# The optical properties of amorphous V$_2$O$_5$ and SiO thin films and of the mixed dielectric system SiO/V$_2$O$_5$

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The optical absorption of amorphous thin films of V$_2$O$_5$, SiO and of SiO/V$_2$O$_5$ is studied in the photon energy range 0.42 to 6.53 eV. The optical absorption edge of evaporated V$_2$O$_5$ films can be described by direct forbidden transitions while that of SiO films follows the non-direct transitions in **k**-space. The data of the SiO/V$_2$O$_5$ oxide mixtures are fitted to new values of the exponent in the well-known absorption equation and the corresponding optical band gaps are determined. Experimental data on the wavelength dependence of the refractive index of SiO films are presented. The dispersion of the refractive index follows a single oscillator model. The infrared spectra show that some bonding occurs between the two oxides so that the mixed dielectric system SiO/V$_2$O$_5$ cannot be considered as a simple physical mixture.

## 1. Introduction

The study of optical absorption may give a considerable amount of information about the electronic structures in amorphous non-metallic materials. The fundamental absorption edge in such solids is less abrupt and well defined than in comparison with crystalline non-metallic solids. In the high-absorption region Tauc *et al.* [2] and Davis and Mott [2] gave an equation, derived independently, for the optical absorption coefficient $\alpha(\omega)$ as a function of photon energy $\hbar\omega$:

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^n / \hbar\omega \qquad (1)$$

where $n$ is an exponent, $\omega$ is the angular frequency of the incident radiation, $B$ is a constant and $E_{opt}$ is the optical energy gap of the material. Equation 1 with $n = 2$ as originally postulated by Tauc *et al.* [1] and as predicted by Davis and Mott [2] for indirect transitions has been found to represent the experimental results particularly at the higher values of absorption at the edge for oxide and chalcogenide glasses [3, 4] and for thin oxide films [5, 6] including SiO. Nevertheless an exponential dependence of the absorption coefficient on the energy near the fundamental absorption edge is frequently found for amorphous semi-

conductors of the form

$$\alpha(\omega) = A \exp\left(\frac{\hbar\omega}{E_1}\right) \qquad (2)$$

where $E_1$ is interpreted as a measure of the width of the tail of localized states in the band gap. Equation 2 was originally proposed by Urbach [7].

For vanadium pentoxide [8, 9] and for some vanadate glasses the dominant absorption process is one involving direct forbidden transitions, represented by Equation 1 with $n = 3/2$. Amorphous films of V$_2$O$_5$ are known to exhibit semiconducting properties arising from electron hopping between V$^{4+}$ and V$^{5+}$ centres. A thin film composed of two oxides including V$_2$O$_5$ has not previously been reported and in the present work, which forms part of a general research programme on complex dielectrics, we have studied thin films of the co-evaporated SiO/V$_2$O$_5$ system. We are concerned with modifications to various properties of such films. As part of our recent activities the optical constants of V$_2$O$_5$ thin films have been studied by an ellipsometry technique [10] and it was found that the high absorption made it difficult to obtain reliable

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| $V_2O_5$ specimen | Thickness (nm) | Refractive index |
|---|---|---|
| 1 | 170 | 2.10 |
|   | 182 | 1.97 |
| 2 | 160 | 2.19 |
|   | 155 | 2.25 |
| 3 | 222 | 1.71 |
|   | 220 | 1.72 |
|   | 221 | 1.71 |
| 4 | 167 | 2.11 |
|   | 165 | 2.14 |
|   | 175 | 2.03 |
| 5 | 160 | 2.20 |
|   | 148 | 2.34 |

thickness and refractive index measurements using a fixed angle of incidence and wavelength. Some tentative results obtained by this method are included in Table I. A recent report by Michailovits *et al.* [11] suggests that the optical constants vary with film thickness. It is our concern to establish whether the properties of $SiO/V_2O_5$ are equivalent to those of a simple mixture or whether some local bonding occurs as has been suggested following measurements of unpaired electron densities by electron spin resonance (e.s.r.) studies [12]. Amorphous $V_2O_5$ has been studied using X-ray diffraction by Mosset *et al.* [13]. Our optical results are consistent with the idea of some bonding in the $SiO/V_2O_5$ films. We have also studied some of the effects of vacuum annealing on the properties of the films. Finally the refractive index dispersion parameters for some SiO films are obtained.

