

## THERMOLUMINESCENCE OF ANODIC AND THERMAL ZIRCONIUM OXIDE LAYERS

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This work concerns natural and induced thermoluminescence of anodic and thermal  $ZrO_2$  layers. It was found that anodic layers display natural thermoluminescence in the temperature range from 540°K to 700°K, whereas thermal layers display induced thermoluminescence in the 90° to 530°K temperature range. The natural thermoluminescence curves are characterized by broad maxima, the position of which depends on the formation voltage. The induced thermoluminescence curves are characterized by the position of maxima at the temperatures of 133°K, 247°K and 485°K.

## 1. Introduction

The electric and dielectric properties of anodic  $ZrO_2$  layers are known to some extent in the literature, *e.g.*, [1, 2, 3, 4, 6]. The author, in the papers [5, 7, 8], presented some of the results of his research on the luminescent properties of anodic  $ZrO_2$  layers.

During the writing of this paper an article by Bettinali and collaborators [16] concerning the thermoluminescence of  $ZrO_2$  appeared. Bettinali *et al.* found that  $ZrO_2$ , of nuclear purity and titanium activated alike, exhibit within a range of temperatures from 100°K to 350°K an intense thermoluminescence, and the thermostimulated glow curve has sharp, distinct thermoluminescence peaks at the temperatures 135°K, 195°K, 245°K and 275°K. The spectral distribution of this glow, analyzed by the same authors, is characterized by a single maximum at a wavelength of approximately 498  $m\mu$ .

It is known [1, 2, 5, 6, 9] that anodic  $ZrO_2$  layers are formed during the process of electrolytic oxidation of metallic zirconium in appropriate electrolytes (by constant voltage or constant density of formation current). The physical properties and structure of these layers depend above all on the conditions of formation (the type of electrolyte, temperature, *etc.*).

Thermal layers of zirconium oxide are formed in the process of annealing zirconium in

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an atmosphere of air or oxygen. The crystalline structure of these layers depends, among other things, on the temperature and duration of annealing (formation).

Figure 1 presents a photograph of the cross-section of a thermal  $ZrO_2$  layer (after Phalnikar and collaborators) formed at a temperature of 1373°K during one hour.

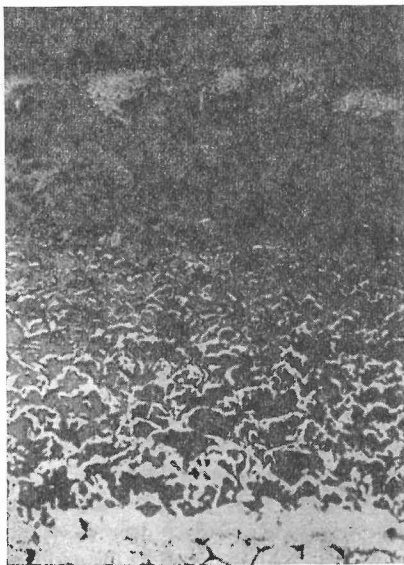


Fig. 1. Cross-section of thermal layer of zirconium oxide (after Phalnikar *et al.* [10]) formed at 1373°K during 1 hr

## 2. Equipment and sample preparation

The subject of this study was the thermoluminescence of anodic and thermal layers of zirconium oxide on zirconium substrate plates of a purity of 99.7 per cent. The layers were obtained by two techniques:

- electrolytic oxidation of zirconium by constant voltage (15 V, 25 V and 35 V) in a 10 per cent solution of nitric acid. The second electrode during oxidation was a platinum platelet, and the temperature of the electrolyte fluctuated about room temperature,
- thermal annealing of zirconium in a resistance furnace in an atmosphere of air for 0.5 hour at temperatures of 773°K, 873°K, 973°K and 1073°K.

From the oxidized plates samples of an area of approximately 0.4 cm<sup>2</sup> were cut and then mounted on the plate of the resistance furnace.

The furnace was placed in a vessel from which air was pumped off (by a rotary pump) to a pressure of the order of 10<sup>-2</sup> mm Hg. The cross-section of the furnace and vessel is shown in Fig. 2.

