

# REACTIVE EVAPORATION OF $\text{TiO}_2$ AND $\text{SiO}_2$ FILMS FOR MULTILAYER COATINGS

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## ABSTRACT

*The optimum deposition parameters for  $\text{TiO}_2$  and  $\text{SiO}_2$  films for the multilayer coatings are reported. The influence of residual pressure of oxygen in the range of  $10^{-4}$ – $10^{-5}$  torr, rate of evaporation between 1 and  $22 \text{ \AA sec}^{-1}$  and different oxides of titanium on the refractive index and transmittance of quarter wave films are studied. The characteristic absorption peaks are at  $7.0 \mu$  for  $\text{TiO}_2$  and  $9.5 \mu$  for  $\text{SiO}_2$ . 11 to 21 layers of quarter wave multilayer stacks were tested for their durability and stability and found to be good.*

**Keywords.**  $\text{TiO}_2$  and  $\text{SiO}_2$  films; Optical properties; Reactive evaporation; Multilayer films of  $\text{TiO}_2$  and  $\text{SiO}_2$ ; and Laser Mirrors.

## 1. INTRODUCTION

Multilayer dielectric films find a wide application in several optical devices and instruments. The multilayer stack consists of alternate layers of high and low refractive index materials such as, ZnS (2.3), ZnSe (2.5),  $\text{TiO}_2$  (2.3),  $\text{MgF}_2$  (1.38), Cryolite (1.33) and  $\text{SiO}_2$  (1.50). Most of the films except those of the oxides are soft in nature and sensitive to different environmental conditions. Multilayer stacks produced with the  $\text{TiO}_2$  and  $\text{SiO}_2$  combination are mechanically, chemically and thermally stable and are known as "hard coatings".

Films of these oxides can be prepared either by reactive evaporation of lower oxides such as  $\text{TiO}$ ,  $\text{SiO}$  in the presence of oxygen or by electron beam evaporation of  $\text{TiO}_2$  and  $\text{SiO}_2$ . In the process of reactive evaporation, the sub-oxide vapours and the oxygen molecules will arrive onto the substrate simultaneously and react with each other forming a strongly oxidised film, when the mean free path of the oxygen molecules is greater than the source to substrate distance.

According to Auwarter [1] non-absorbing and durable  $\text{TiO}_2$  and  $\text{SiO}_2$  films can be obtained if the partial pressure of oxygen in the chamber is in the range of  $7 \times 10^{-5}$  to  $9 \times 10^{-5}$  torr and also the direction of flow of the oxygen molecules and the vapours must be the same. Ritter [2] observed  $\text{Si}_2\text{O}_3$  as a main phase in the film produced by evaporation of  $\text{SiO}$  in the presence of oxygen at  $1 \times 10^{-4}$  torr.  $\text{SiO}_2$  films produced by electron beam evaporation of quartz are free from absorption down to  $0.2 \mu$  whereas  $\text{Si}_2\text{O}_3$  films absorb below  $0.3 \mu$ . The reported values of refractive indices for silicon oxide films, vary from 2.0 to 1.46 as the phase of the film changes from  $\text{SiO}$  to  $\text{SiO}_2$ . Anastasio [3] and Howson *et al.* [4] found that there is an unique relationship between the properties of Silicon oxide film and the parameter  $p/r$  which is defined as the ratio of oxygen molecules to the vapour molecules, where  $p/r = 1.06 \times 10^6 \times P/R$  where  $P$  is the partial pressure of oxygen in torr and  $R$  is the deposition rate in  $\text{\AA sec}^{-1}$ . Further, they observed that the three phases  $\text{SiO}$ ,  $\text{SiO}_2$ ,  $\text{Si}_2\text{O}_3$  could be obtained by varying the values of  $p/r$ , with the values larger than 10 favouring the formation of  $\text{SiO}_2$  phase.

Investigations of Ritter [5] on  $\text{TiO}_2$  films showed that the refractive index and the hardness of the films decreased with an increase of oxygen pressure. Dundenhausen *et al.* [6] studied the effect of substrate temperature on refractive index of reactively evaporated films of  $\text{TiO}_2$  and reported that the refractive index of  $\text{TiO}_2$  films was 1.9 when the substrate was at room temperature and 2.8 at  $400^\circ \text{C}$ . Heitman [7, 8] introduced ionized oxygen instead of neutral oxygen to improve the oxidation during the deposition of  $\text{TiO}_2$  and  $\text{SiO}_2$  films and produced non-absorbing, durable films with the evaporation rate of  $3 \text{\AA sec}^{-1}$  for  $\text{TiO}$  and  $5 \text{\AA sec}^{-1}$  for  $\text{SiO}$ . The corresponding refractive indices were reported as 2.3 and 1.42 at  $5500 \text{\AA}$ . Also, he observed that  $\text{TiO}_2$  and  $\text{SiO}_2$  films exhibit opposite stresses and therefore it could be possible to produce multilayers with low residual stresses using the above combination.

