

Tadeusz Marcinów, Cecylia Wesółowska, Tadeusz Wiktorczyk\*

# Optical properties of the thin ytterbium oxide films\*\*

The results of investigations concerning the methods of thin ytterbium oxide film production are presented. A description of optical properties contains the optical constants  $n$  and  $k$  of the  $\text{Yb}_2\text{O}_3$  films evaporated from the tungsten heaters and by electron-beam gun in the 0.2–2.5  $\mu\text{m}$  wavelength range. Besides, the structural examinations of  $\text{Y}_2\text{O}_3$  films are reported as well as the X-ray microanalysis results of the chemical compound for films evaporated from the tungsten boats.

## 1. Introduction

Thin films of the rare earth oxides are intensively examined because of advantageous properties of those materials [1]. In several papers devoted to the optical properties of the compounds belonging to this group [2, 3] there are no reliable data referring to the ytterbium oxide films. In other papers either preliminary results are presented [4, 5, 6] or the investigations have been stopped because of technological difficulties [3].

The present paper is devoted to production of  $\text{Yb}_2\text{O}_3$  films, and to investigations of their optical properties.

## 2. Experimental part

The films of ytterbium oxide have been obtained by applying three methods:

- evaporation from the resistor heaters,
- electron-beam evaporation,
- oxidizing the ytterbium films of thickness 100 nm in the air atmosphere (400°C, 30 h).

All the films were evaporated in the Edwards Model 19 E-7 unit equipment with an electron gun of 1.5 kW output power of Polish make [7]. In the course of experiments with different resistor heaters (W, Mo, Ta) it has been stated that only tungsten boats are useful for evaporation of  $\text{Yb}_2\text{O}_3$ , though they suffer from quick damage, as reported earlier in [3].

The influence of condensation conditions on the properties of films are determined for fixed parameters in the following intervals:

- pressure  $2 \times 10^{-5}$ – $7 \times 10^{-5}$  Tr,
- substrate temperature 50–250°C,
- evaporation rate 1–3.5 nm/s.

\* Institute of Physics, Wrocław Technical University, Wrocław, Poland.

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For evaporation the ytterbium oxide of 99.9 % purity has been used. The layers were deposited onto the optical wedges and plane parallel plates made of quartz, and next subjected to the optical and structural investigations. The film thickness has been determined by the Tolansky's method.

## 3. Structure of films and their chemical composition

The structural properties of  $\text{Yb}_2\text{O}_3$  films of thickness above 400 nm were examined with a X-ray diffractometer, type DRON-1. A diffractogram of the powdered  $\text{Yb}_2\text{O}_3$  used during evaporation is presented in fig. 1a.

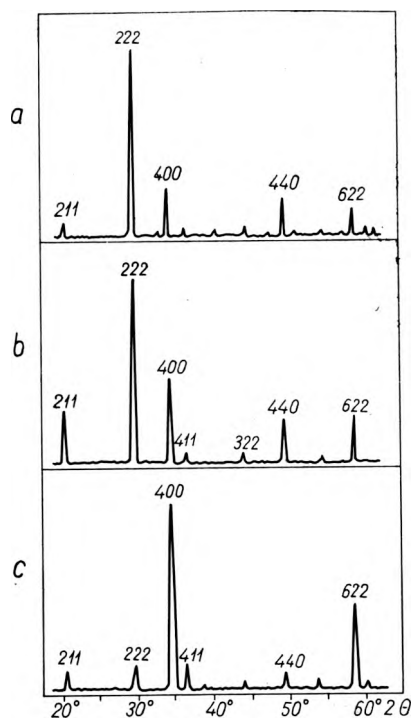


Fig. 1. Diffractograms for ytterbium oxide: a) powdered material; b) film deposited with an electron-beam on a substrate at 250°C and  $10^{-6}$  Tr; c) film deposited on a substrate at 250°C and  $2 \times 10^{-5}$  Tr;

The films obtained by evaporation from the tungsten boats are amorphous independently of the condensation parameters and the subsequent both thermal and temporal aging of the films. On the other hand, the films evaporated with the help of an electron-gun are amorphous or polycrystalline depending on the condition under which they were obtained.

The main parameters which influence the ordering of the film structure are: increased temperature of the substrate, and increased pressure during evaporation.