The flat wall of the furnace with the sample placed on it was cooled by liquid nitrogen to a temperature of about 85°K and subsequently heated at a constant rate ( $\beta_1 = 0.6^\circ/\text{sec}$  or  $\beta_2 = 0.1^\circ/\text{sec}$  or  $\beta_3 = 1^\circ/\text{sec}$  in the temperature range from 85°K to 723°K.

- The changes in luminescence intensity with temperature were studied:
- without prior illumination with ultraviolet light (natural thermoluminescence), and
  - after previous excitation by ultraviolet radiation at the temperature 85°K (excited or induced thermoluminescence).

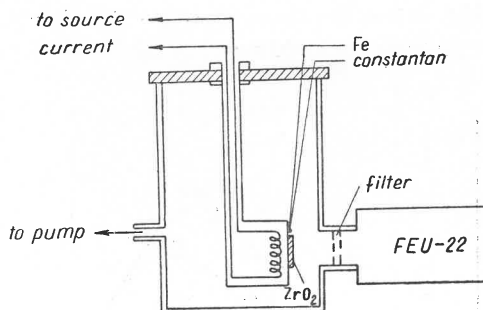


Fig. 2. Diagram of furnace and vessel in which samples were first cooled and then heated

In the latter case, before the process of thermostimulated emission of radiant energy of the sample placed on the resistance furnace cooled to 85°K, the sample next it was excited through a quartz window by ultraviolet radiation emitted from a  $Q - 400$  [Hg] lamp. The glow appearing during heating of the sample was detected by an FEU-27 photomultiplier (the interval of spectral sensitivity of which is from 360 m $\mu$  to 750 m $\mu$ ). The photomultiplier current was amplified by a d. c. amplifier and recorded on a "Norma" recording milliammeter.

### 3. Experiments and results

#### 3.1. Natural thermoluminescence of anodic $ZrO_2$ layers

On the basis of experiments made in this study it was found that anodic layers of zirconium oxide on a zirconium substrate, formed by constant voltage of values of 15 V, 25 V and 35 V in a 10 per cent solution of nitric acid, display natural thermoluminescence during heating in the temperature range from 533°K to 723°K. Figure 3 shows three thermostimulated glow curves of three samples of practically the same areas formed by constant voltages of 15 V, 25 V and 35 V.

The heating rate of each sample and the amplification of the photomultiplier current were always the same.

The experiment shows that identical shapes of the glow curves of anodic layers are obtained independently of whether or not the sample is excited with ultraviolet radiation prior to the emission process. The natural and induced thermoluminescences of anodic layers of zirconium oxide are identical.

The temperature at which the thermoluminescence maximum occurs depends on the formation voltage. The curves of natural thermoluminescence are very broad (half-width  $T \approx 200^\circ$ ). This suggests that in anodically formed zirconium oxide there are traps (donor levels) of depths comprised within a rather wide energy interval  $\Delta E$ .

It should be emphasized that the samples, whose glow curves are illustrated in Fig. 3, were flushed and dried at room temperature in air atmosphere after the electrolytic process.

Visual observations and measurements proved that the anodic  $\text{ZrO}_2$  layers do not exhibit thermoluminescence (natural or UV excited) at temperatures below  $530^\circ\text{K}$ .

It is also seen from Fig. 3 that the thermoluminescence temperature (the temperature at which the curve passes through the maximum) is the lowest for the sample whose  $\text{ZrO}_2$

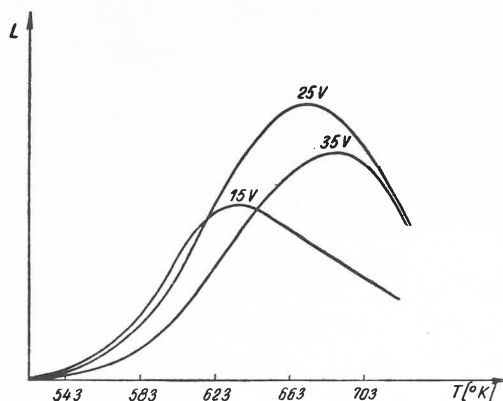


Fig. 3. Natural thermoluminescence curves of three samples formed in 10%  $\text{HNO}_3$  solution by constant voltage of values 15 V, 25 V and 35 V

layer was formed by the lowest value of voltage (15 V), and with increasing formation voltages the thermoluminescence temperature shifts towards the higher temperatures. One might think that the dependence of  $T^*$  on formation voltage is only an apparent one.