In view of the profound influence of evaporation parameters such as oxygen pressure, evaporation rate and substrate temperature on the properties of the films in the reactive evaporation technique, electron beam evaporation technique has been preferred for the production of multilayer films with  $\text{TiO}_2$  and  $\text{SiO}_2$ . In spite of the advantage in producing stable and pure films of oxides, the electron beam technique leads to undesirable scatter centres and damage sites in the films. However the potentialities of the reactive evaporation technique need not be ruled out in view of the simplicity both in technique and evaporation. It could also be observed

that the limited or no information exists in the published literature on the fabrication of multilayer stacks with the oxides of titanium and silicon by either of the techniques. Hence it is proposed to adopt the reactive evaporation technique to study the optimum deposition parameters to produce reliable multilayer films of  $TiO_2$  and  $SiO_2$  with desired properties. The optical properties of individual films of  $TiO_2$  and  $SiO_2$  have been studied by varying the deposition parameters to find the suitable conditions for matching these films for the production of the multilayer films [9, 10]. Durable single layer films were deposited with the evaporation rate of  $2.5 \text{ \AA sec}^{-1}$  and  $5 \text{ \AA sec}^{-1}$  of  $TiO$  and  $SiO$  respectively at the oxygen pressure of  $1 \times 10^{-4}$  torr and the substrate being at room temperature. The corresponding refractive indices were measured and found to be 2.30 and 1.50 at  $6328 \text{ \AA}$ .

These optimized parameters have been used in the fabrication of dielectric mirrors consisting of 21 alternate layers of  $TiO_2$  and  $SiO_2$  and with the transmission 0.05%.

## 2. EXPERIMENTAL TECHNIQUES

Titanium dioxide and silicon dioxide films were produced in conventional 19" vacuum coating plant. The films were deposited on well polished B.S.C. glass and on fused quartz substrates for the optical measurements in both visible and ultra violet regions respectively. The substrates are first cleaned with liquid detergent using soft linen cloth and then rinsed in tap water followed by distilled water and deionised water. Then the substrates are vapour degreased in trichloroethylene bath, after which they were immediately transferred to the deposition plant. The materials  $TiO$  and  $SiO$  used for the evaporation are supplied by Balzers. Tantalum boat with a perforated cover, was used for the evaporation of  $SiO$  and a tungsten boat for evaporating  $Ti$ ,  $TiO$ ,  $Ti_2O_3$  and  $TiO_2$ . In all these experiments the bell jar was evacuated to a pressure less than  $1 \times 10^{-6}$  torr. Then the oxygen was admitted into the bell jar and maintained at the desired pressure by means of a needle valve. The films of quarter wave thicknesses were monitored using a modulated beam photometer.

The refractive index of the titanium dioxide films were calculated from the transmission measurements of the coated substrates [11]. The transmittance  $T$  of an uncoated substrate [12] is given by:

$$T = \frac{1 - R}{1 + R} \quad (1)$$

where  $R$  is the reflectance for normal incidence of substrate single surface. If the surface is coated with a non-absorbing film of reflectance,  $R_f$ , the transmittance  $T_f$  of the film is given by

$$T_f = \frac{(1 - R)(1 - R_f)}{(1 - R R_f)} \quad (2)$$

combining the equations (1) and (2)  $R_f$  is given by

$$R_f = \frac{2(T/T_f) - 1 - T}{2(T/T_f) - 1 + T} \quad (3)$$

Also the transmittance  $T_f$  of the coated substrates will be a minimum when  $n_f > n_s$  and the optical thickness of a film is  $m(\lambda/4)$ ,  $m = 1, 3, 5 \dots$  where  $\lambda$  is the desired wavelength,  $n_f$ ,  $n_s$  are the refractive indices of the film and the substrate respectively. Titanium dioxide films were deposited to a quarter wave thicknesses at 6328 Å and the ratio  $T/T_f$  was measured using a Unicam SP 700 double beam UV and visible spectrophotometer. The transmittance of the substrate was calculated from the Fresnel's equation for normal incidence. The values thus obtained for  $T$  and  $T/T_f$  are substituted in equation (3) to determine  $R_f$ . The refractive index  $n_f$  [11] of the film is now calculated using the equation,

$$n_f^2 = n_s \left[ \frac{1 + \sqrt{R_f}}{1 - \sqrt{R_f}} \right] \quad (4)$$

The above measurements of  $n_f$  is accurate to  $\pm 0.005$ . The refractive index of silicon oxide films was determined by Abeles [11] method. This method rests on the fact that in the absence of significant optical absorption, the reflectance of p-polarized light from the film is the same as that of the bare substrate for a particular angle of incidence. The refractive index of the film  $n_f$  is given by

$$n_f = n_0 \tan \phi_0 \quad (5)$$

where  $n_0$  is the refractive index of the medium of incidence and  $\phi_0$  is the angle of incidence. The angle  $\phi_0$  was measured by photo-electric Ellipsometer. The measurements are accurate to  $\pm 0.002$ . This method applies accurately to the film where the difference of  $n_f$  is not greater than 0.3 of that of the substrate.

The I.R. transmission characteristics of the films between  $2\mu$  and  $14\mu$  were studied by depositing films on NaCl substrates and using Carl Zeiss I.R. 10 infrared spectrophotometer. In the above experiments film

thicknesses were measured using multiple beam interferometer built in the laboratory.

### 3. RESULTS AND DISCUSSION

#### (i) Titanium Dioxide Films

Figure 1 represents the variation of transmittance of titanium dioxide and silicon dioxide single layer films of quarter wave thickness at 6328 Å at different wavelengths. U.V. absorption edge was observed at  $0.38\mu$  and the refractive index of the film was calculated from the transmission curve was 2.30 at 6328 Å. Due to heat treatment the transmission of the  $TiO_2$  film has not changed significantly in the visible region but has increased slightly at the U.V. edge without any shift in the absorption peak. U.V. absorption edge was observed at  $0.32\mu$  for  $SiO_2$  film.

