

Presented at the 8th International Workshop on Glasses and Ceramics From Gels, Faro, Portugal, September 18-22, 1995, and to be published in the Journal of Sol Gel Science.

## **Structural and Optical Properties of Sol-Gel Deposited Proton Conducting Ta<sub>2</sub>O<sub>5</sub> Films**

Nilgun Ozer and Carl M. Lampert  
Building Technologies Program  
Energy and Environment Division  
E.O. Lawrence Berkeley National Laboratory  
University of California  
Berkeley, CA 94720

August 1995

**MASTER**

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED  
*DIC*

## **DISCLAIMER**

**Portions of this document may be illegible  
in electronic image products. Images are  
produced from the best available original  
document.**

# Structural and Optical Properties of Sol-Gel Deposited Proton Conducting $Ta_2O_5$ Films

NILGUN OZER<sup>a</sup> AND CARL M. LAMPERT<sup>b</sup>

<sup>a</sup>Istanbul University, Faculty of Science, Physics Department, Vezneciler, Istanbul, Turkey

<sup>b</sup>University of California, E.O. Lawrence Berkeley National Laboratory, Energy and Environment Division., 1 Cyclotron Road , MS. 62-203, Berkeley, CA 94720, USA

**Abstract:** Proton conducting tantalum oxide films were deposited by spin coating using a sol-gel process. The coating solutions were prepared using  $Ta(OC_2H_5)_5$  as a precursor. X-ray diffraction studies determined that the sol-gel films, heat treated at temperatures below 400°C, were amorphous. Films heat treated at higher temperatures were crystalline  $Ta_2O_5$ . The solar transmission values ( $T_S$ ) of tantalum oxide films on glass generally range from 0.8-0.9 depending on thickness. The refractive index and the extinction coefficient were evaluated from transmittance characteristics in the UV-VIS-NIR regions. The refractive index values calculated at  $\lambda=550$  nm increased from  $n=1.78$  to 1.97 with increasing heat treatment from 150 to 450°C. The films heat treated at different temperatures showed low absorption with extinction coefficients of less than  $k=1\times 10^{-3}$  in the visible range. Spectrophotometric and impedance spectroscopic investigations performed on  $Ta_2O_5$  films revealed that these films have protonic conductivity of  $3.2\times 10^{-6}$  S/cm. The films are suitable for proton conducting layers in electrochromic (EC) devices.

**Keywords:** optical properties, proton conductor, tantalum oxide, electrochromic devices

## 1. Introduction

Tantalum oxide films are of considerable interest in optical and optoelectronic technology [1]. Tantalum oxide also has been studied as an ion conductor for applications in electro-optical devices such as chromogenic glazing in windows and large scale information displays [2-3]. Because of its high protonic conductivity, tantalum oxide is a candidate for inorganic type solid electrolyte in electrochromic (EC) devices [4]. In general practice, tantalum oxide films have been prepared by conventional techniques, such as reactive evaporation [5], reactive sputtering [6], reactive ion plating [7], pulsed-laser assisted deposition [8], chemical vapor deposition [9-10]. Tantalum oxide has been used commercially by Donnelly Corp.(Holland, MI) in electrochromic mirror devices for vehicle applications. Recently, the sol-gel deposition process has been adopted to prepare tantalum oxide films [2,11]. The sol-gel process allows the formation of tantalum oxide films using low temperatures with very low capital investment compared to physical vapor deposition techniques. Sol-gel processing also allows control of the microstructure of the coating by adjusting the complexing of the precursor chemicals, changing the pH and viscosity of the solution, modifying the firing conditions and coating technique. Using microstructure modification and porosity control, one can enhance the kinetics, durability and ion insertion capability of  $Ta_2O_5$  film. Therefore the investigation of the properties of tantalum oxide heat treated over a wide temperature range is of great interest. Furthermore, no data concerning the effect of heat treatment temperature on the optical properties and protonic conductivity of sol-gel deposited tantalum oxide films have been published. In this study, we investigate the structure optical properties and proton conductivity of tantalum oxide films at the heat treatment temperatures in the range of 150-450°C.