It is known that the thickness of the oxide layer depends on the value of the formation voltage, and it follows from Refs [1, 2, 5] that the thickness of the anodic  $\text{ZrO}_2$  layer is proportional to the formation voltage.

Whence the supposition that the observed shift of natural thermoluminescence temperature is due to the low thermal conductivity of zirconium oxide.

The temperature of the surface layer of  $\text{ZrO}_2$ , the thermoluminescent glow of which is examined in the experiment, is lower than the temperature of the substrate to which the thermocouple measuring the temperature adheres. Therefore, there was some concern over whether or not the increase in temperature difference with increased layer thickness is the cause for the shift of the thermoluminescence peak with layer thickness (formation voltage).

An idea for a simple verification of this supposition by means of induced thermoluminescence was conceived, namely, to investigate the effect of the oxide layer thickness on the temperature of excited thermoluminescence peaks.

Figur 4 presents two excited thermoluminescence curves of two samples anodically formed in nitric acid by constant voltages 10 V and 30 V, which were then annealed for 0.5 hr at  $973^\circ\text{K}$  and excited by ultraviolet light at a temperature of  $85^\circ\text{K}$ .

As is seen in Fig. 4, the two samples of different oxide layer thicknesses are characterized by the position of thermoluminescence peaks at the same temperatures of  $133^\circ\text{K}$  and

247°K. On the basis of these data it may be surmised that the thickness of the oxide layer is not the reason for the shift of the thermoluminescence temperature. It is to be noted that the electric conductivity of thermal layers, compared to the conductivity of anodic layers, is subject to a slight change.

Hence, the observed shift of thermoluminescence temperatures towards the higher temperatures for layers formed at higher voltages corresponds to an increase in the energy

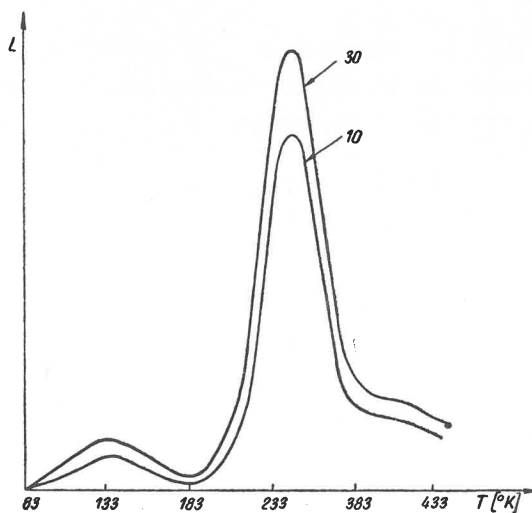


Fig. 4. Induced thermoluminescence curves of two samples formed by constant voltages of values 10 V and 30 V and annealed for 0.5 hr at 973°K (the emission process of these samples was examined in the 90°K to 350°K temperature range)

depth of electron traps in the oxide layers formed by those higher voltage values. Finally, it may be surmised that with an increase in formation voltage the initial number of levels occupied by electrons becomes decreased, what consequently leads to a shift of the thermoluminescence maxima towards the higher temperatures, as had been shown by N. Antonov-Romanovski [14, 15]. At a fixed occupation of electron traps, electrons primarily occupy the deep traps under equilibrium conditions (retrapping). This explanation of the shift of the thermoluminescence maximum seems hardly probable; notwithstanding, this requires further research.

### 3.2. Excited thermoluminescence

Thermal layers formed in a furnace in air do not exhibit natural thermoluminescence, but are luminescent only when excited by ultraviolet light. It follows from observations and measurements that this glow appears in a temperature range different than for the thermoluminescence of unannealed anodic layers, while the intensity of this glow is much larger as compared to the intensity of anodic layer emission. This glow also is blue in color.

Further experiments show that zirconium oxide formed anodically, after being addi-

tionally annealed in a furnace at appropriate temperatures, gives off an excited thermoluminescence analogous to the thermoluminescence of thermally formed  $ZrO_2$  layers.