Figure 2 shows the dependence of refractive index of  $TiO_2$  films produced by evaporating Ti,  $TiO$ ,  $Ti_2O_3$  and  $TiO_2$  in oxygen atmosphere at different pressures between  $1.0 \times 10^{-5}$  torr to  $5 \times 10^{-4}$  torr. When titanium monoxide was evaporated at  $O_2$  pressures lower than  $7.5 \times 10^{-5}$  torr the film became absorbing. Similarly for Ti and  $Ti_2O_3$  the pressure region is indicated as dotted line in Fig. 2 where the absorbing films are obtained. This phenomena might be due to the presence of metallic titanium obtained by the partial dissociation of evaporant or insufficient oxygen for recombination. When these absorbing films were heated to  $400^\circ C$  for 4 hours in air, they were found to be non-absorbing. The values of the refractive index of the above heat treated films are also shown as the dotted curve. The optimum pressures required for Ti,  $Ti_2O_3$  are  $2 \times 10^{-4}$  and  $5 \times 10^{-5}$  torr respectively for obtaining non absorbing films. However, a high temperature is required for evaporating  $TiO_2$  which results in thermal dissociation of  $TiO_2$ . These films are porous and having low refractive index. Figure 3 shows the relation between the refractive index and the wavelength of  $TiO_2$  films at two evaporation rates. The refractive index decreases with increasing wavelengths.

#### (ii) Silicon Oxide Films

Figure 5 shows the evaporation rate *versus* the refractive index of the silicon oxide films. During the evaporation of the films, the pressure of oxygen was maintained at  $1 \times 10^{-4}$  torr. Due to heat treatment the values of the refractive index of the films have decreased for the deposition rates above  $5 \text{ \AA sec}^{-1}$  whereas the values increased for the films deposited at

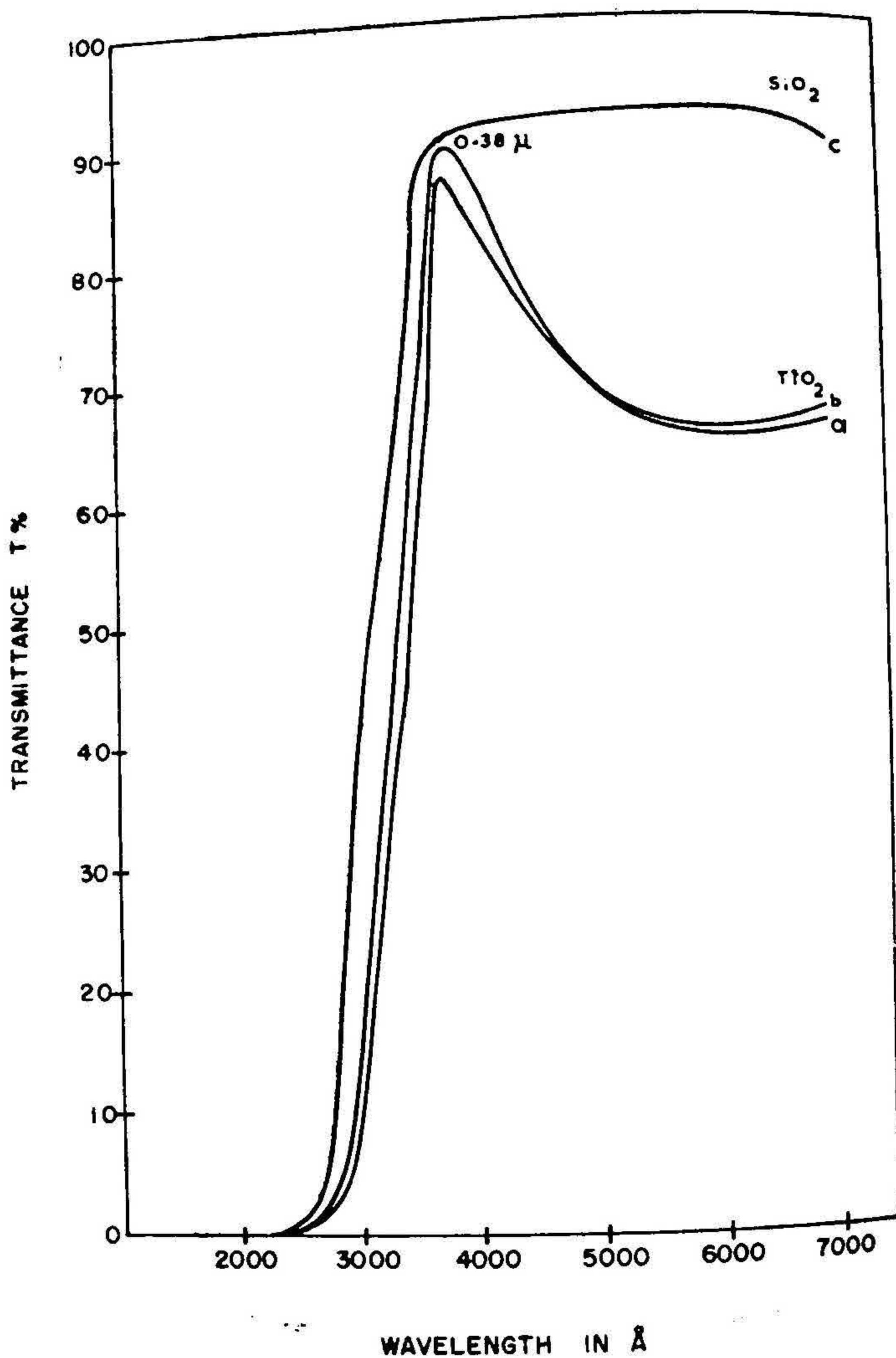


FIG. 1. Transmittance of TiO<sub>2</sub> and SiO<sub>2</sub> films of quarter wave thickness at 6328 Å. (a) TiO<sub>2</sub> film condensed on substrate at room temperature, (b) Effect of heat treatment on the same TiO<sub>2</sub> film at 400° C for 4 hours in air.