## 2. Experimental work
Thin layers of $V_2O_5$, SiO and $SiO/V_2O_5$ were deposited onto clean Corning 7059 glass substrates held at temperature $\geqslant 100°$ C and at a pressure of $\simeq 5 \times 10^{-6}$ torr in a Balzers 510 coating unit. The co-evaporation technique used here has been established and described by Hogarth and Wright [14]. Vanadium and silicon oxides were evaporated from molybdenum and tantalum boats respectively. The thicknesses of the films were determined by multiple-beam interferometry using Fizeau fringes of equal thickness. Annealing of $V_2O_5$ films was carried out for 4 h at 220° C in a vacuum of $\sim 5 \times 10^{-6}$ torr followed by cooling to room temperature at a rate of $1°C\,min^{-1}$. The absorption measurements of the fundamental edge were taken at room temperature using a Perkin–Elmer spectrophotometer model 402. The optical data in the near infrared up to 3000 nm were obtained at room temperature using a Beckman Acta M-series spectrophotometer M IV. Discs of KBr of 2 cm diameter were prepared by hot pressing in vacuum. Thin $V_2O_5$, SiO and $SiO/V_2O_5$ films were then deposited on these discs and their infrared absorption spectra were recorded using a Perkin–Elmer 577 grating infrared double-beam spectrometer and also by a Unicam SP 2000 double-beam recording infrared spectrometer. The structure of our films was obtained from a JEOL, JEM7 electron microscope with a magnification × 38 000 and by X-ray techniques suitable for distinguishing between amorphous and crystalline states.

## 3. Results and discussion
Curves of the optical absorbance as a function of wavelength for different compositions of the SiO/$V_2O_5$ evaporated layers are presented in Fig. 1. The absorption coefficient $\alpha(\omega)$ is calculated from
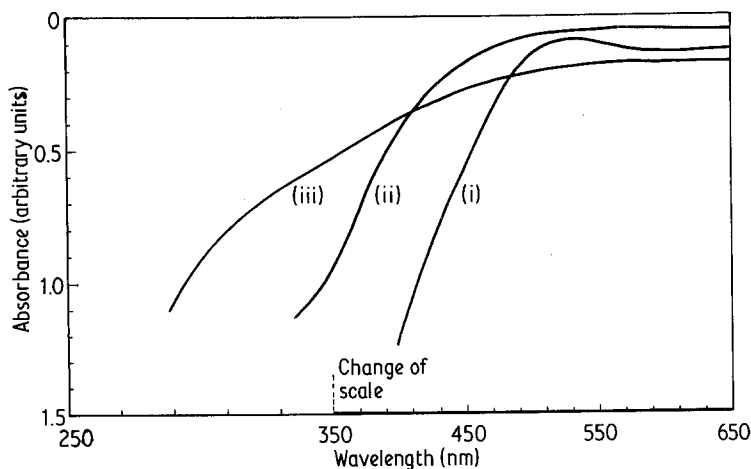