Additional annealing of anodic layers leads to the decay of natural thermoluminescence in them (observed for anodic layers in the temperature range from  $533^\circ K$  to  $723^\circ K$ ) and the appearance of induced thermoluminescence in a temperature range identical to the one where the thermal layer emission was.

The positions of the thermoluminescence peaks of samples made from plates formed thermally and samples made from plates formed anodically, and additionally annealed at the same temperatures at which the thermal layers were formed, are identical.

The thermoluminescent emission measurements presented in Fig. 5 were made for samples of thermal zirconium oxide and annealed anodic oxide. The temperatures of thermal

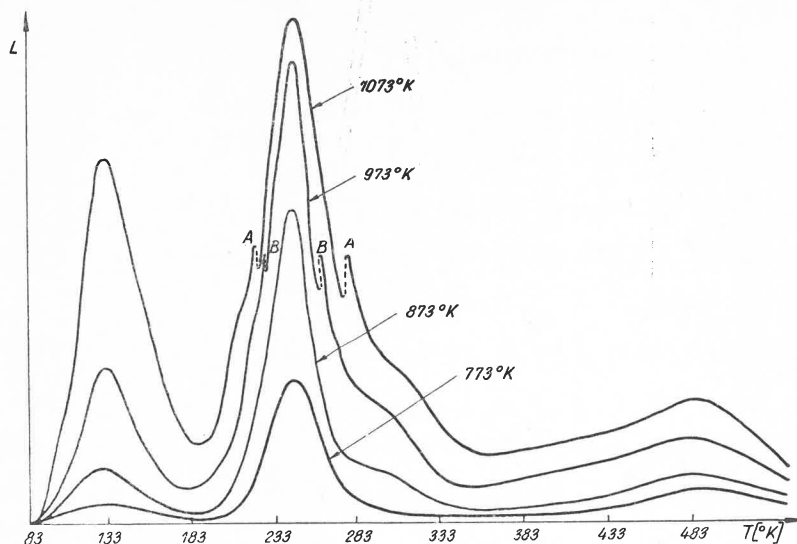


Fig. 5. Induced thermoluminescence curves of four samples formed at the temperatures  $773^\circ K$ ,  $873^\circ K$ ,  $973^\circ K$ ,  $1073^\circ K$  during 0.5 hr. At the points *A* and *B* the amplification of the photomultiplier current was changed 10 and 6 times, respectively

ayer formation and the temperatures of annealing the anodic layers were as follows:  $773^\circ K$ ,  $873^\circ K$ ,  $973^\circ K$  and  $1073^\circ K$ . The time of formation and annealing was 0.5 hr.

Owing to the fact that the positions of the thermoluminescence maxima and the heights of the peaks (under identical conditions of observation and excitation) for both types of samples (thermal and annealed anodic) are identical, only the changes in intensity of the induced thermoluminescence (in arbitrary units) are shown in Fig. 5 for four of the samples prepared from thermal  $ZrO_2$  layers. These changes arise during heating of the samples from  $85^\circ K$  to  $573^\circ K$  at a constant rate of about 0.6 degrees per second.

It is seen from Fig. 5 that the emission process recorded by the equipment used here begins at a temperature of approximately  $95^\circ K$ , then with increasing temperature the intensity of this glow passes through three distinct maxima at definite temperatures. Figure 5

also shows that an increase in formation temperature leads to a distinct increase in the integral luminescence intensity. Moreover, there is at the same time a sharpening of the thermoluminescent peaks lying at 133°K, 247°K and 485°K, of which the middle one (at 247°K) is the strongest, whereas the high-temperature peak is the weakest.

The method of thermostimulated glow curves, among other things applied in studies on the energy distribution of electron traps, is one of the most commonly used techniques in solid state physics, above all thanks to the work of Urbach, Randall and Wilkins, G. Curie, D. Curie [17, 18, 19, 11], Antonov-Romanovski [14, 15] and Wrzesińska [12, 13]. The method of thermoluminescence curves was proposed by Urbach [17] in 1930. As a result of research on the thermoluminescence of KCl-Tl Urbach found an empirical formula which enables making an estimate of the energy depth of traps when the heating rate is  $\beta = 1$  degree per sec,

$$E = \frac{500}{T^{*2}} \text{ [eV]}.$$

With the assumption of first order kinetics the theoretical formula for thermoluminescence curves [12, 18] is

$$L = n_0 S e^{-E/kT} \exp \left[ - \int_{T_i}^T S e^{-E/kT} \frac{dT}{\beta} \right]$$

where  $n_0$  is the number of traps filled at the initiation of heating, and  $S$  is a certain constant which in the literature is sometimes called the "frequency of escape attempts".