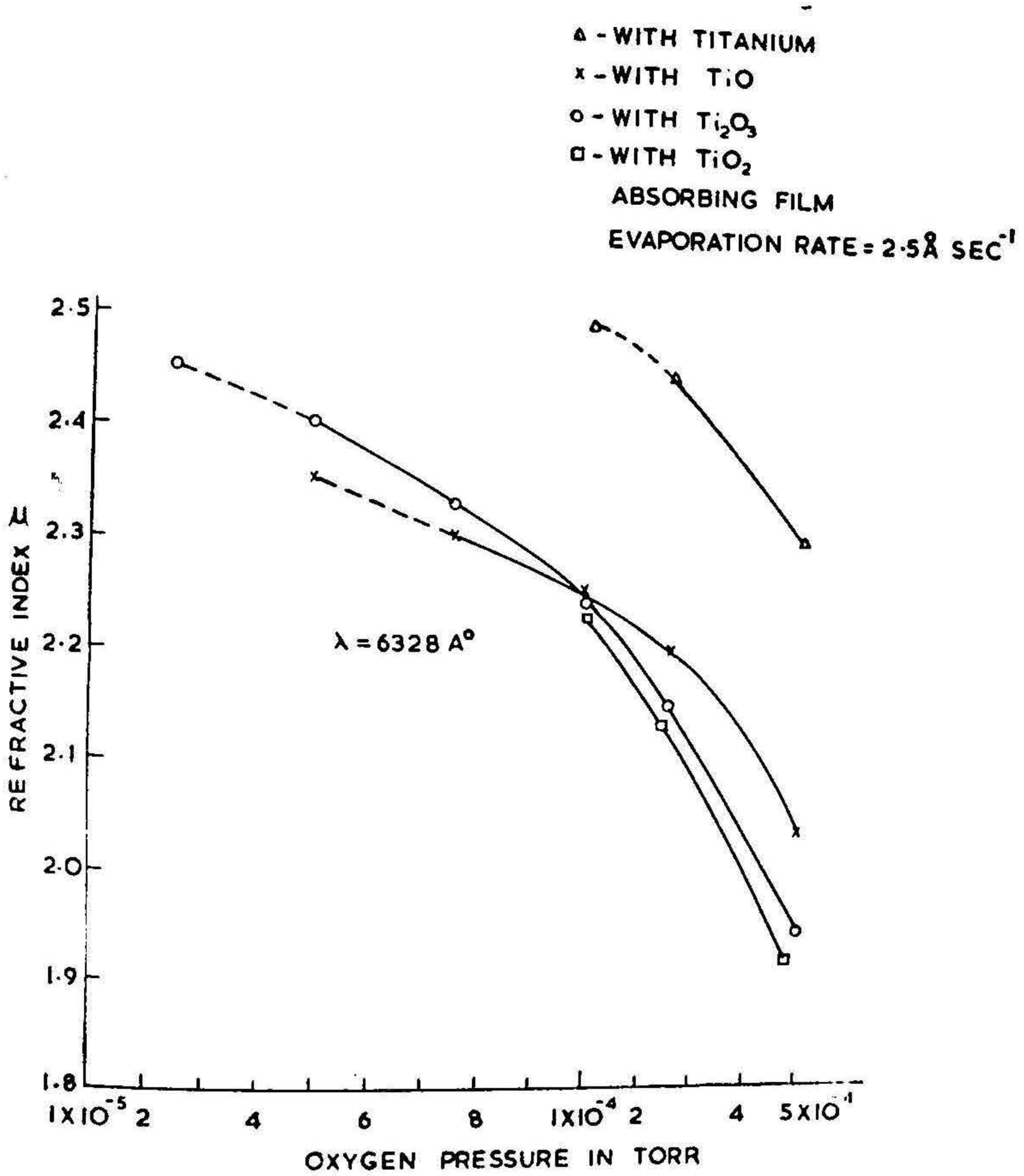


FIG. 2. Refractive index of titanium dioxide films with pressure.