## 2. Experimental

### 2.1. Coating Characterization

Structural investigation was performed by a Siemens Kristallofex X-ray diffraction (XRD) with Ni filtered  $\text{CuK}\alpha$  excitation. The surface morphology of the films were examined by scanning electron microscopy (SEM) with accelerating voltage of 10keV. A gold coating was applied onto the films to avoid the charging of the surface by the beam. The chemical composition and residual carbon content of the films were examined by a Kratos (XSAM 800) X-ray photoelectron spectrometer (XPS) with  $\text{MgK}\alpha$  excitation. The spectrometer was calibrated so that the Au ( $4f_{1/2}$ ) electron binding energy was at  $83.3 \pm 0.1\text{ eV}$  and adventitious carbon occurred at  $285 \pm 0.1\text{ eV}$ .

Thickness measurements were performed with a surface profiler Dektak II (Veeco Inst. Inc.) having a maximum resolution of 5 nm/ 100 nm. The optical transmittance of the films deposited on a quartz substrate were measured in the spectral range 290-2100 nm with Perkin Elmer Lambda 9 double beam spectrophotometer which has high photometric accuracy (<0.1 %).

The proton conductivities of the  $\text{Ta}_2\text{O}_5$  films were measured by an a-c complex impedance spectroscopy technique. The equipment used was a Schlumberger (model S-11260) Impedance/Gain analyzer, and a PAR (model 273) potentiostat/galvanostat and electrochemical interface. These were programmed by a desktop computer for data collection and analysis. The electrochemical cell consisted of a three electrode configuration in a sealed cell. The electrolyte was 0.2M  $\text{H}_2\text{SO}_4$ . All potentials in the present work are quoted against a standard calomel reference electrode (SCE).

### 2.2. Preparation of Solutions and Coatings

The coating solutions were prepared by hydrolytic polycondensation.  $\text{Ta}(\text{OC}_2\text{H}_5)_5$  was used as molecular precursor. The starting solution was prepared by mixing one part  $\text{Ta}(\text{OC}_2\text{H}_5)_5$  with 2/3 part ethanol and 0.003 part glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) by volume. Addition of acetic acid played a specific role in the sol-gel processing of tantalum it is not only a catalyst but it forms ligands with alkoxide. The polymeric solutions were stable up to 3 months when they were kept at 5°C. The coating solutions from freshly prepared and aged solutions were of the same quality. The  $\text{Ta}_2\text{O}_5$  films were deposited using spin-coating. The spinning rate was 2500 rpm and substrate was span 4 times to increase the film thickness (240 nm). Between each spin coat, heat treatment of the coating at 70°C was necessary; this was because the gel film dried and solidified too slowly in ambient. After final deposition, the films were heat treated in air at a temperature within the range of 150-450°C, to densify the newly formed oxide coatings. All films investigated in this work were transparent, hard, durable and chemically stable.

### 2.3. Optical Measurements

Before fabrication of EC devices, it is important to know the optical properties of the layers. In this investigation a simple method described by Demiryont et al.[12] were used to determine the optical constants and thickness of the films for thicker films. The optical parameters of  $\text{Ta}_2\text{O}_5$  films, namely the refractive index  $n(\lambda)$ , the extinction coefficient  $k(\lambda)$ , and the thickness of the coatings

were calculated by this model. The numerical analysis requires construction of the envelop curves of the interference extreme in the transmission spectra. Sample thicknesses were chosen so we could obtain a sufficient number of interference maxima and minima to determine the refractive index and extinction coefficient accurately. The thickness values also examined by surface profiler for comparison with the spectrophotometric analysis. The optical constants were evaluated over the wavelength interval of 0.3 to 1.3  $\mu\text{m}$ .