The  $\text{Yb}_2\text{O}_3$  films evaporated onto unheated substrate at the pressure  $10^{-5}$  Tr are amorphous. Polycrystalline structure is characteristics of the films evaporated on the heated substrate (fig. 1b). As can be seen in this figure the film diffractogram is analogous to that of powdered material.

The highest degree of order in the film structure has been obtained in the case of evaporation of  $\text{Yb}_2\text{O}_3$  on the heated substrates of ( $250^\circ\text{C}$ ) at the  $2 \times 10^{-5}$  Tr air pressure. Fig. 1c shows that the films may be partially textured with a privileged orientation of the [400] plane.

In order to explain the difference in the properties of the examined films obtained in different ways the X-ray microanalysis have been made (JOEL-JXA-5A type). From the measurement results and the additional evaluations it follows that the films evaporated from the tungsten boat contain about 18 weight percent of tungsten in nonstoichiometric  $\text{WO}_3$ .

#### 4. Optical properties

Optical properties of the  $\text{Yb}_2\text{O}_3$  films obtained by various methods are different, especially in the vicinity of the absorption edge. In fig. 2 the dependence of the transmission coefficient  $T$  upon the wavelength  $\lambda$  is shown for the following films:

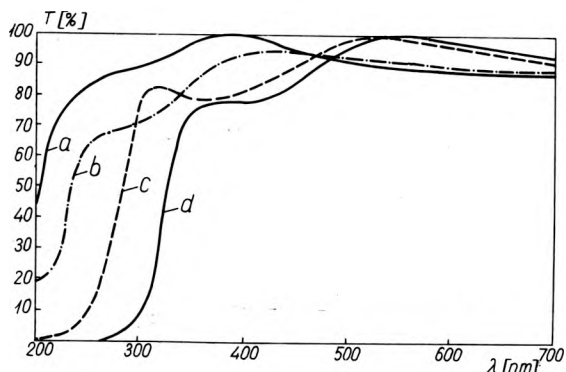


Fig. 2. The dependence of the transmission coefficient  $T$  upon the wavelength, for  $\text{Yb}_2\text{O}_3$  films obtained by different methods, and for the  $\text{WO}_3$  films:

- a)  $\text{Yb}_2\text{O}_3$  film evaporated by an electron gun,  $d = 100$  nm; b)  $\text{Y}_2\text{O}_3$  film obtained by oxidizing the ytterbium film  $d = 81$  nm; c)  $\text{Yb}_2\text{O}_3$  film evaporated from a tungsten boat,  $d = 128$  nm; d)  $\text{WO}_3$  film,  $d = 139$  nm

- a) deposited by an electron-beam evaporation,  
b) obtained by oxidizing the ytterbium,  
c) evaporated from a tungsten heater,  
d)  $\text{WO}_3$  films.

From the figure it may be seen that  $\text{Yb}_2\text{O}_3$  films evaporated by an electron-beam (curve *a*) have a shifted absorption edge by about 70 nm toward shorter waves if compared to those evaporated from the tungsten boats (curve *c*).

On the other hand, the mutual course of the curves *a*, *b*, and *c* indicates that the films evaporated from the tungsten heaters are mixtures of ytterbium and tungsten oxides. A considerable discrepancy of the curves *a* and *b* (fig. 2) may be explained by an unfinished process of ytterbium film oxidation. Ytterbium oxidation occurs very slowly, and is characterized in fig. 3. This figure shows the changes of the transmission coefficients  $T$  for three wavelengths during oxidation of the ytterbium film of 79 nm thickness.

Besides, the ytterbium oxide films evaporated reactively from the tungsten boat possess considerable

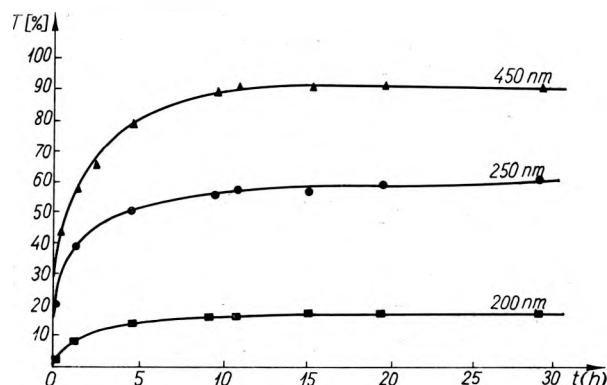


Fig. 3. The oxidizing process for ytterbium film of thickness 79 nm at  $400^\circ\text{C}$ , illustrated by transmission changes in the films for various wavelengths