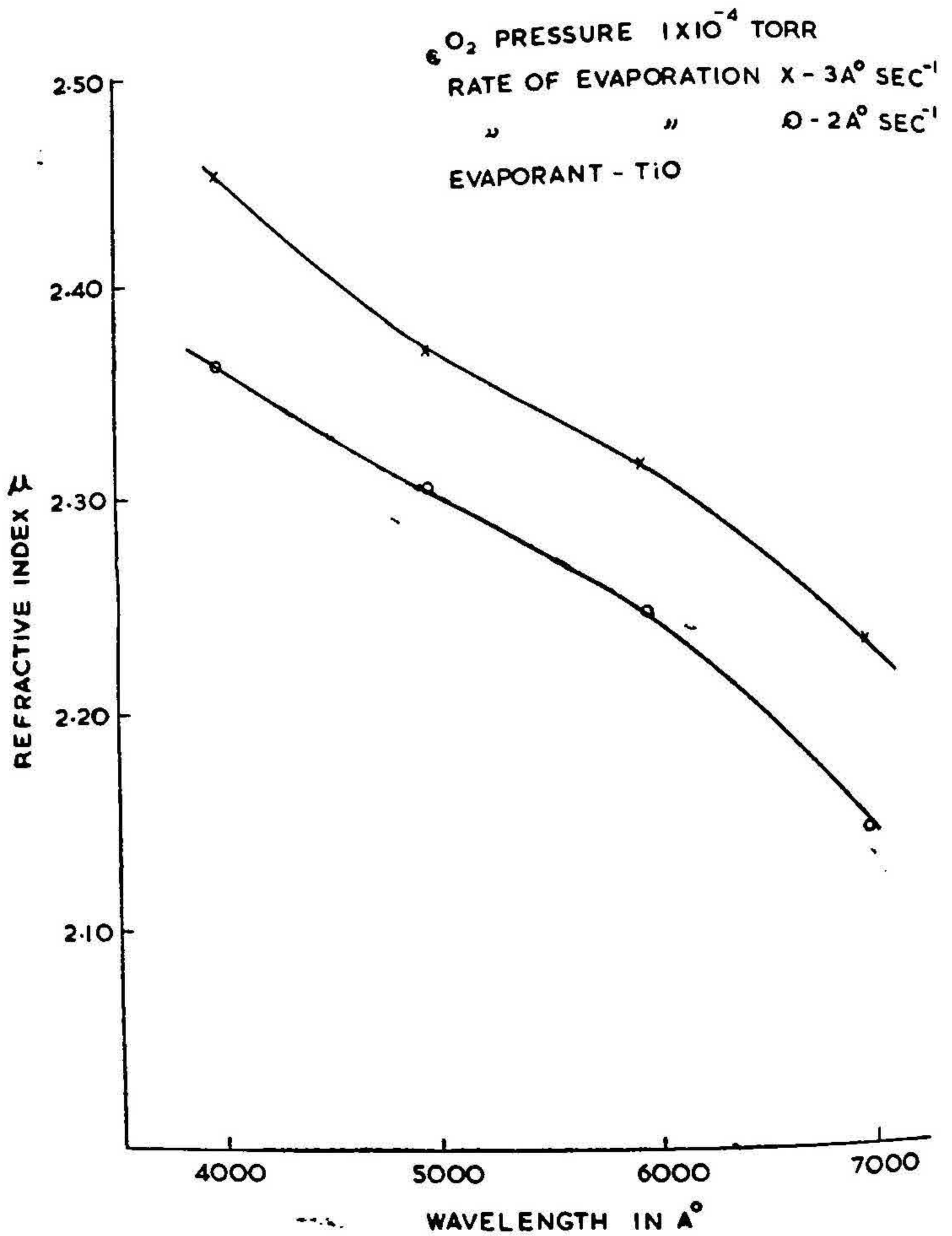


FIG. 3. Refractive index of  $\text{TiO}_2$  films deposited at  $1 \times 10^{-4}$  torr with wavelength.