### 3. Results and Discussion

Thickness profile measurement of the sol-gel deposited  $\text{Ta}_2\text{O}_5$  films indicate that the average thicknesses of a single coating heat treated at 150 and 450°C are 85 and 68 nm respectively. The coatings used in this study were deposited in 4 coating cycles. The thicknesses of the resulting films are about 240 and 182 nm respectively. These films were examined by scanning electron microscopy and exhibited a smooth adherent surface with very few pinholes or microcracks over a large region of the film. Multiple coating increased thickness, but did not affect the uniformity of the film. Figure 1 shows the results of the broad energy scan XPS spectrum of the tantalum oxide film. The relatively high content of carbon residues at a heat treatment temperature of 150°C (12.7%) decreases rapidly to 3.3% at 450°C. The stoichiometry of the films are given as the atomic concentration ratio of oxygen to tantalum O:Ta. The variation in O:Ta is less than 2% over the entire heat treatment temperature range investigated while the mean value of O:Ta is equal 4.8:2. This is close to the ratio frequently found for stoichiometric  $\text{Ta}_2\text{O}_5$  [13]. The structures of films deposited on glass substrates were studied by XRD. Figure 2 shows the XRD patterns of  $\text{Ta}_2\text{O}_5$  films. XRD analysis shows that all of the films heat treated at lower temperatures (<450°C) are amorphous and those heat treated at higher temperatures (>450°C) are polycrystalline. The films heat treated at 450°C and higher temperatures exhibited characteristic peaks of hexagonal  $\delta$ - $\text{Ta}_2\text{O}_5$ .

Ionic conductivity measurements were determined from a-c impedance spectroscopy. The measurements were made over the frequency range of 100 mHz to 20 Hz. Figure 3 shows a typical complex impedance plane diagram which consists of an arc of circle at the high frequencies followed by a straight line at the lower frequencies. A simplified equivalent circuit representing the sample was used to calculate ionic conductivity (shown in the inset in Figure 3) where  $R_e$  is the ohmic resistance of electrode,  $C_d$  is the double layer capacitance of the electrode / electrolyte interface,  $R_i$  is the ionic resistance arising from the diffusion of protons,  $C_g$  is the geometric capacitance between electrodes. From impedance analysis, the intercept of the high frequency semicircle with  $\text{Re}(Z)$  axis gives the  $R_i$  ionic resistance. These values were used to determine ionic conductivity of  $\text{Ta}_2\text{O}_5$  films together with geometrical factors (film thickness and the electrode area) [14]. The semi-circle observed at high frequency part of the diagram corresponding to the proton diffusion into the electrode material. The proton conductivity decreased with an increase in heat treatment temperature. The value of protonic conductivity is  $3.2 \times 10^{-6}$  S/cm for  $\text{Ta}_2\text{O}_5$  films heat treated at 150°C and  $10^{-6}$  S/cm for the films heat treated above 350°C. The electrical resistivity of the films was about  $150 \Omega/\text{cm}^2$ . This value was found to be high for proper device operation.

Figure 4 shows the spectrophotometric transmittance plot of  $\text{Ta}_2\text{O}_5$  film heat treated at 150°C. It can be seen that film has good optical quality. The  $T_0$ ,  $T^+$  and  $T^-$  plots correspond to the transmittance of bare substrate and maximum and minimum envelopes passing through the transmittance extrema. The number of interference extrema in a given spectral region is