*Figure 1* Absorption spectra as a function of wavelength for samples of (i) $V_2O_5$ (190 nm), (ii) 70% $V_2O_5$/30% SiO (140 nm), (iii) 30% $V_2O_5$/70% SiO (140 nm).
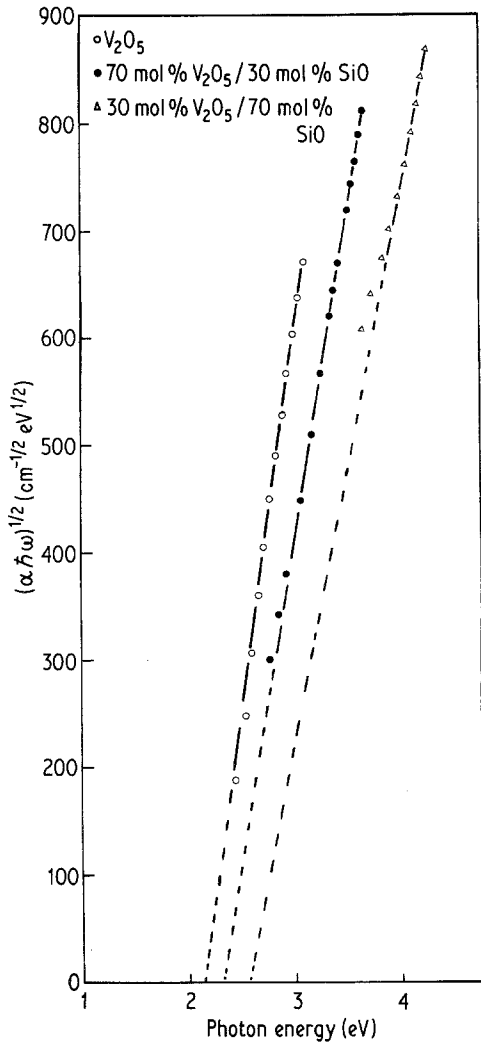
*Figure 2* Data of Fig. 1 replotted to estimate $E_{opt}$ using the equation for indirect transitions. ($\circ$ $V_2O_5$; $\bullet$ 70 mol% $V_2O_5$/30 mol% SiO; $\triangle$ 30 mol% $V_2O_5$/70 mol% SiO.)

*Figure 3* Data for Fig. 1 replotted to estimate $E_{opt}$ using the equation for direct transitions. ($\circ$ $V_2O_5$; $\bullet$ 70 mol% $V_2O_5$/30 mol% SiO; $\triangle$ 30 mol% $V_2O_5$/70 mol% SiO.)

the thickness of the specimen $d$ and the corresponding absorbance. The optical absorption edge of a $V_2O_5$ film as shown in Figs. 2 and 3 fits Equation 1 with $n = 3/2$ better than with $n = 2$ and giving a value of $E_{opt}$ of 2.33 eV. The fit with $n = 2$ gives a line which deviates, albeit to a small extent, from the straight line drawn through the points. It also leads to a value of $E_{opt}$ which is smaller than the value of 2.33 eV earlier reported
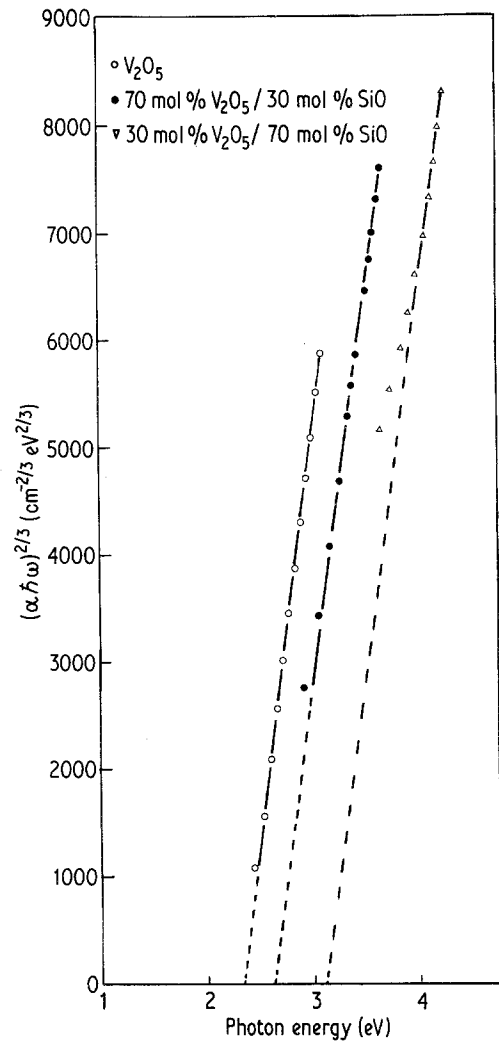
for $V_2O_5$. The optical absorption edge of a SiO film has however been extensively investigated [6] and it was concluded that Equation 1 for nondirect transitions, i.e. $n = 2$, offers the best fit for the experimental data. The edges of the intermediate compositions 30 mol% SiO/70 mol% $V_2O_5$ and 70 mol% SiO/30 mol% $V_2O_5$ are also displayed in Figs. 2 and 3 in accordance with assumed values of $n = 2$ and $n = 3/2$ respectively. The values of