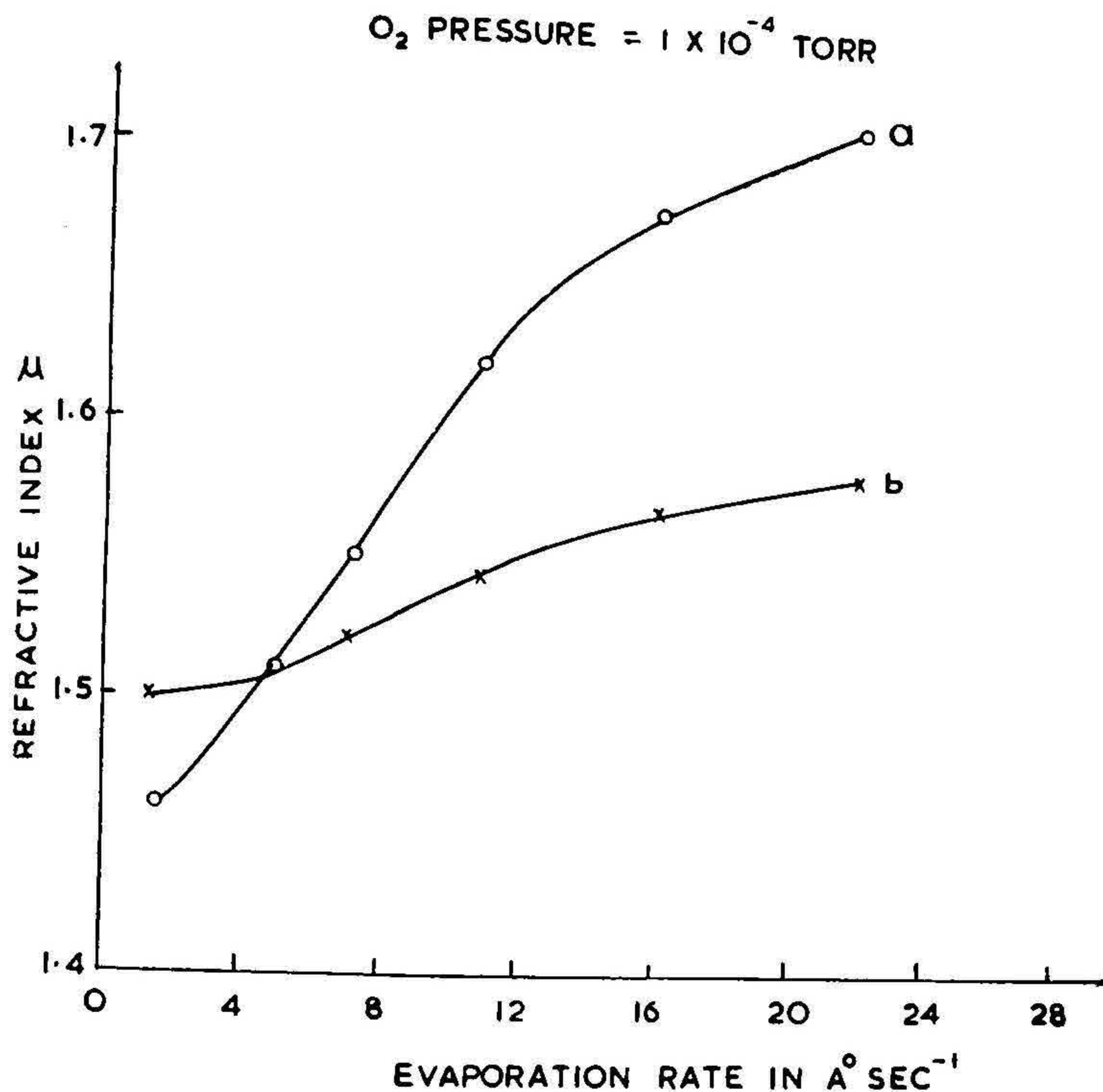


FIG. 4. Refractive index of silicon oxide films with deposition rate. (a) condensed on the substrate at room temperature; (b) Effect of heat treating the film at  $250^\circ\text{C}$  for 10 hours.

lower rates. The above phenomenon may be explained on the basis of the conversion of lower oxides to higher oxides in the case of low refractive index films and the transformation of the loosely bound structure to the closed packed one for higher refractive index films. Some of the related optical properties of silicon oxide films are summarised in Table I with the varied deposition parameters. Keeping the pressure at  $1 \times 10^{-4}$  torr the refractive index has increased with the increase of rate of deposition.

Figure 5 represents the infrared transmittance of  $\text{TiO}_2$  film and silicon oxide films for three samples deposited under different conditions, between  $2\mu$  and  $14\mu$ . Curve (A) represents the  $\text{SiO}$  phase deposited at the oxygen

TABLE I  
*Optical properties of silicon oxide films by evaporating SiO*

Sample No.	Pressure in torr	Deposition rate in Å sec <sup>-1</sup>	Thickness in Å	Refractive index at 6328 Å	Strong absorption edges	
					UV region in μ	I.R. region in μ
1	1 × 10 <sup>-4</sup>	22	2700	1.71	0.40	9.68
2	1 × 10 <sup>-4</sup>	7	3000	1.55	0.33	9.56
3	1 × 10 <sup>-4</sup>	5	3150	1.50	0.32	9.50
4	1 × 10 <sup>-4</sup>	1.5	3300	1.46	0.30	9.37
5	1 × 10 <sup>-5</sup>	17	2525	1.90	0.51	10.0

pressure of  $1 \times 10^{-5}$  torr and at the rate of  $17 \text{ Å/sec}^{-1}$ . It has a characteristic absorption peak at  $10 \mu$  and the U.V. absorption edge at  $0.51 \mu$ . The refractive index of the film was measured and found to be 1.9. Curve (B) represents the  $\text{Si}_2\text{O}_3$  phase obtained when the deposition rate is  $7 \text{ Å sec}^{-1}$  and oxygen pressure at  $1 \times 10^{-4}$  torr. The strong absorption band at  $9.56 \mu$ , the weak band at  $11.5 \mu$  and UV edge at  $0.33 \mu$  are observed. These results confirm the validity of the earlier results except a slight shift of UV edge to  $0.33 \mu$  instead of  $0.3 \mu$ . Curve (C) represents silicon oxide film of refractive index 1.46 with a weaker absorption band at  $11.8 \mu$ . Even though this refractive index value corresponds to bulk  $\text{SiO}_2$ , the IR absorption band ( $11.8 \mu$ ) deviates from the reported value of  $12.5 \mu$  for  $\text{SiO}_2$  film obtained by electron beam evaporation of quartz. This discrepancy may be explained on the basis of the presence of a small amount of  $\text{Si}_2\text{O}_3$  in  $\text{SiO}_2$  films. The above film corresponding to curve (C) was deposited with the rate of  $1.5 \text{ Å sec}^{-1}$  and the oxygen pressure of  $1 \times 10^{-4}$  torr. Curve D is the I.R. transmission of  $\text{TiO}_2$  film. Absorption bands were observed at  $3.2 \mu$  and  $7.0 \mu$  when the rate of evaporation is  $2.5 \text{ Å sec}^{-1}$  and the oxygen pressure is  $1 \times 10^{-4}$  torr.