proportional to the film thickness and the refractive index. The differences between the  $T^+$  and  $T^-$  and the  $T_0$  and  $T^+$  couples are measures of the refractive index and absorption of the film respectively [12].  $T(\lambda)$  spectra exhibit high transparency throughout the range studied. Figures 5 and 6 show the spectral dependence of the refractive index and extinction coefficient of spin-coated  $Ta_2O_5$  films. It can be seen from Figures 5 and 6 that the refractive index has the same characteristics as the extinction coefficient since both of them increase sharply in the strong dispersion region ( $\lambda < 450$  nm). The  $n$  value decreased from 1.88 at 400 nm to 1.79 at 550 nm and remain at 1.78 in the near infrared for the films heat treated at 150°C. The refractive index of the films are  $n = 1.78 \pm 0.04$ ,  $1.88 \pm 0.05$  and  $1.97 \pm 0.05$  at  $\lambda = 550$  nm for the films heat treated at 150, 300 and 400°C respectively. The last value is within experimental error, the same as that obtained by Kukli et al. [15] for tantalum oxide films grown by atomic layer deposition. All deposited films had homogeneous refractive index. No signs of inhomogeneity were observed. The optical band gap value  $E_g$  were calculated from the absorption coefficient ( $\alpha = 4\pi k/\lambda$ ) values of the film. The extrapolated value of the linear part of  $(E\alpha)^{1/2}$  vs  $E$  curves at zero absorption provides  $E_g$  [12]. The absorption coefficient of  $Ta_2O_5$  films follows well  $(E - E_g)^2$  energy dependence characteristics of indirectly allowed transitions. The optical band gap of the  $Ta_2O_5$  films is found at around 3.9 eV. The lowest energy gap is found to be 3.89 eV for crystalline  $Ta_2O_5$  films. The transition from the amorphous phase to crystalline phase caused a decrease in the band gap value. The optical band gap values of sol-gel films are lower than the values obtained by other researchers and range from 4.0 to 4.5 eV [15]. We also observed bandgap widening upon proton intercalation but not studied in detail. The characteristics of sol-gel spin coated films are tabulated in Table 1.

**Table 1. Main characteristics of proton conducting tantalum oxide films**

HT Temp. °C (1hr.)	$n_{(500nm)}$	$k$ (500nm) (eV)	$E_g$ ( $S\text{ cm}^{-1}$ )	$\sigma$	Structure
150	1.78	$8 \times 10^{-4}$	3.93	$3.2 \times 10^{-6}$	Amorphous
250	1.84	$8 \times 10^{-4}$	3.92	$2.4 \times 10^{-6}$	Amorphous
350	1.91	$7 \times 10^{-4}$	3.88	$1.2 \times 10^{-6}$	Amorphous
450	1.97	$7 \times 10^{-4}$	3.82	$8.6 \times 10^{-7}$	Polycrystalline

#### 4. Conclusion

The present investigation shows that the properties of tantalum oxide films deposited by sol-gel process depend significantly on the heat treatment temperature. The films heat treated below 400°C were amorphous. Amorphous  $Ta_2O_5$  films had room temperature conductivities of  $3.2 \times 10^{-6} \text{ Scm}^{-1}$  and crystalline  $Ta_2O_5$  had  $8.6 \times 10^{-7} \text{ Scm}^{-1}$ . These films exhibited low absorption with an extinction coefficient of less than 0.001 in the visible region. Uniform, transparent proton conducting  $Ta_2O_5$  films with refractive index and optical band gap ranging between  $1.78 < n < 1.97$  and  $3.82 \text{ eV} < E_g < 3.92 \text{ eV}$  were deposited by the spin coating technique. The film properties were altered by heat

treatment temperatures. The properties of low absorption and a relatively high proton conductivity at room temperature make these  $Ta_2O_5$  films potentially useful as protonic ion conductors in electrochromic devices. However, it is necessary to increase their electrical resistivity in order to reduce electrical leakage in devices. With further study we believe it will be possible to use sol-gel  $Ta_2O_5$  coating in protonic electrochromic devices.

## 5. Acknowledgments

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The authors wish to thank Dr. Temel Büyüklimanlı, Evans East, for performing XPS measurements.

