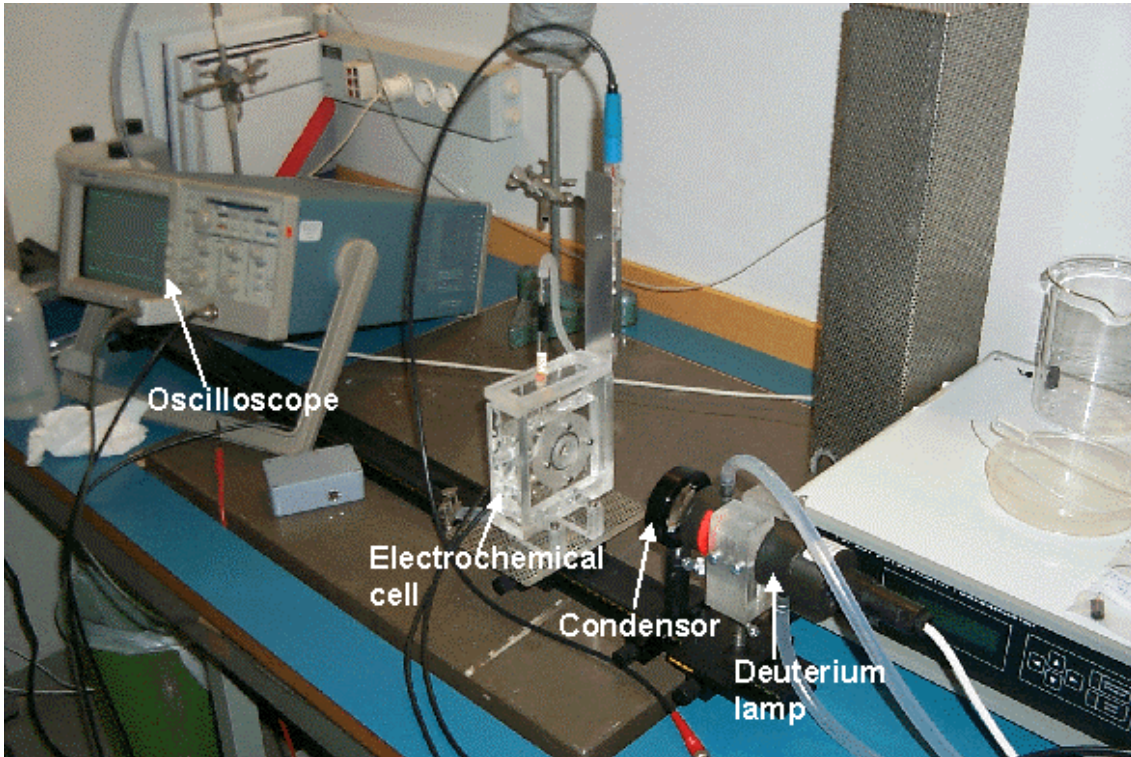


Figure 3: Photo of the experimental setup showing the electrochemical cell, oscilloscope, condenser and deuterium lamp.

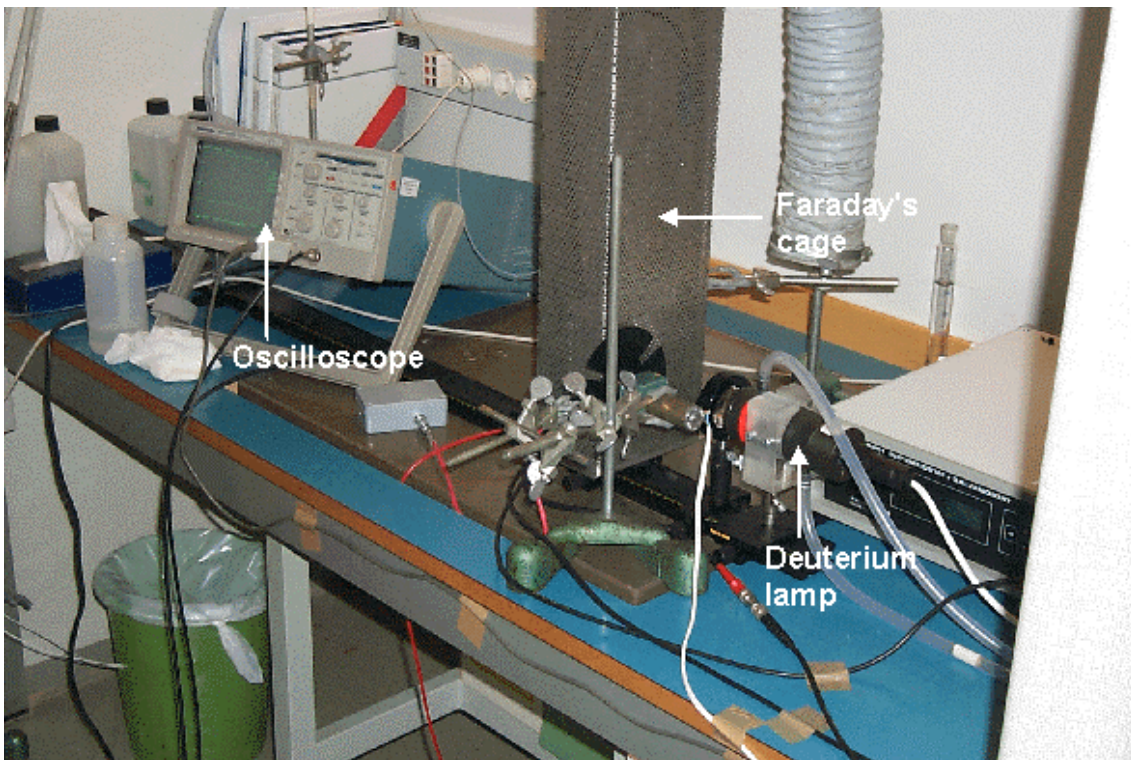


Figure 4: Photo of the experimental setup, showing the Faraday's cage, chopper, oscilloscope and deuterium lamp.