TABLE II Some optical properties of evaporated $V_2O_5$ and of SiO/$V_2O_5$ films

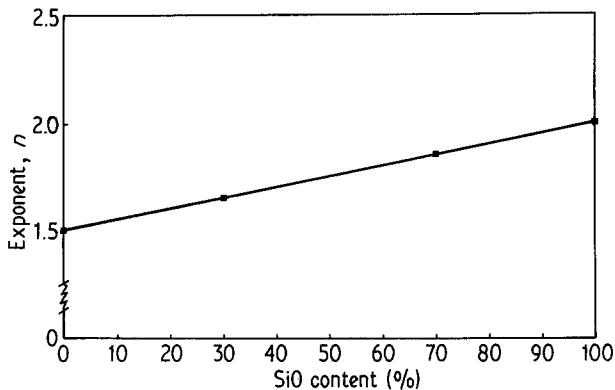| Specimen | Optical energy gap (eV) | | | | $E_1$ (eV) |
|---|---|---|---|---|---|
| | $(\alpha\hbar\omega)^{1/2}$ | $(\alpha\hbar\omega)^{2/3}$ | $(\alpha\hbar\omega)^{0.60}$ | $(\alpha\hbar\omega)^{0.541}$ | |
| $V_2O_5$ | 2.15 | 2.33 | — | — | 0.22 |
| 30 mol% SiO/70 mol% $V_2O_5$ | 2.30 | 2.60 | 2.50 | — | 0.58 |
| 70 mol% SiO/30 mol% $V_2O_5$ | 2.55 | 3.10 | — | 2.85 | 1.27 |

Figure 4 Estimation of values of $n$ for mixed films assuming a linear variation with film composition.

$E_{opt}$ obtained from the extrapolation of the nearly linear regions in these figures are presented in Table II. As is clear, the fits in both figures are not entirely satisfactory and this has posed the question of whether the evaporated complex is a simple physical mixture or whether local bonds may have some effect. In a recent paper by Al-Ramadhan *et al.* [15] concerned primarily with electron spin resonance measurements on the $SiO/V_2O_5$ system but linking them with optical absorption edges, the data were analysed using $n = 2$ and served to demonstrate qualitatively the differences in $E_{opt}$ with composition. Nevertheless

it was found that the fits even at high values of $\alpha$ were not entirely satisfactory. Indeed Timson and Hogarth [12] have shown by e.s.r. measurements that the density of unpaired electrons associated with dangling bonds in a complex of $SiO/B_2O_3$ is less than the comparable density in SiO films. Hence in an attempt to improve our interpretation of the behaviour of the experimental data, a linear dependence of the exponent $n$ has been drawn in Fig. 4 as a function of the molar percentage of the constituent oxides. The experimental compositions were then fitted to the appropriate new values of $n$. Fig. 5 shows the new values of $n$. For these absorption edges the values of $E_{opt}$ obtained by extrapolation are listed in Table II.
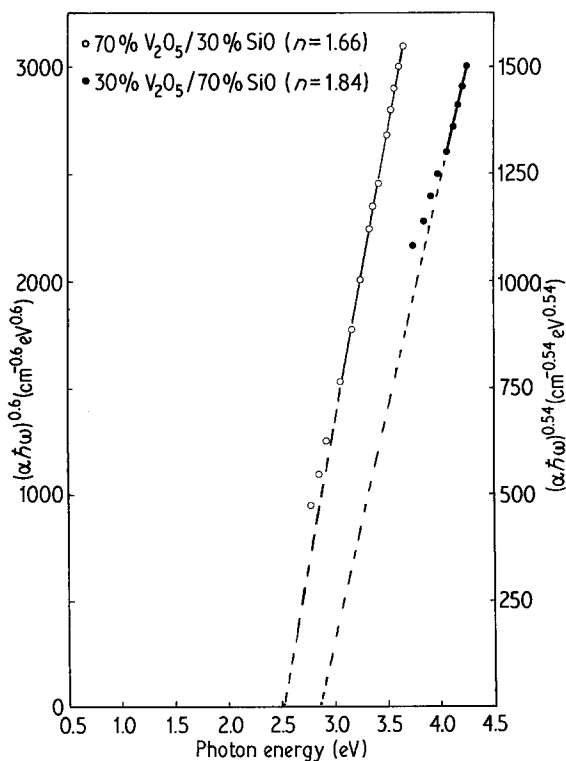
The present investigation on infrared absorption spectra plotted in Fig. 6 reveals three important features:

