DETERMINATION OF THE THICKNESS AND THE REFRACTIVE INDEX OF V_2O_5 THIN FILMS FROM REFLECTANCE INTERFERENCE SPECTRA

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The thickness and the refractive index of V_2O_5 thin layers on silicon single-crystal plates were determined from the reflectance interference spectra measured at 45° and 29.2° angle of incidence in the wavelength range of 360 nm—900 nm. The thin V_2O_5 layers were prepared by evaporating vanadium layers of different thickness onto silicon single-crystal plates and oxidizing the vanadium layer at 400° C. For evaluation of the reflectance spectra an approximate calculation was applied. The density of thin layers was determined from the thickness of vanadium measured during the evaporation and from the thickness of vanadium pentoxide layers measured by optical method. For the density of the V_2O_5 films an average value of 3.1 g/cm³ was obtained. A reflectance peak found at about 420 nm was attributed to the V^{4+} concentration present in the vanadium pentoxide.

Introduction

The mechanisms of carrier transport, the voltage dependence of capacitance, and the photoconductivity of V_2O_5-nSi system were reported in earlier communications [1, 2]. We measured some physical parameters of the V_2O_5 layers, but concerning the thickness and refractive index were restricted only to estimations. The subject of the present paper is the determination of the thickness and the refractive index of vanadium pentoxide thin films — prepared by evaporation and subsequent oxidation of vanadium on silicon single-crystal plates — from reflectance interference spectra.

As it is known, if a non-absorbing planparallel slab with a thickness of d and a refractive index of n is bordered on its sides by two non-absorbing media I and II with refractive indices of n_0 and n_1, respectively, ($n_0 < n$; $n_1 < n$ for all wavelengths taken into account), then the light beams *1* and *2* reflected from the upper and the lower surfaces of the slab will interfere (Fig. 1). Due to this interference the intensity of the light beams reflected at α angle will exhibit maxima and minima at the following wavelength:

$$\lambda_{max} = \frac{4d\sqrt{n^2(\lambda_{max}) - n_0^2(\lambda_{max})\sin^2\alpha}}{2k-1} = \frac{A(\lambda_{max})}{2k-1} \tag{1}$$

$$\lambda_{min} = \frac{4d\sqrt{n^2(\lambda_{min}) - n_0^2(\lambda_{min})\sin^2\alpha}}{2k} = \frac{A(\lambda_{min})}{2k}, \tag{2}$$

where $k=1, 2, 3, \ldots$. In Eqs. (1) and (2) the wavelength dependence of the refractive indices should be taken into account. If medium I is air, then $n_0=1$ is true with a good approximation in a wide spectral region.

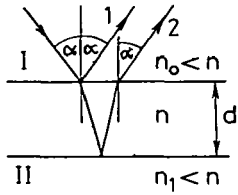

Fig. 1.

For our reflectance spectra we can write;

$$\text{maxima:} \quad \lambda_1 = A(\lambda_1), \quad \lambda_3 = \frac{A(\lambda_3)}{3}$$

$$\text{minima:} \quad \lambda_2 = \frac{A(\lambda_2)}{2} \quad \lambda_4 = \frac{A(\lambda_4)}{4}, \tag{3}$$

i.e. we have taken into account only the first and second order extrema. Knowing the $n=n(\lambda)$ function the thickness of the layers can be calculated from Eqs. (1) and (2). Although the $n(\lambda)$ function is known for the crystallographic directions *a*, *b*, *c* in the case of vanadium pentoxide single-crystal [3–5], we cannot use directly these values of refractive indices, because the prepared layers are certainly not single-crystals, and the optical properties of thin films generally differ from that of bulk materials. The method applied for the evaluation of interference spectrum and for determination of the thickness and the refractive indices of the thin V_2O_5 layers will be discussed in the last section.

Experimental

Vanadium layers (thickness: 57 nm, 52 nm, 45 nm, 20 nm and 11.5 nm) were evaporated onto freshly etched silicon single-crystal plates of 15 mm×15 mm×0.2 mm in size or onto chemically cleaned mica sheets in 5×10^{-6} torr vacuum. The thickness of the condensed metal layer was determined during the evaporation process by a Thin Film Thickness and Deposition Rate Monitor instrument type MSV-1841; made by the Hungarian Research Institute for Precision Engineering. The vanadium covered silicon plates (in the followings referred to as samples) and mica sheets (in the followings referred to as sheets) were held in an oxigen stream of atmospheric pressure in an oven of 400° C temperature. The vanadium layers which differed in thickness were oxidized for different time-periods. From time to time the oxidation process was interrupted and the reflectance spectra of the samples and the sheets were determined.