## 6. References

1. Waldorf, A. J., Dobrowski, J. A., Sullivan, B. T., and Plante, L. M., *Appl. Opt.* **32**, 5583 (1993).
2. Ozer, N., He, Y. X., and Lampert, C. M., *Proc. SPIE* **2255**, 456 (1995).
3. Duggan, M. J., Saito, T., and Niva, T., *Solid State Ionics* **62**, 15 (1993).
4. Slade, R. C. T., Barker, J. and Halstead, T.K., *Solid State Ionics* **24**, 147 (1987).
5. Rubio, F., Denis, J., Albella, J. M., and Martinez-Duart, J. M., *Thin Solid Films* **90**, 405 (1982).
6. Gurtler, K., Bange, K., Wagner, W., Rauch, F., and Hantche H., *Thin Solid Films* **175**, 185 (1989).
7. Shimizu, K., Katayama, M., Funaki, H., Arai, E., Nakata, M., Ohji, Y., and Imura, R., *J. Appl. Phys.* **74**, 375 (1993).
8. Sankur, H. O., and Gunning, W., *Appl. Opt.* **28**, 341 (1989).
9. Desu, S. B., *Mater. Chem. Phys.* **31**, 314 (1992).
10. Lo, G. Q., Kwong, D. L., and Lee, S., *Appl. Phys. Lett.* **62**, 97 (1993).
11. Ozer, N., and Lampert, C. M., *Proc. of Conf. Window Innovations 95* (Minister of Supply and Services, Govt. of Canada, Ottawa, Canada, 1995), p.372.
12. Demiryont, H., Sites, J. R., and Geib, K., *Appl. Opt.* **24**, 490 (1985).
13. Wagner, C. D., Riggs, W. N., Davis, L. E., and Moulder, J. F., *Handbook of X-ray Photoelectron Spectroscopy* (Physical Electronics Industries, Eden Prairie, MN, 1979).
14. Slade, R. C. T., and Hall, G. P., *Solid State Ionics* **37**, 29 (1989).
15. Kukli, K., Aarik, J., Aidla, A., Kohan, O., Ustare, T., and Sammelserg, V., *Thin Solid Films* **260**, 135 (1995).

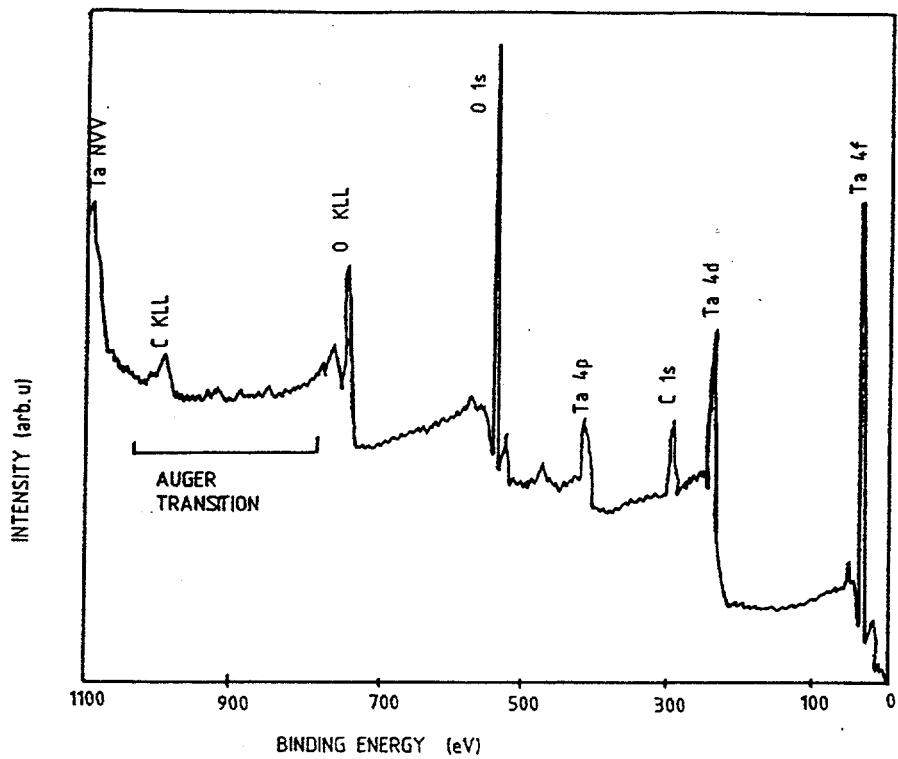


Figure 1. XPS survey scan of tantalum oxide films.