1. The existence of a large absorption peak near $1000\,cm^{-1}$ corresponds to a large excess of SiO in the mixture.

2. The disappearance of the $V_2O_5$ film peak near $650\,cm^{-1}$ is noted.

3. The appearance of a small shoulder (peak) at $870\,cm^{-1}$ following the SiO absorption peak and another new peak at $430\,cm^{-1}$ are observed.

Therefore it may be concluded that there is some chemical interaction between SiO and $V_2O_5$, i.e. we cannot treat the evaporated film as a simple physical mixture of the two oxides. (Table III summarizes these results.) The exper-



Figure 5 Data of Fig. 1 replotted for new values of $n$.

TABLE III Characteristic infrared (IR) absorption band positions $(cm^{-1})$ for SiO, $V_2O_5$ and $SiO/V_2O_5$ evaporated films

| Specimen | IR absorption band position $(cm^{-1})$ | | | |
|---|---|---|---|---|
| SiO | – | – | – | 1000 |
| $V_2O_5$ | – | 650 | – | – |
| $SiO/V_2O_5$ | 430 | – | 870 | 1025 |
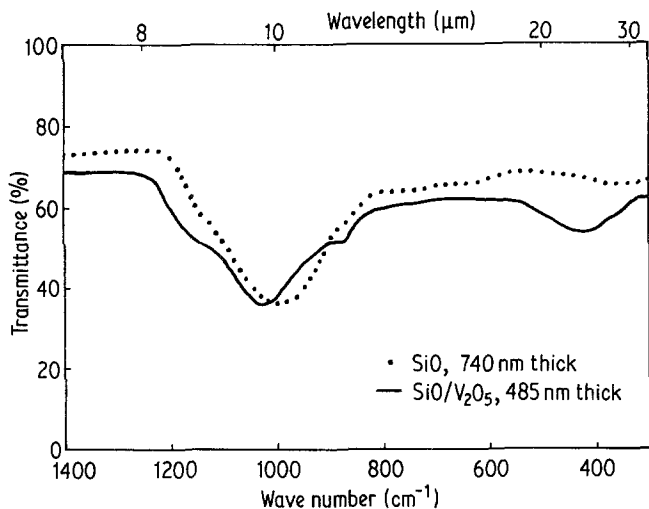
imental data in Fig. 1 have been re-plotted in Fig. 7 to test the Urbach behaviour for these films and the values of $E_1$ are given in Table II. Higher temperature measurements [16], however, showed that these edges shift with temperature towards longer wavelengths. The present values of $E_1$ are larger than those reported for typical amorphous semiconductors [3], and as they increase with film composition, electronic transitions between localized states in the band-edge tails [17] may also be involved.