The reflectance spectra were measured at an angle of $\alpha=45°$ and $\alpha=29.2°$ changing the wavelength of the monochromatic light beam in 5 nm or 10 nm steps in the 360 nm–900 nm range. The intensity ratio of the light reflected from the layer $(I_R(\lambda))$ and incident onto the layer $(I_o(\lambda))$ at the same λ was measured with a PIN silicon photodiode (sensitive area 1 cm², type UDT 500, United Detector Technology Inc.). The output voltage of the FET operation amplifier built in the photodiode housing was detected by a digital voltmeter. The sensitivity of the detector considerably depended on the wavelength, however the relation between the output voltage of the photodiode-amplifier system and the light intensity at all fixed wavelength and intensity used was found to be linear with a good approximation. Therefore,

the reflectance was determined from the relation $R(\lambda)=\frac{I_R(\lambda)}{I_o(\lambda)}=\frac{U_R(\lambda)}{U_o(\lambda)}$, where $U_R(\lambda)$ and $U_o(\lambda)$ denote the measured output voltages. On a given sample the reflectance spectrum minima and maxima could be reproduced within 5 nm in all cases; the maximum relative error of $R(\lambda)$ was 6% in the most unfavourable case.

Results and discussion

During the oxidation process the metallic vanadium gradually transformed to yellow vanadium pentoxide. In an early stage of the oxidation, a peak at about 420 nm appeared in the reflectance spectrum, but interference structure could not be resolved (Fig. 2). In the following only the results obtained with samples in the last stage of oxidation process will be discussed, *i.e.* the oxidation was first stoppey when the yellow colour of V_2O_5 on the sheets which were heat treated parallele with the samples had already appeared. It is reasonable to assume that at this stagd the composition of the layers was very near to that of the vanadium pentoxide, but the layers were not totally stochiometric, especially beyond a certain depth.

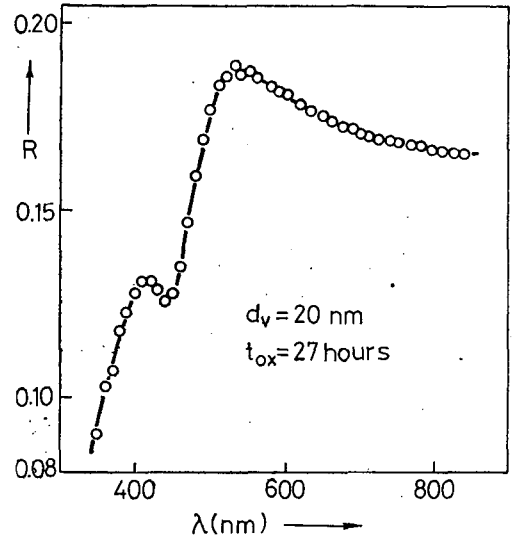

Fig. 2. The reflectance spectrum of a sample measured at $\alpha=45°$ angle of incidence in an early stage of oxidation. d_v and t_{ox} are the thickness of evaporated vanadium layer and the oxidation time, respectively.

In Figs. 3a–d the reflectance spectra of a sample covered with evaporated vanadium layer (thickness $d_v=57$ nm) are shown. The spectra were measured at an angle of $\alpha=45°$ and $\alpha=29.2°$ after an oxidation time (t_{ox}) of 35, 59, 109 and 205 hours, respectively. The shortest wavelength maximum was found at $\lambda_0=430$ nm (Figs. 3a–d). This λ_0 belonging to the first maximum practically did not depend on the angle of incidence, but the wavelength belonging to other maxima and minima were generally shifted towards longer wavelength with decreasing angle of incidence. Quite generally λ_0 was found to be independent of α, whereas the maxima and minima strongly depended on α in all reflectance spectra presented below. As it is seen in Figs. 3a–d the maxima and minima are red-shifted with increasing oxidation time for both angles, however, λ_0 remained constant (see Table I). The reflectance spectra of different samples are shown in Figs. 4–7.

It has to be mentioned that the peak belonging to λ_0 could not be observed in the thinnest layer (Fig. 7), probably due to the overlaping intense maximum.