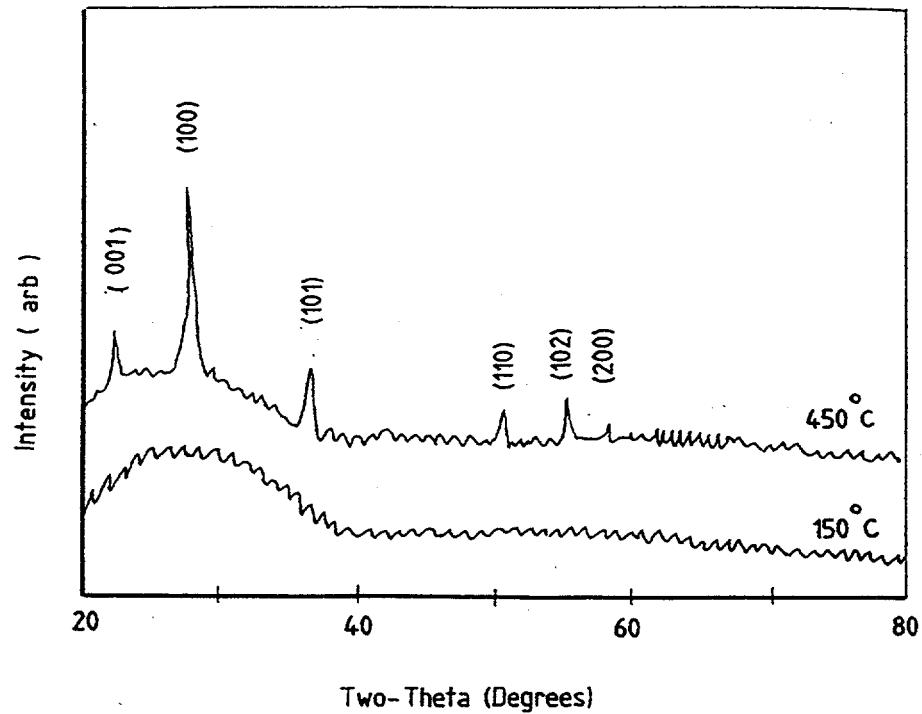


Figure 2. XRD patterns of tantalum oxide films deposited on glass substrates.