Regardless of the exact value of the exponent $n$, the extrapolated $E_{opt}$ has increased with the addition of the SiO and this indicates that the degree of disorder in the system is increased. This increase is accompanied by an increase of $E_1$ taken as a measure of the width of the tails of localized states in the band gap region. The results demonstrate some of the complexities of the optical absorption edges in these amorphous non-metallic materials. In the absence of further quantitative information, a genuine density-of-states
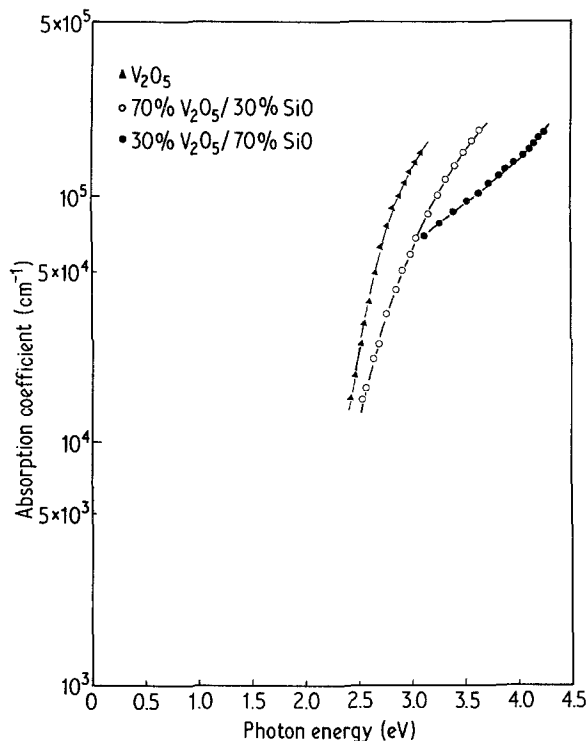


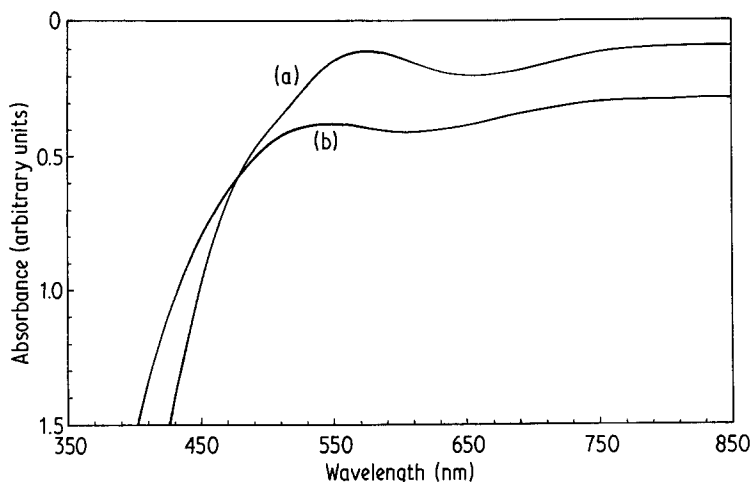*Figure 7* Absorption coefficient as a function of photon energy for the data of Fig. 1.

*Figure 8* The absorption edge for an evaporated thin film of $V_2O_5$ (thickness 223 nm), (a) as evaporated, (b) after annealing.

model is not applicable. Essentially, $E_{opt}$ and $E_1$ are two different features of the band structure which depend on the disorder but do not necessarily change in the same direction.

The absorption edge of an annealed $V_2O_5$ film shown in Fig. 8 exhibits similar properties but it shifts to short wavelengths after annealing, so that the values of $E_{opt}$ in general increase. The value of $E_1$ for this film is increased from 0.30 to 0.48 eV due to the effect of annealing. Freshly deposited films may contain many defects such as voids, grain boundaries and dislocations. The annealing process can be associated with stress relief which may cause local structural rearrangements [18] and also cause observable changes in the optical parameters.