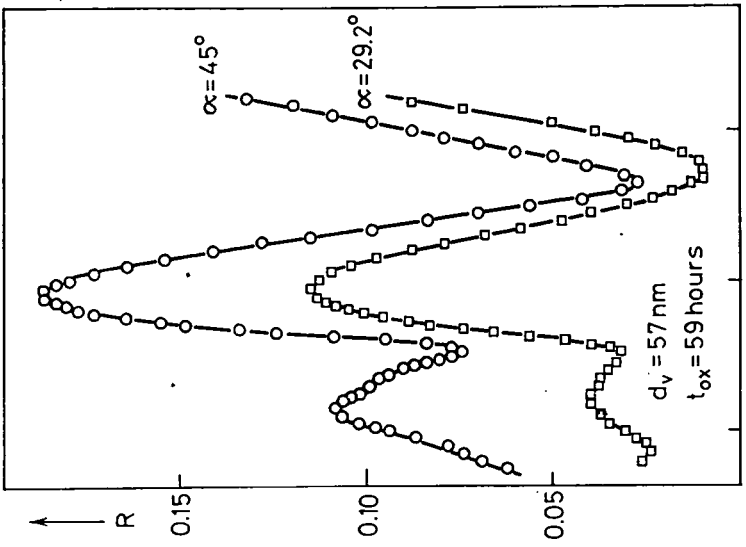
α=45°
α=29.2°
d_v = 57 nm
t_ox = 59 hours
R
0.15
0.10
0.05
400
600
800
λ(nm)

Fig. 3b

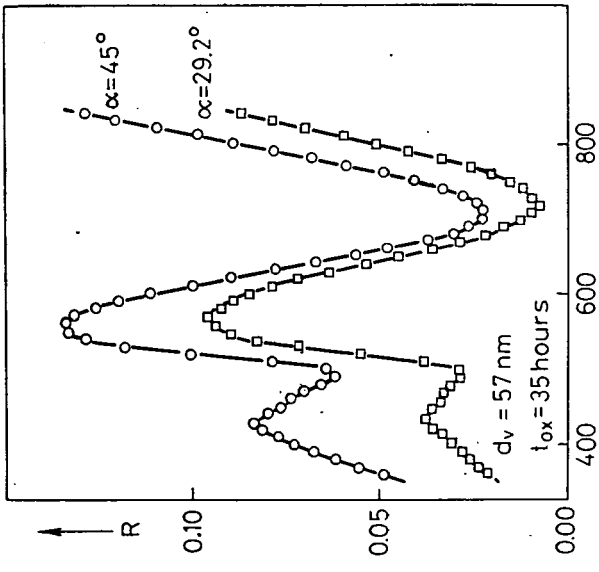
α=45°
α=29.2°
d_v = 57 nm
t_ox = 35 hours
R
0.10
0.05
0.00
400
600
800
λ(nm)

Fig. 3a

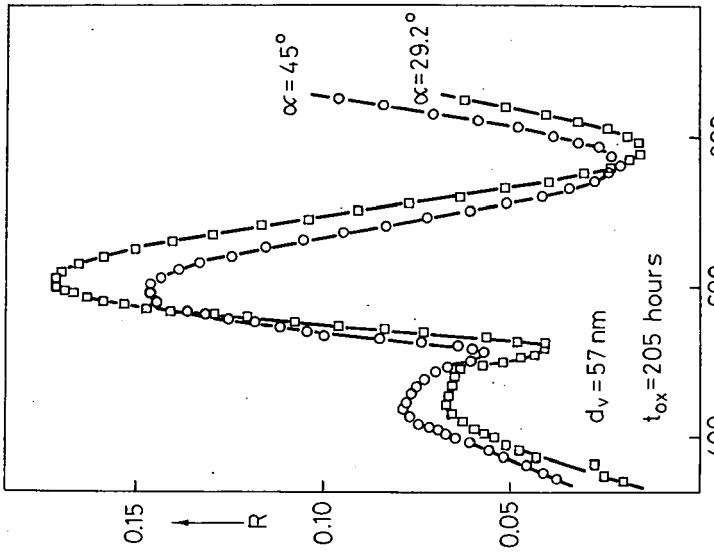
α=45°
α=29.2°
d_V = 57 nm
t_ox = 205 hours
R
0.15
0.10
0.05
400
600
800
λ(nm)

Fig. 3d

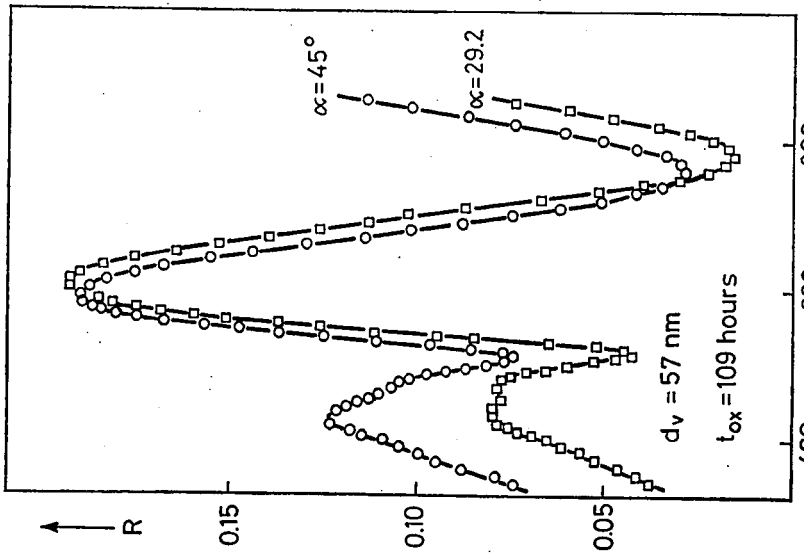
α=45°
α=29.2
d_V = 57 nm
t_ox = 109 hours
R
0.15
0.10
0.05
400
600
800
λ(nm)