From the condition for the extreme of this formula the following relation between the energy depth of the traps  $E$  and the thermoluminescence temperature  $T^*$  is obtained,

$$\frac{E}{kT^{*2}} = S e^{-E/kT^*}.$$

This formula was used by G. Curie and D. Curie [19] and Wrzesińska [12] for calculating trap depths. By numerical integration the authors of [19] unravelled this relation with an accuracy better than 1 per cent, getting the following dependence:

$$E = \frac{T^* - T_0}{K}$$

where  $\Theta = \frac{\beta}{S}$ ,  $T_0(\Theta)$  and  $K(\Theta)$  are certain constants which were calculated by D. Curie in the range from  $10^{-4}$  to  $10^{-16}$ .

Wrzesińska [12] found  $E$  from the unravelled dependence by a graphical technique.

All of these methods of finding the depths of electron traps from the thermoluminescence temperature require knowledge of the value of  $S$  for the given group of traps.

In this work an attempt was made to estimate  $S$  for thermal and annealed anodic layers by the use of the method of two heating rates,  $\beta_1 = 1^\circ/\text{sec}$  and  $\beta_2 = 0.1^\circ/\text{sec}$ .

If we write the formula for the extreme values of the thermoluminescence curves for the rate  $\beta_1$  and the rate  $\beta_2$ , we can eliminate  $S$  by simple division by sides, thus receiving the equation

$$\frac{E}{k} \left[ \frac{1}{T_2^*} - \frac{1}{T_1^*} \right] = \ln \left[ \frac{\beta_1}{\beta_2} \cdot \frac{T_2^{*2}}{T_1^{*2}} \right].$$

If  $E$  is known, we can calculate  $S$  from the following relationship given in Ref. [12]:

$$\ln \frac{Sk}{E} = \frac{T_2^* \ln \frac{T_2^{*2}}{\beta_2} - T_1^* \ln \frac{T_1^{*2}}{\beta_1}}{T_1^* - T_2^*}.$$

Calculations show that in thermal  $ZrO_2$  layers and in annealed anodic layers there are three different values of  $S$  corresponding to the three principal groups of electron traps of thermoluminescence temperatures 133°K, 247°K and 485°K. For the group of electron traps whose thermoluminescence temperature is about 133°K the value of  $S$  is  $1.9 \times 10^4 \text{ sec}^{-1}$ . For traps of a thermoluminescence temperature of 247°K  $S = 9.3 \times 10^8 \text{ sec}^{-1}$ , and for the high-temperature group of traps of a thermoluminescence temperature of 485°K  $S$  is of the order of  $2.1 \times 10^{11} \text{ sec}^{-1}$ . Whence it follows that the values of  $S$  are different for different groups of traps and increase with their depths.

With the use of the described methods of determining the energy depth of electron traps calculations were made in this work of the energy depths of three groups of traps which may be distinguished for the thermal and annealed anodic  $ZrO_2$  layers.

The obtained results are arranged in the Table.

TABLE I

| No. | Method<br>Thermolum. temp. | 133°K   | 247°K   | 485°K   |
|-----|----------------------------|---------|---------|---------|
| 1   | F. Urbacha                 | 0.27 eV | 0.49 eV | 0.97 eV |
| 2   | D. Curie                   | 0.12 eV | 0.50 eV | 1.07 eV |
| 3   | A. Wrzesińska (graphical)  | 0.13 eV | 0.53 eV | 1.10 eV |
| 4   | Two heating rate           | 0.13 eV | 0.51 eV | 1.08 eV |

The depths of electron traps calculated in this work from the thermoluminescence temperatures 133°K and 247°K agree very well with the results for the energy values for the 135°K and 249°K thermoluminescence maxima obtained by the Italian researchers [16] via the method of thermoluminescence curve analysis.