### (iii) Multilayer Films

Figure 6 shows a comparison of the experimental curves of transmittance with wavelength for multilayer high reflecting mirrors with 11 to 21 alternate layers of  $\text{TiO}_2$  and  $\text{SiO}_2$ . Quartz substrates were held at

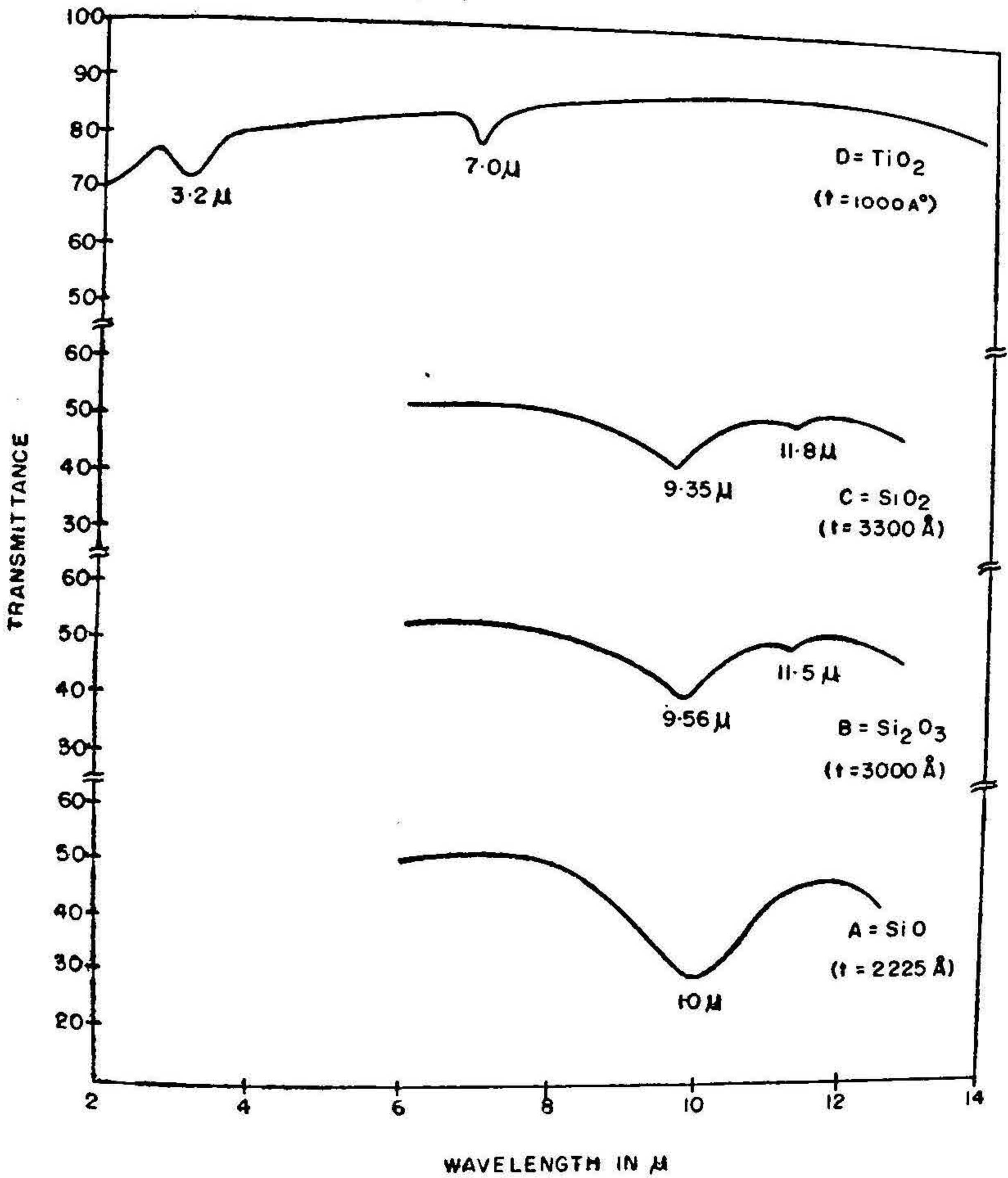


FIG. 5. Infrared transmittance of silicon oxide and  $TiO_2$  films.