Fig. 3c

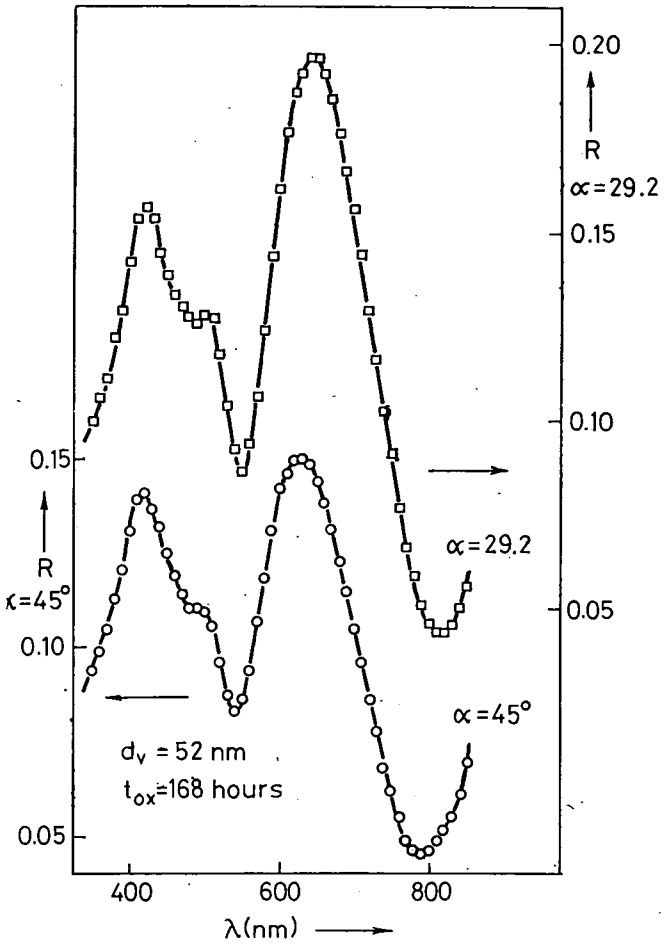

Fig. 4. The reflectance spectrum of a sample measured at an angle of $\alpha=45°$ and $\alpha=29.2°$ after an oxidation time of 168 hours. Scales for $\alpha=45°$ and $\alpha=29.2°$ are given on the left-hand and righthand sides of the figure, respectively.

The reflectance spectra of V_2O_5 films on mica sheets were also determined. The main features of these were as follows:

(i) in the case of all but the thinnest layer (with different d_v and t_{ox}) λ_0 was found to be 415 nm and its amplitude was slightly higher than that observed in the samples;

(ii) in the case of the thinnest layer ($d_v=11.5$ nm and $t_{ox}=40$ hours) the λ_0 maximum could not be observed;

(iii) the maxima and minima within a deviation of 0–20 nm were observed close to the same features of the samples.

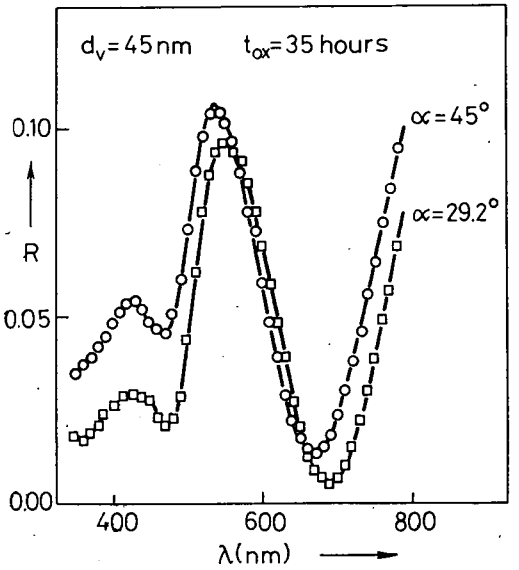
d_v = 45 nm
t_{ox} = 35 hours
α = 45°
α = 29.2°
0.10
R
0.05
0.00
400
600
800
λ(nm)