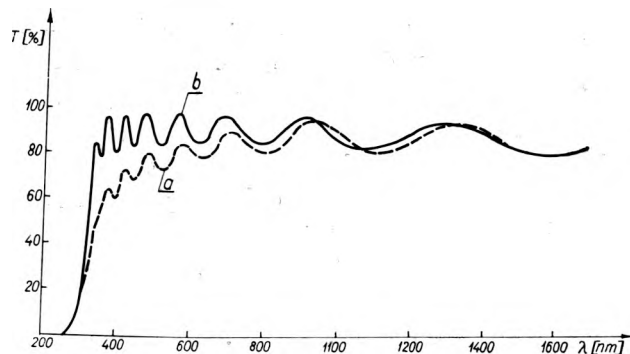


Fig. 4. The dependence of the transmission coefficient for a  $\text{Yb}_2\text{O}_3$  film evaporated on an unheated substrate at the  $10^{-4}$  Tr oxide pressure:  
a) before heating; b) after heating

rable absorption in the visual spectrum. The absorption disappears after a multi-hours heating of the films in the air atmosphere at the temperature of 400°C. This is illustrated in fig. 4 in which the relation  $T = t(\lambda)$  for a  $\text{Yb}_2\text{O}_3$  film evaporated onto a heated substrate (250°C) is shown (curve *a*), and the same relation after heating this film in the air atmosphere (400°C, 4 hours; curve *b*).

The optical constants  $n$  and  $k$  have been calculated for uniform films of thickness above 200 nm.

In the absorptionless region the refractive indices of the films has been determined from the positions of minima and maxima of the transmission coefficients  $T$ , reflection coefficients  $R$ , and the geometrical thickness  $d$  of the film [8].

In the region of small absorption ( $k^2 \ll (n-n_0)^2$ ),  $n$  and  $k$  have been determined with the help of HALL-FERGUSON method [9]. In the vicinity of the absorption edge, where interference effects are attenuated, the optical constants are determined by a method of SCHULTZ-TANGHERLINI [10].

In fig. 5 (curve *a*) optical constants  $n$  and  $k$  are presented as a function  $\lambda$  for the film evaporated from the tungsten boats onto a substrate of 250°C temperature at  $10^{-4}$  Tr oxygen pressure. Curve *b* shows optical constants for the same films after heating in air atmosphere at 400°C for 4 hours. The heating of the layers causes a slight lowering of the refractive index (2%) and some essential index of absorption in the visual and ultraviolet parts of the spectrum. The refractive indices of the films are greater than for the monocrystalline material [11], this may be explained by the presence of the tungsten oxides in the film. Fig. 6 presents the optical constants of the films evaporated from an electron-beam gun onto a substrate at temperature 250°C and  $2 \times 10^{-5}$  Tr constant pressure. The refractive index  $n = 1.9$  for  $\lambda = 600$  nm is slightly lower than for a  $\text{Yb}_2\text{O}_3$  mono-

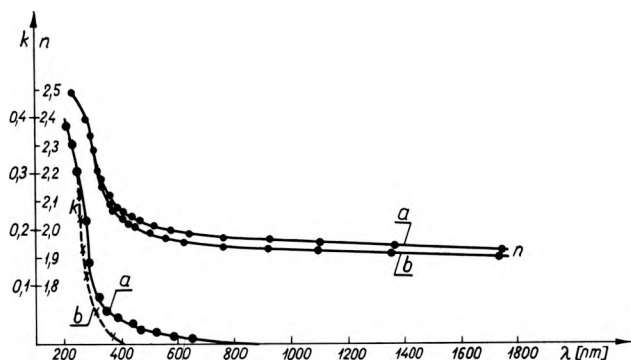


Fig. 5. Optical constants  $n$  and  $k$  for the  $\text{Yb}_2\text{O}_3$  film evaporated from a tungsten boat on a substrate of temperature of 250°C (curve *a*), and after heating (curve *b*) in the air atmosphere (400°C, 4 hours)