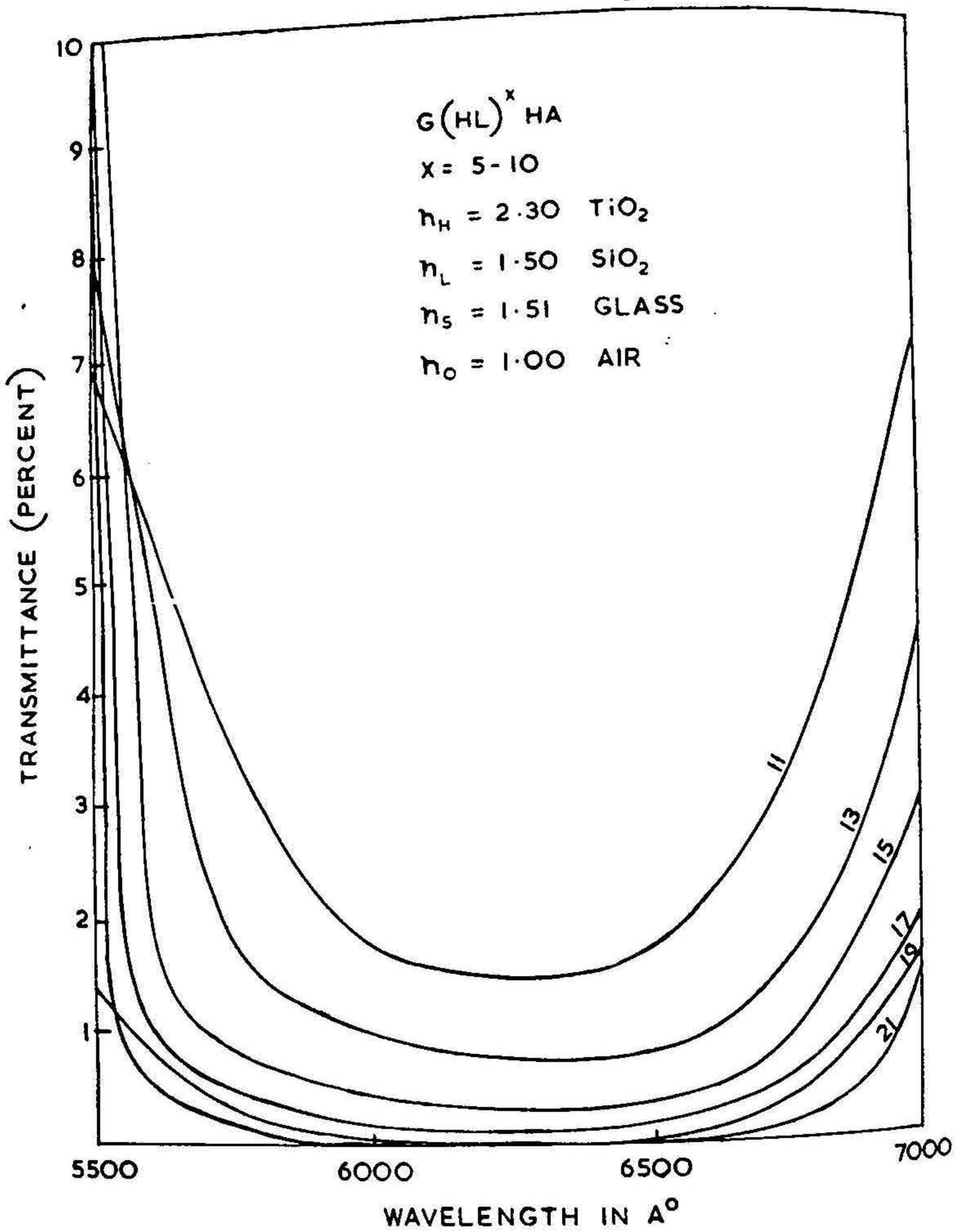


FIG. 6. Experimental curves of transmittance *verses* wavelength with  $\text{TiO}_2$  and  $\text{SiO}_2$ .

TABLE II

Transmission values of  $\text{TiO}_2$ - $\text{SiO}_2$  multilayers  $n_H = 2.30$ ,  $n_L = 1.50$ ,  
 $n_S = 1.51$

No. of layers	Transmission		Evaporation conditions
	Experimental	Theoretical	
3	38.80	38.60	Rate of evaporation: $\text{TiO}_2 = 2.5 \text{ \AA sec}^{-1}$
5	18.80	18.67	
7	8.00	7.74	$\text{SiO}_2 = 5 \text{ \AA sec}^{-1}$
9	3.85	3.66	Partial pressure of oxygen = $1 \times 10^{-4}$ torr
11	1.60	1.57	
13	0.70	0.67	
15	0.30	0.28	
17	0.15	0.12	
19	0.05	0.05	
21	<0.05	0.02	

room temperature in vacuum chamber and they attained the temperature of about  $150^\circ \text{C}$  during the deposition of multilayer. The above mirrors were deposited taking optimum deposition parameters as:

- (a) (i) Partial pressure of oxygen  $1 \times 10^{-4}$  torr.
- (b) (ii) The deposition rate  $2.5 \text{ \AA sec}^{-1}$  and  $5 \text{ \AA sec}^{-1}$  for  $\text{TiO}_2$  and  $\text{SiO}_2$  respectively.

The corresponding refractive indices are measured and found to be 2.30 and 1.50 at  $6328 \text{ \AA}$ .

The above conditions were maintained constant during the deposition of the multilayers. The transmittance of the 21 layer mirror is nearly zero ( $< 0.05$ ).

(iv) *Stability and Structure of the Films*

The following tests were carried out to establish the adhesion and stability of the films.

(1) A strip of scotch tape was fixed to the surface of the mirror and pulled perpendicular to the substrate. This did not cause any damage to the mirror.

(2) No damage was observed by rubbing the films with the usual pencil eraser.

(3) No change was observed on the surface and in the reflectance values of the mirrors, when they were immersed in water for 24 hours and also in 5% sodium chloride solution for 24 hours.

(4) The mirrors were not affected by acids like Concentrated, HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> and organic solvents.

(5) The mirrors were stable even at 400° C.

(6) The surfaces of the single and multilayer films of TiO<sub>2</sub> and SiO<sub>2</sub> appear to be uniform, free from structural defects and scattering centres as observed under high magnification microscope ( $\times 50$ ).

These mirrors can be cleaned with acetone and soft linen cloth without causing any damage. Removal of the films can be done only by repolishing the substrate.

## 4. CONCLUSION

The optimum deposition parameters for the fabrication of multilayer films of TiO<sub>2</sub> and SiO<sub>2</sub> are summarised as follows:

- (i) Partial pressure of oxygen should be at  $8 \times 10^{-5}$  to  $1 \times 10^{-4}$  torr.
- (ii) Deposition rates should be  $2.5 \text{ \AA}/\text{sec.}^{-1}$  and  $5 \text{ \AA}/\text{sec.}^{-1}$  for TiO and SiO respectively.

The characteristic absorption bands in IR and UV regions for SiO, Si<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> and TiO<sub>2</sub> and the above optimum deposition parameters are in good agreement with the reported values. A new absorption band is observed for TiO<sub>2</sub> film at  $7.00 \mu$ .

The multilayer films produced by the above technique are durable, stable reproduceable.

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