Fig. 5a

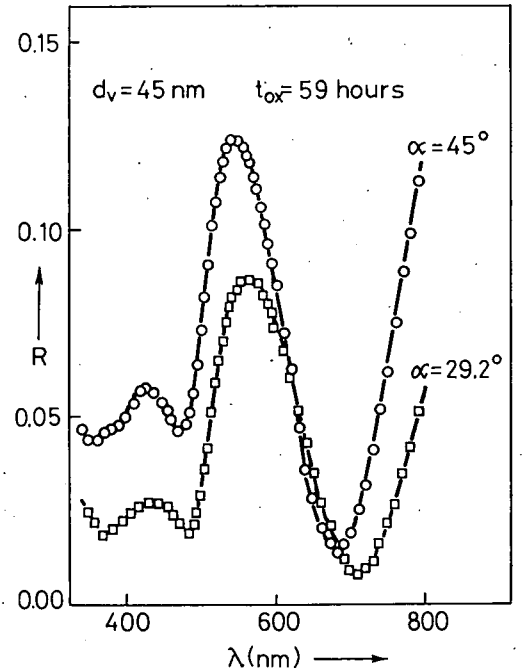
d_v = 45 nm
t_{ox} = 59 hours
α = 45°
α = 29.2°
0.15
0.10
R
0.05
0.00
400
600
800
λ(nm)

Fig. 5b

Because the reflective index of mica is smaller than that of V_2O_5 in the total wavelength range investigated (for instance at $\lambda = 600$ nm the refractive index of mica is between 1.56 and 1.60 depending on crystallographic orientation), the light beam reflected from the V_2O_5-mica interface does not suffer phase change. Since the spectra of the samples and the sheets with the same parameters agreed relatively well with each other as the position of maxima and minima were concerned, we concluded that no phase jump could take place at the V_2O_5-Si interface either. The major part of the light intensity probably reflected from the thin layer between the V_2O_5 and the silicon [1]. If so this thin interface layer should have smaller refractive index than that of the vanadium pentoxide film in the investigated wavelength range; the refractive index of silicon itself is higher than that of V_2O_5 [6]. Had the light thus reflected from the silicon surface, a phase change should have been observed.