The values of refractive index $n_f$ of SiO films obtained from interference fringes are shown in

Fig. 9. It is known from simple dispersion theory that in the region of low absorption the index of refraction is expected to be given [19] in a single-oscillator model presented by

$$n_f^2 - 1 = \frac{S_0 \lambda_0^2}{1 - (\lambda_0/\lambda)^2} \qquad (3)$$

where $\lambda$ is the light wavelength, $S_0$ is the average oscillator strength and $\lambda_0$ the average oscillator position. The validity of this assumption can be checked by plotting the quantity $(n_f^2 - 1)^{-1}$ against $\lambda^{-2}$ in Fig. 10. The parameter $S_0$ can then be derived from the slope of the straight line while $\lambda_0$ follows from the infinite wavelength intercept. These parameters as well as the refractive index dispersion parameter $E_0/S_0$ of Fig. 10 are listed in Table IV and are near to values published for other materials [19, 20]. For SiO/$V_2O_5$ films of thick-
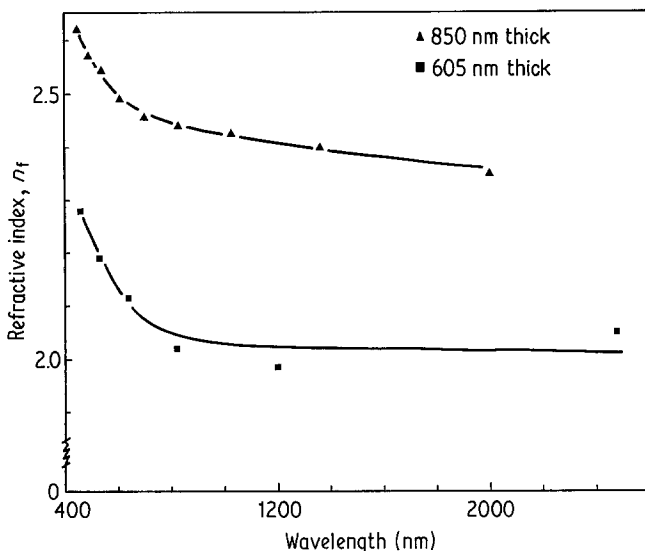


*Figure 9* Dependence of refractive index of thin SiO films on wavelength. (▲ 850 nm thick; ■ 605 nm thick.)
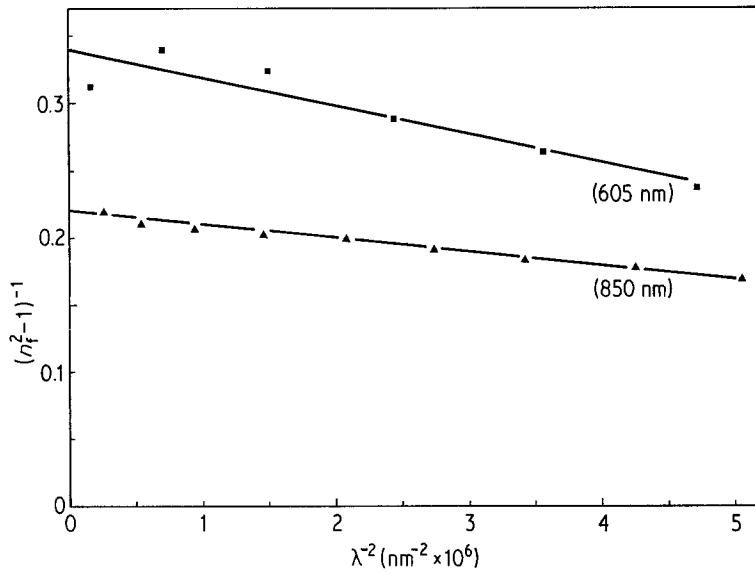
*Figure 10* Data of Fig. 12 replotted to show $(n_f^2 - 1)$ against $\lambda^{-2}$.
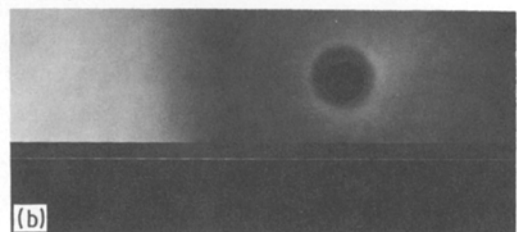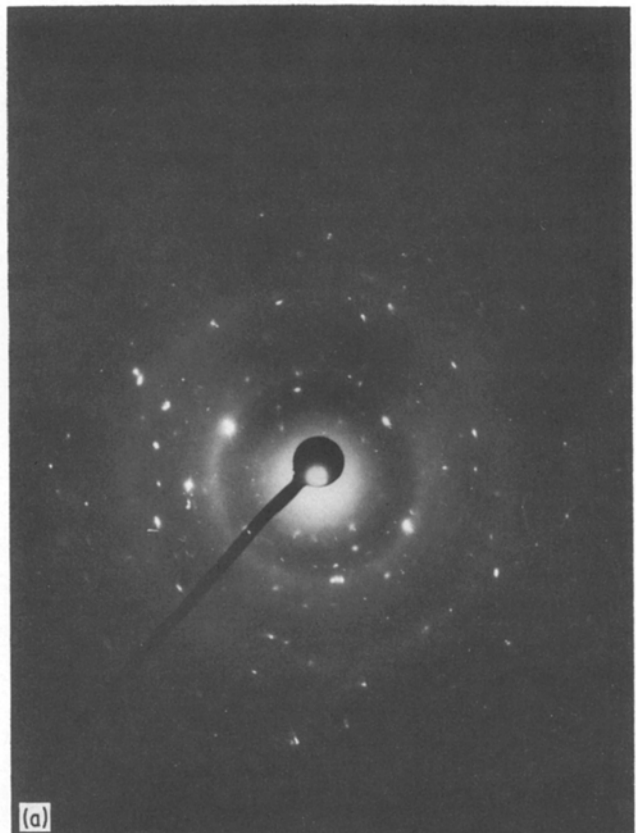