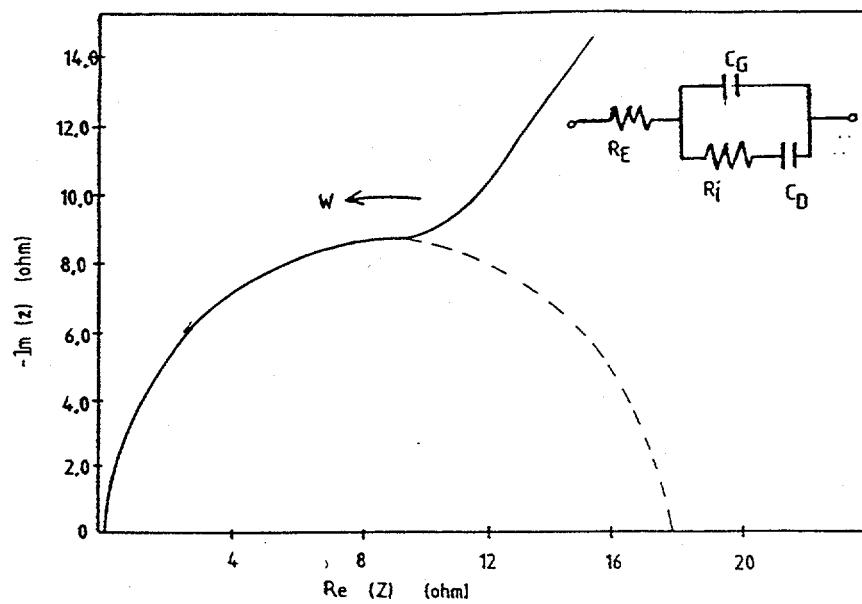


Figure 3. Impedance plot of amorphous tantalum oxide film (580 nm thick). The inset shows the circuit model used for analysis where  $R_E$  is the ohmic resistance of electrode,  $C_D$  is the double layer capacitance of the electrode/electrolyte interface,  $R_I$  is the ionic resistance arising from the diffusion of protons,  $C_G$  is the geometric capacitance between electrodes.

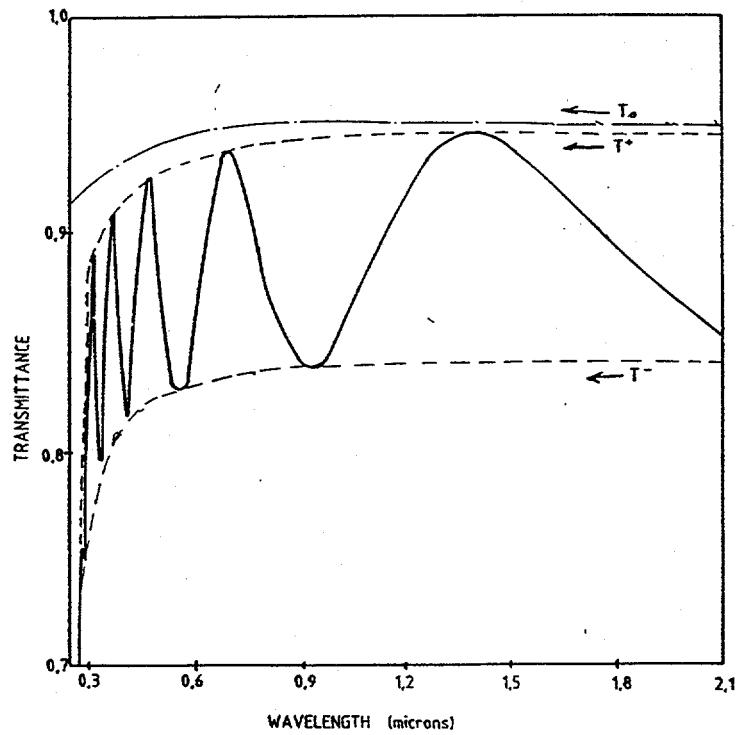


Figure 4. Transmittance spectrum of tantalum oxide film heat treated at 150 C. The film thickness calculated from this spectrum is 245 nm.  $T_0$  is the transmittance of the bare glass substrate.  $T^+$  and  $T^-$  are the transmittance maxima and minima respectively.