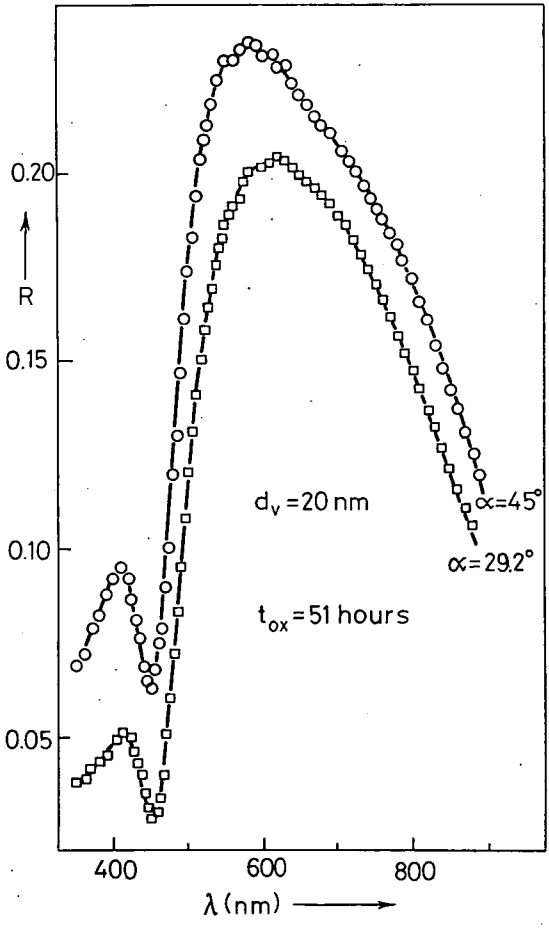

Fig. 6

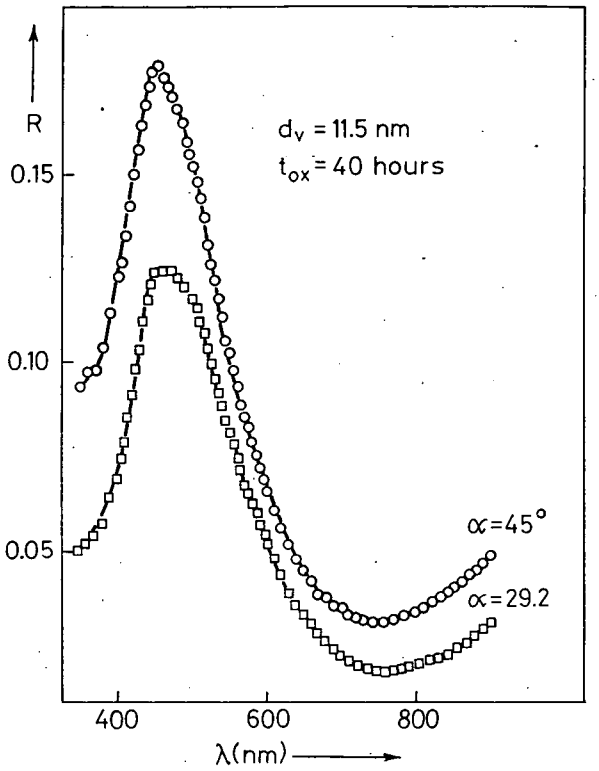

Fig. 7

However, no maximum-minimum interchange was observed indicating that the light was mainly reflected from the thin interface layer.

Taking into account that the vanadium pentoxide single-crystals were found to be non-absorbing* with a good approximation in the wavelength range used [3] the same can hold for V_2O_5 layers, too. Therefore Eqs. (1) and (2) can be applied for the evaluation of the reflectance spectra.

Notation used in Table I: m_d denotes the so called "mass thickness" *i.e.* the mass of vanadium layered on 1 cm^2 area of the silicon substrate. It has to be noted that by longest oxidation times we mean the time period which was necessary to the total oxidation of the vanadium layer at a given thickness. After prolonged oxidation listed in Table I as "longest" no changes could be observed in the reflectance spectra.

On evaluating the reflectance spectra the following assumptions were made:

(i) Eqs. (1)–(2) are valid;

(ii) the $n=n(\lambda)$ function is nearly the same for all V_2O_5 layers investigated and $n(\lambda)$ is a continous function of λ;

(iii) the reflectance peak belonging to λ_0 did not produce interference.

* More exactly: the refractive index n is much more higher than the absorption index k.

Table I

Results of measurements

d_v (nm)	m_d $\left(\times 10^{-5}\frac{g}{cm^2}\right)$	t_{ox} (hours)	(λ_0) (nm)	$\alpha=45°$				$\alpha=29.2°$			
				λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)
57	6.06	35	430	—	705	555	490	—	720	570	495
57	6.06	59	430	—	730	580	505	—	745	582	505
57	6.06	109	430	—	760	585	510	—	782	603	515
57	6.06	205	430	—	763	590	510	—	785	608	517
52	5.53	168	425	—	790	625	545	—	815	645	550
45	4.79	35	425	—	670	535	465	—	690	550	470
45	4.79	59	425	—	680	545	473	—	710	565	480
20	2.13	51	405	590	446	—	—	620	450	—	—
11.5	1.22	40	—	453	—	—	—	465	—	—	—

For notation $\lambda_1-\lambda_4$ see Eq. (3).

Since we did not know the $n(\lambda)$ function for V_2O_5 thin films there was one way to calculate the thicknesses and refractive indices belonging to different wavelength: inserting simultaneously all the results obtained into an iteration. By averaging and interpolating the values of refractive indices given in the literature [3–5] for different crystallographic directions and wavelength for V_2O_5 single-crystal, an approximate $n=n_h(\lambda)$ function was constructed (dotted line in Fig. 8). First we supposed that

$$\frac{n_h(\lambda_{i45°})}{n_h(\lambda_{i29,2°})}=\frac{n_{(0)}(\lambda_{i45°})}{n_{(0)}(\lambda_{i29,2°})}, \tag{4}$$

where $i=2, 3, 4$; and $n_{(0)}(\lambda)$ is the value of refractive index at wavelength λ in zeroth order approximation. The values of λ_{ix} were taken from the 1st–7th lines of Table I. Using the values standing on the right side of Eq. (4) three different values of thickness were obtained for each sample with the same d_v and t_{ox} from Eqs. (1)–(3). The average of these values was taken as zeroth order approximate value for the thicknesses. Substituting these values into Eqs. (1)–(3) the numerical values of $n_{(1)}(\lambda)$ could be obtained for all λ can be found in the 1st–7th lines of Table I. Inserting the appropriate values of $n_{(1)}(\lambda)$ into the left-hand side of Eq. (4) we got the new values of $\frac{n_{(2)}(\lambda_{i45°})}{n_{(2)}(\lambda_{i29,2})}$. The iterative calculation was continued as long as the values obtained for the thickness were the same in three digits for all λ_i. At last the iteration was expanded over the two samples with thinner V_2O_5 layer (8th and 9th lines in Table I).