A comparison of the temperatures of all thermoluminescence peaks obtained in this work and those cited in Ref. [16] reveals, apart from the conformity of these temperatures ( $\Delta T = 2^\circ$  lies within the limits of experimental error) for the two above-mentioned peaks, a distinct discrepancy for other peaks.

In particular, in the cited work [16] no high-temperature thermoluminescence peak ( $T = 485^\circ\text{K}$ ) was found to appear. This may be due perhaps to the difference in the process of thermally procuring  $ZrO_2$  and different purity of the material.



The effect of these factors is confirmed by observations and measurements conducted by this author on spectrally pure zirconium oxide manufactured by Johnson Matthey Chemicals (London, England) and oxide obtained by annealing zirconium (powdered and without the zirconium substrate).

The results of these measurements are illustrated in Fig. 6, where there are two curves of thermoluminescence excited by ultraviolet light for the spectrally pure oxide (dashed curve — 1) and for the oxide obtained from 99.7 per cent pure zirconium by thermal sintering in a furnace (continuous curve — 2).

As is seen in Fig. 6, both curves have the characteristic two peaks at thermoluminescence temperatures of 133°K and 247°K, but there are large differences in the intensity ratios of these maxima.

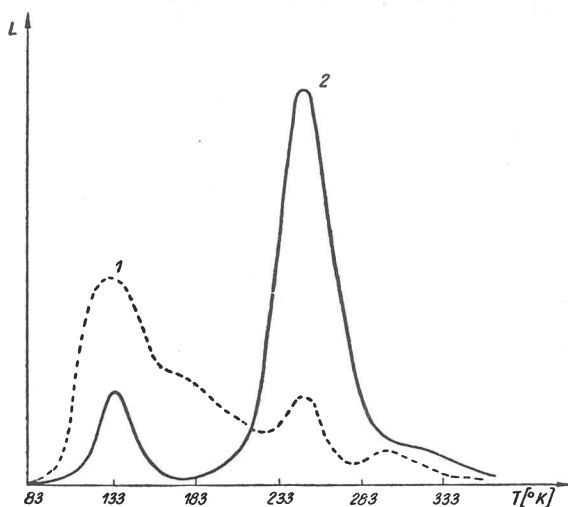


Fig. 6. Induced thermoluminescence of two samples: in spectrally pure zirconium oxide (curve 1) and in thermal zirconium oxide obtained from 99.7% pure zirconium (curve 2). The amplification of the photomultiplier current for curve 1 was 10 times that for curve 2 (the curves are taken for the 90°K to 350°K temperature range)

#### 4. Conclusions

The results obtained in this work, concerning the thermoluminescent properties of anodic  $ZrO_2$  layers imply that structural defects of this oxide are very sensitive to annealing.

Annealing of anodic layers for 0.5 hour at temperatures over 733°K causes the decay of the original deep electron traps responsible for natural thermoluminescence and the appearance of three groups of shallow traps responsible for excited thermoluminescence.

$ZrO_2$  layers formed thermally reveal only induced thermoluminescence; analogous excited thermoluminescence is also the property of annealed anodic layers.

The conformity of positions of the thermoluminescent peaks of the thermal layers and annealed anodic layers gives rise to the suggestion that thermal treated of anodic layers essentially alters the physical structure of the oxide. Visual observations and measurements

reveal that the intensity of induced thermoluminescence of thermal and annealed anodic layers is much larger than the intensity of the natural thermoluminescence of anodic layers. It follows thus that the defects responsible for induced thermoluminescence, *i. e.* for the electron traps of depths from 0.13 to 1.08 eV, are of thermal origin. This conclusion is supported by the fact that with a rise in temperature at which the thermal oxides are formed the intensity of the thermoluminescence increases distinctly (Fig. 5), and particularly distinct is the increase of the participation of the trap level to which the thermoluminescence temperature of 247°K at  $\beta = 0.6^\circ/\text{sec}$  corresponds.

It appears that further studies on the identification of the defects in the structure of zirconium oxide and the luminescence centers alike are necessary, and they will be continued.

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