3.3 Testing conditions

The amplitude of the photoresponse should be independent of the the chopper frequency to avoid leakage of carriers through the interface between the oxide and electrolyte. The frequency was in this experiment set to 15 Hz, as a result of an experiment when the frequency was varied.

The electrolyte of the electrochemical cell was 0.1 M NaOH and the testing temperature was room temperature.

The working sample surface was 7 mm², the platinum foil surface was 1100 mm² and the volume of the electrolyte was 120 ml.

3.4 Modifications

This experimental setup was modified compared to earlier tests [2, 3].

A deuterium lamp was used instead of a xenon lamp since the wave length interval of a deuterium lamp is more suitable for the band gap of ZrO₂.

A better signal/noise ratio was obtained by means of a new oscilloscope with an amplifier.

4 Results

The results from the testing are given in Table 4 and in Figure 6.

Table 4: Results from the testing at 15Hz. The amplification (10x) is included in the results

Alloy	Vpep signal No autocl.	Vpep signal Autocl. 288°C, 20h	Vpep signal Autocl. 288°C, 168h	Vpep signal Autocl. 360°C, 96h
Zr-2P	-0.5	-1.6	-2.0	-2.8
Zr-2	-0.9	-1.5	-2.3	-3.0
LK-2	-0.9	-1.8	-2.2	-3.7
LK-3	-1.0	-1.5	-2.1	-2.7
Zr-4	-0.8	-1.5	-2.0	-2.3

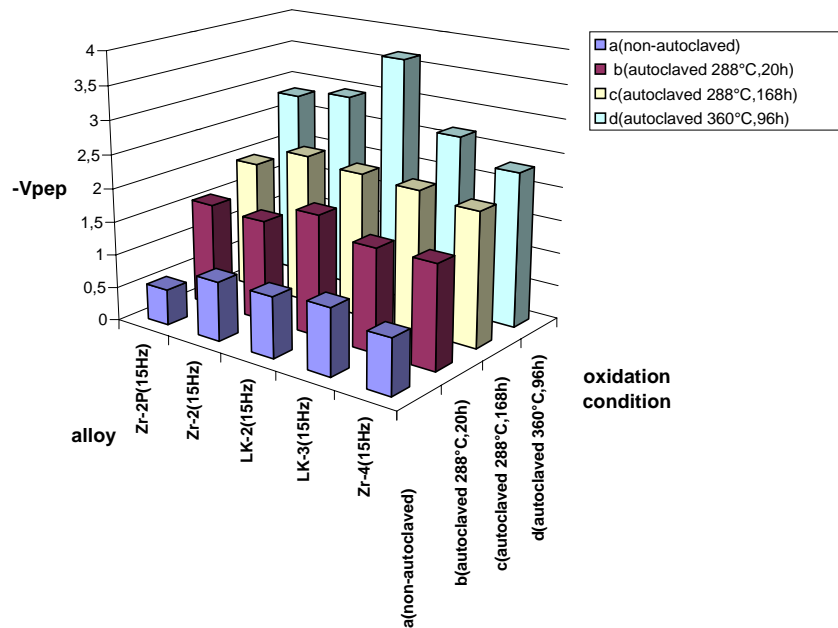


Figure 6: Vpep signal as a function of alloy and oxidation condition.

5 Discussion

The results show that the photoresponse is negative for all types of cladding and under all kind of oxidation regimes and that the photoresponse increases by oxidation time. According to Oshe [1] the magnitude and sign of the photoresponse in volts are determined by the concentration and nature of defect and impurity. This could be expressed by

$$V_{pep} = \frac{k_B T}{e} \ln \frac{p}{n} \quad (3)$$

This means that a negative photoresponse corresponds to a semiconductor with a n-type conductivity and hence an oxide with oxygen deficiency. From literature ZrO_2 is considered to be a n-type semiconductor [5].

By assuming that a number of conditions are fulfilled, discussed in chapter 2, equation (3) can be expressed as

$$V_{pep} = \frac{1}{16.5} \log(x) \quad (10)$$

where x is the deviation from stoichiometry. The deviation from stoichiometry is found to be very small for all types of cladding and oxidation regimes if we assume that equation (4) can be used. From these results the deviation from stoichiometry increases by oxide thickness in the oxide thickness interval tested in this work ($< 1\mu m$). The deviation from oxide stoichiometry is 1.002 for non-autoclaved Zr-2P according to equation (4) and 1.01 for Zr-2P when autoclaved at $360^\circ C$ for 96 h.

If we assume that we have measured the V_{pep} signal according to Oshe's theory this will give us useful information for understanding the relationship between defect chemistry and corrosion behaviour. But so far there are several other oxide parameters that might influence the V_{pep} signal, e.g. oxide grain boundaries, oxide pores and secondary phase particles.

In order to separate these parameters from the actual defect stoichiometry, semiconductors with a known defect concentration should be tested by using this method. There should also be a comparison with other methods for studying defect structure, e.g. impedance spectroscopy.

6 Conclusions

The conclusions from the experiments are as follows:

- The modifications of the experimental setup by means of a new source of light (deuterium lamp) and a new oscilloscope with an amplifier gave distinct V_{pep} signals.
- The photoresponse is negative for all types of cladding and under all kind of oxidation regimes and hence the oxides are n-type semiconductors with deficiency of oxygen.
- The method need to be verified by testing semiconductors with a known defect concentration.

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