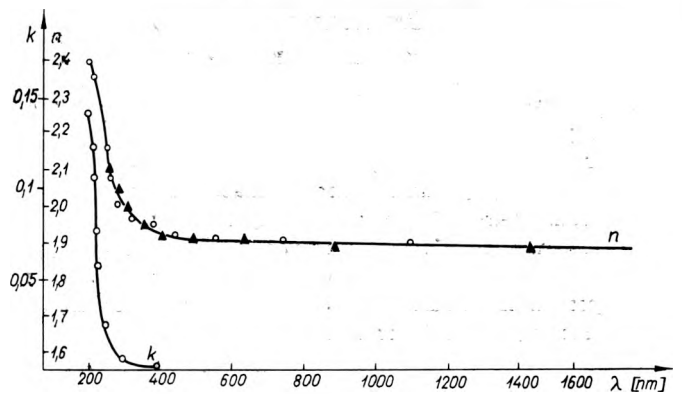


Fig. 6. The optical constants  $n$  and  $k$  for  $\text{Yb}_2\text{O}_3$  film evaporated on a substrate at the temperature of 250°C

crystal. The evaluation of the packing density based on Lorentz-Lorenz relation gives the value 0.975. During the examination it has been stated that the optical constants of the  $\text{Yb}_2\text{O}_3$  films evaporated with the help of an electron-gun do not differ considerably from one another, if the parameters kept constant during the evaporation are contained within the following intervals:

- the residual gas pressure:  $2 \times 10^{-5}$  Tr– $7 \times 10^{-5}$  Tr,
- the condensation rate of films: 1–3.5 nm/s, at the substrate temperature 250°C.

If, however, the pressure is not kept constant during the evaporation because of dosing of the air or oxygen, then the pressure in the vacuum chambers drops down by a factor of 1.5. Ytterbium oxide film evaporated under such conditions are optically nonuniform. This like in the case of ytterbium oxide [12] — may be due to the dependence of the stoichiometric composition of the film upon the conditions of its creation, i.e. upon the pressure in the case considered.

## 5. Conclusions

The most proper method of producing the  $\text{Yb}_2\text{O}_3$  films is the evaporation with the help of the electron-beam.

The films evaporated by the electron-beam exhibit advantageous optical properties for wavelength range 0.55–2.0  $\mu\text{m}$ . The refractive indices change very slowly. Immediately after evaporation onto a heated substrate the films are absorptionless in the visual and infrared parts of the spectrum. They are also characterized by a high mechanical resistance and stability of optical constants in the course of heating and temporal ageing.

**Оптические свойства  
тонких пленок окиси иттербия**

Представлены результаты исследований по методам получения тонких пленок окиси иттербия. В описании оптических свойств содержатся оптические константы  $n$  и  $k$  пленок  $Yb_2O_3$ , напыливаемых испарением из вольфрамовых нагревателей и электронной пушкой в диапазоне длины волн от 0,2 до 2,5 мкм. Кроме того, выполнены структурные исследования пленок  $Yb_2O_3$  а также рентгеновские микроанализы химического состава пленок, напыливаемых с помощью вольфрамовых челноков.

**References**

- [1] TAYLOR K., DARBY M., *Physics of Rare Earth Solids*, Chapman and Hall Ltd, London 1972.  
[2] HASS G., RAMSEY J. B., THUN R., *JOSA* **49**, 116, 1959.

- [3] HEITMAN W., *Vakuum Technik* **22**, 2, 49, 1973.  
[4] FRANK B., GROTH R., *Thin Solid Films* **3**, 41, 1969.  
[5] JAWALEKAR R., *Indian J. Pure Appl. Phys.* **7**, 801, 1969.  
[6] SEMILETOV S. A. et al., *Thin Solid Films*, **32**, 2, 325-328, 1976.  
[7] MARCINÓW T., *Własności fizyczne cienkich warstw tlenku iterbu* (Doctor's Thesis), Wrocław 1975.  
[8] HEAVENS O. S., *Physics of Thin Films*, Vol. 2, Academic Press, New York 1964.  
[9] HALL J. F., FERGUSSON W. F., *JOSA* **45**, 714, 1954.  
[10] SCHULZ L. G., TANGHERLINI F. R., *JOSA* **44**, 362, 1954.  
[11] WICKERSHEIM K., LEFEVER R., *JOSA* **51**, 1147, 1961.  
[12] TSUTSUMI T., *Jap. J. of Appl. Phys.* **9**, 7, 735, 1970.

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