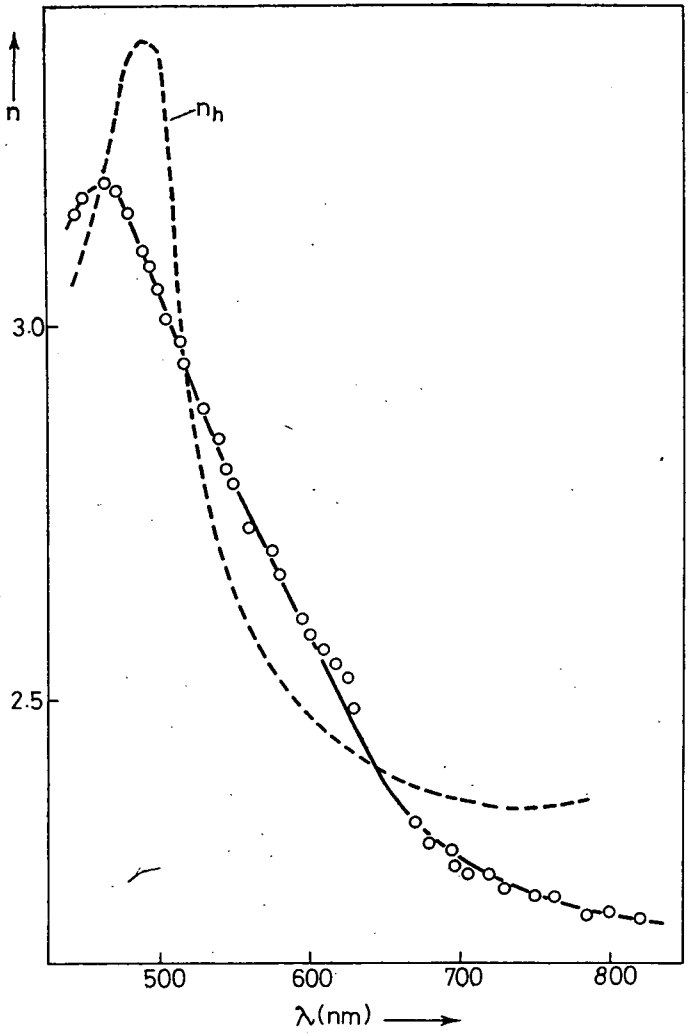

Fig. 8. The calculated values of refractive index for V_2O_5 thin films (empty circles) and the $n_h(\lambda)$ curve (dotted line).

Obviously the results obtained for the thickness and $n(\lambda)$ in this way were independent of $n_h(\lambda)$. If $n_h(\lambda)$ were equal to const. $n(\lambda)$ for example, then the iteration would be completed in the first step. If the form of $n_h(\lambda)$ deviates from that of $n(\lambda)$ the iteration consists of too many steps.

The determination of interference order (k in Eqs. (1)–(2)) was very simple since in Figs. 7 and 6 only one and two extrema could be found, respectively.*

* In Fig. 7 the minimum at about 750 nm is due to the slight increase in the reflectance of the silicon substrate towards the longer wavelength, as measured in Si-SiO_2 system.

Any variation in k implicitely found in Eq. (3) resulted in very unresonable thickness and density values for the vanadium pentoxide layers and, in addition, made the simultaneous evaluation of the reflectance spectra impossible.

In Fig. 8 the calculated values of refractive index (empty circles) and the $n_h(\lambda)$ curve (dotted line) are shown. As it has been expected, the shape of the two curves is similar but the values of the two curves at certain wavelength regions are considerably different.

The obtained results are summarized in Table II. Column 4 of Table II contains the calculated thickness (d) of the vanadium pentoxide layers, while column 5 gives the density calculated from the relation $\varrho=\frac{m_d}{d}$, other columns give the wavelength values recalculated from the refractive indices (Fig. 8) and from the thickness (column 4) obtained by the iterative calculation. Comparing the measured (Table I) and the calculated wavelength values (Table II) for the interference maxima and minima, the agreement is satisfactory except for two λ_1 values in the case of sample with $d_v=20$ nm. The slight increase in reflectance of the substrate towards longer wavelength, the asymmetry of the reflectance peak in Fig. 6 (not experienced by us in other cases), and the poor resolution of the peak may probably contribute to the difference between the measured and calculated values. These factors caused uncertainity in the determination of the λ_1 values.

As it is seen from Table II the thickness of the V_2O_5 layers increase, whereas their density decrease with increasing oxidation time. This thickness increase is about 10% for a sample with $d_v=57$ nm. In the case of the longest oxidizing times presented in Table II the average value of density is 3.1 g/cm³ for V_2O_5 layers of different thickness.