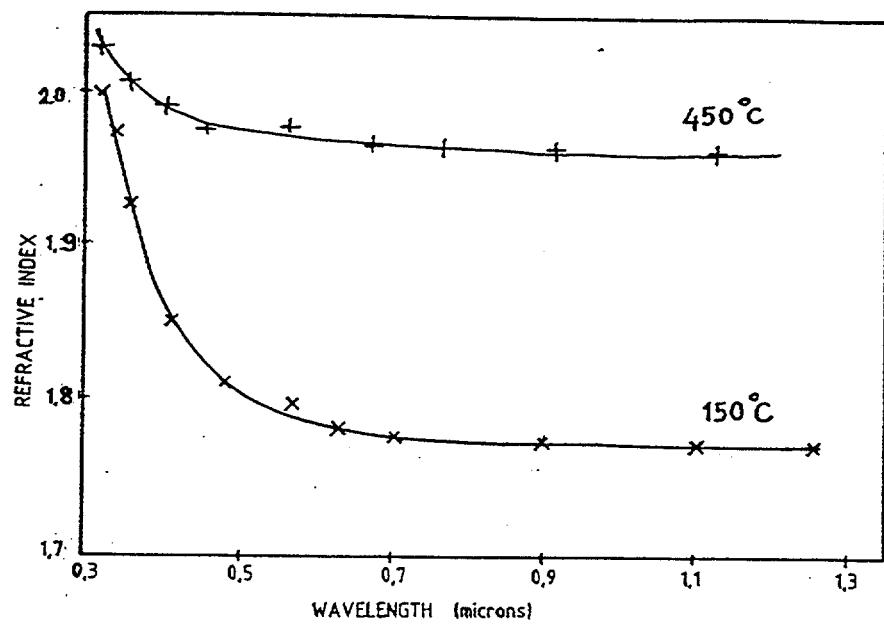


Figure 5. Refractive index spectra of tantalum oxide films heat treated at 150 and 450 C.

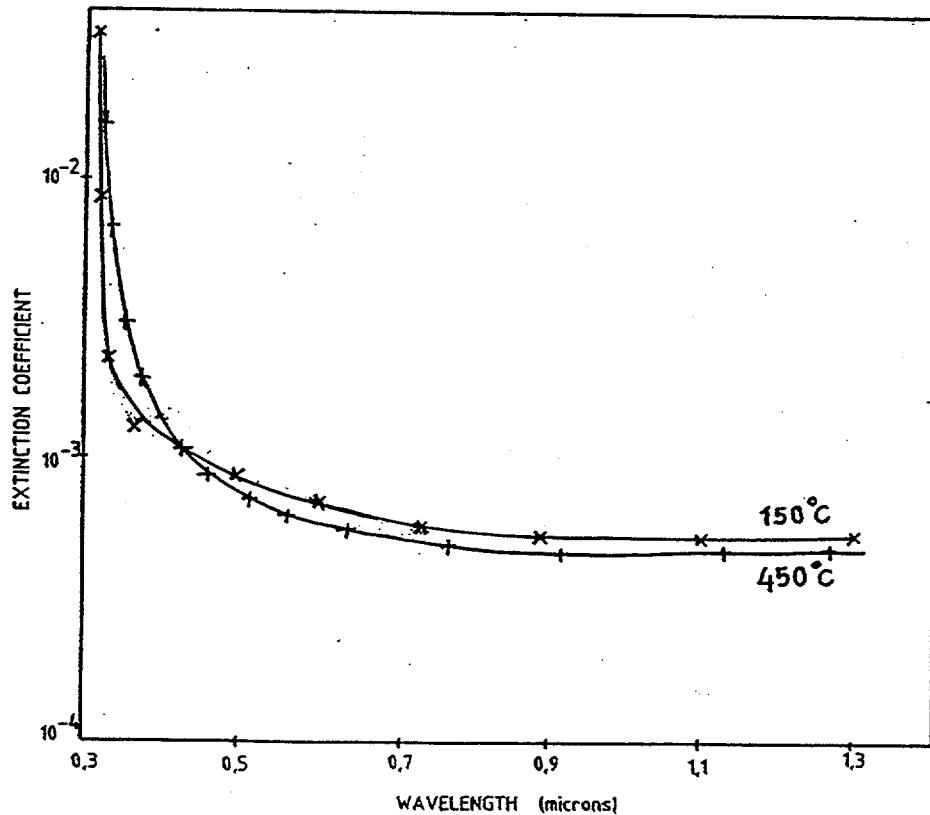


Figure 6. Extinction coefficient spectra of tantalum oxide films heat treated at 150 and 450 C.