*Figure 11* (a) Electron diffraction pattern for a $V_2O_5$ thin film taken at room temperature. (The diffuse rings and diffraction spots indicate a fairly disordered polycrystalline structure.) (b) X-ray diffraction pattern for a $V_2O_5/SiO$ thin film.

TABLE IV Room temperature values of $S_0$, $E_0$ and $E_0/S_0$ of SiO films deposited at a pressure $\sim 10^{-6}$ torr

| | Specimen thickness (nm) | $S_0$ ($\times 10^{13}$ m$^{-2}$) | $E_0$ (eV) | $E_0/S_0$ ($\times 10^{-14}$ eV m$^2$) |
|---|---|---|---|---|
| Rapid evaporation | 655 | 5.05 | 4.41 | 8.73 |
| | 770 | 7.67 | 4.98 | 6.50 |
| Slow evaporation | 605 | 4.84 | 5.03 | 10.40 |
| | 773 | 11.23 | 6.16 | 5.50 |
| | 850 | 10.74 | 6.03 | 5.61 |

ness up to 300 nm the fringes were absent and this may arise because the specimens were not thick enough. Because the electrical conductivities and the optical properties in crystalline vanadium oxides were known to differ significantly from those of vanadate glasses [21], the structure characteristic is expected to be important in the study of evaporated $V_2O_5$ films. The structure of a typical $V_2O_5$ thin film obtained by electron microscopy is indicated in Fig. 11. While the $V_2O_5$ films show some evidence of polycrystallinity the SiO/$V_2O_5$ complex films have an amorphous structure.

## 4. Conclusion
It has been shown that the optical absorption edge of an evaporated $V_2O_5$ film can be described by direct forbidden transitions in k-space. The co-evaporated SiO/$V_2O_5$ oxide films can be fitted to a new exponent index $n$ to match the experimental data when better fitting and more consistent values of $E_{opt}$ are obtained. Ellipsometric measurements of the optical constants and the thickness showed that the $V_2O_5$ films are optically absorbing. For the SiO films, the dispersion of the refractive index may be described by a single-oscillator model with dispersion parameter $E_0/S_0 \simeq 8 \times 10^{-14}$ eV m$^2$ near to the previously reported values. Experimental results on infrared absorption spectra show that bonding occurs between these two oxides and that the sample is not just a simple physical mixture.

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