Table II

The obtained results and the recalculated values of wavelength

					$\alpha=45°$				$\alpha=29.2°$			
d_v (nm)	m_d $\left(\times 10^{-5}\frac{g}{cm^2}\right)$	t_{ox} (hours)	d (nm)	ϱ $\left(\frac{g}{cm^3}\right)$	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)
57	6.06	35	163	3.72	—	705	553	489	—	719	574	494
57	6.06	59	170	3.56	—	728	580	505	—	745	585	504
57	6.06	109	179	3.39	—	761	595	513	—	781	602	516
57	6.06	205	180	3.37	—	764	595	515	—	784	604	520
52	5.53	168	190	2.91	—	796	620	535	—	816	630	540
45	4.79	34	149	3.21	—	667	540	464	—	678	550	470
45	4.79	59	155	3.09	—	683	553	76	—	694	561	485
20	2.13	51	72	2.96	650	446	—	—	662	450	—	—
11.5	1.22	40	37	3.30	453	—	—	—	460	—	—	—

The reflectance peak at about 420 nm can be assigned according to JOHNSTON [7] to V^{4+} ions present in the vanadium pentoxide which play an important role in determining the conductivity of V_2O_5. This assignment can be supported by our observation that the height of the λ_0 peak could be paralleled with the conductance of the vanadium pentoxide layer.

On the basis of the results presented here we arrived at the following conclusions:

(i) Eqs. (1)–(2) could be applied for the evaluation of reflectance spectra of V_2O_5 layers on silicon substrate;

(ii) the reflected light from the V_2O_5 side of V_2O_5-Si interface did not suffer phase change indicating that a thin interface layer should exist between the V_2O_5 and the silicon with lower refractive index than that of V_3O_5 in the wavelength range investigated;

(iii) after prolonged oxidizing time, which depended on the thickness of the V_2O_5 layer, the refractive index of the V_2O_5 layer was independent of the oxidation time, whereas the thickness and the density changed with the oxidation time;

(iv) the refractive index of the V_2O_5 layers prepared by evaporation and subsequent oxidation of vanadium varied with wavelength as shown in Fig. 8, practically independently of the thickness (in the d_v range investigated);

(v) the density of the V_2O_5 layers prepared was 3.1 g/cm^3, ranging between the density of single crystalline V_2O_5 (3.357 g/cm^3) and that of the amorphous V_2O_5 (2.42–2.69 g/cm^3), but it was nearer to the density of V_2O_5 single-crystals [8].

References

[1] *Mačkus, P., Á. Süli, M. I. Török and I. Hevesi:* Thin Solid Films **42**, 17 (1977).
[2] *Süli, Á., S. D. Kurmashev, L. Michailovits and I. Hevesi:* Acta Phys. et Chem. Szeged **22**, 45 (1976).
[3] *Hevesi, I.,* and *Karvaly:* Acta Phys. Hung. **29**, 182 (1970).
[4] *King, B. W.,* and *L. Suber:* J. Am. Ceram. Soc. **38**, 306 (1955).
[5] *Kenny, N., C. R. Kannewurf and D. H. Whitemore:* J. Phys. Chem. Solids **27**, 1237 (1966).
[6] *Wolf, H. F.:* Silicon Semiconductor Data, Pergamon Press, London, 1969.
[7] *Johnston, W. D.:* J. Am. Ceram. Soc. **48**, 608 (1965).
[8] *Neuberger, M.:* Data Compilation on Vanadium Oxides, National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22151, 1971. p. 30.

ОПРЕДЕЛЕНИЕ ТОЛЩИНЫ И КОЭФФИЦИЕНТА ПРЕЛОМЛЕНИЯ ТОНКИХ СЛОЕВ V_2O_5 НА ОСНОВАНИИ ОТРАЖАТЕЛЬНЫХ ИНТЕРФЕРЕНЦИОННЫХ СПЕКТРОВ

А. Шюли, Л. Михайлович и И. Хевеши

Определены толщины и коэффициенты преломления слоев V_2O_5, приготовленных термическим окислением при 400 °C, конденсированных на поверхность монокристаллов кремния, слоев разной толщины ванадия, при $\alpha=45°$ и $\alpha=29{,}2°$ углах падения, с помощью отражательных спектров, снятых в области длин волн 360—900 нм. Для оценки спектров был принят метод приближений. Удельный вес слоев V_2O_5 определяли исходя из толщины конденсированных слоев ванадия и оптических измерений толщины слоев V_2O_5. Средний удельный вес слоев V_2O_5 составлял 3,1 г·см$^{-3}$. Полоса отражения, найденная в области 420 нм, независимая от угла падения света, отнесена к концентрации V^{4+} находящегося в V_2O_5.