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Optical absorption spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films

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The optical absorption spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films have been studied. For higher photon energies, the absorption is found to be due to a direct forbidden electronic transition process from the oxygen 2p band to the vanadium 3d band in a similar way to that observed in crystalline V_2O_5. The exponential behaviour of absorption edge for lower photon energies is attributed to the electronic transitions between the tailed-off d–d states corresponding to V^{4+} ions. For co-evaporated V_2O_5/B_2O_3 films the optical energy gap is observed to increase with the increase in V_2O_5 content of the composite films.

1. Introduction

The optical absorption spectra of many non-crystalline semiconductors near the edge show typically two types of overlapping parts when the energy of incident photons lies in the range comparable to the energy gap of the material. For the energy of the incident photon less than the band gap, the absorption follows an exponential type of behaviour as

$$\alpha(\omega) \propto \exp\{-\delta[(E_{\text{opt}} - \hbar\omega)/kT]\} \qquad (1)$$

where $\alpha(\omega)$ is the absorption coefficient, $\hbar\omega$ is photon energy, E_{opt} is the optical energy gap, T is absolute temperature and k is Boltzmann constant. This type of behaviour was first observed by Urbach [1] in silver bromide. The quantity kT/δ is related to the steepness of the absorption curve and usually interpreted as the width of tails of localized states in the band gap (also known as the Urbach energy). Equation 1 is also known as the Urbach rule.

The exponential dependence of optical absorption is attributed to the intraband transitions between the sites which have tailed-off into the forbidden gap. It is agreed that the random fluctuations in potential associated with any lattice distortions like thermal vibration, dislocations, electric field of defects etc., can affect the energy bands and cause the tailing-off of energy states into the forbidden gap [2–4]. Redfield [2] showed quantitatively that such a tailing-off of states could modify the direct band-to-band transitions and cause an exponential energy dependence of absorption at the edge. Esser [5] proposed that the optical absorption was due to the influence of some random field present in the disordered system. A similar argument has been given by Bonch-Bruevich [6] for the existence of an exponential edge in disordered systems. Esser and Kleinert [7] suggested that in amorphous semiconductors, the exponential tail might be related to the optical transitions involving electronic states localized in semiclassical potential wells near the band edges. Esser and Herzon [8] proposed that if the valence band and the conduction band were bent in one and the same way a random Franz-Keldysh effect due to internal field would take place.

If the tail states are filled, the dominant transition process will be the more usual direct band-to-band transitions which will cause the absorption coefficient to have a power dependence on the photon energy [9].

In many amorphous materials, the optical absorption at higher values of absorption coefficient ($>10^4\,\text{cm}^{-1}$) above the exponential tail follows a power law of the general form

$$\alpha\hbar\omega \propto (\hbar\omega - E_g)^n \qquad (2)$$

where the exponent n can take the values 2, 3, 1/2, and 3/2 for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively [10]. Considerable attention has been paid to the electrical properties of V_2O_5-based glasses. These glasses are n-type semiconductors and it has been reported that in such glasses the electronic transitions occur by the transfer of polarons between transition metal ions of different valence state [9–16]. The absorption spectra of V_2O_5-based glasses have not received much attention in the ultraviolet range of energy. Some authors [9, 17–19] have reported that the fundamental absorption edges of amorphous as well as crystalline V_2O_5 show a fit to Equation 1 appropriate to direct forbidden (three-halves power law) rather than that for direct allowed transitions (half power law). Atia *et al.* [20] reported that for sputtered V_2O_5 films, the optical absorption edge showed two distinct regions of behaviour. A high photon energy region in which absorption coefficient varies linearly with $(\hbar\omega)^2$ was associated with the valence-to-conduction band transitions. A low energy tail was related to the interband transitions involving impurity states within the gap. Nguyen The Quang and Hevesi [21] measured the value of the optical energy gap following the Urbach rule in V_2O_5. The band gap was in good agreement with that calculated at room temperature following forbidden direct trans-

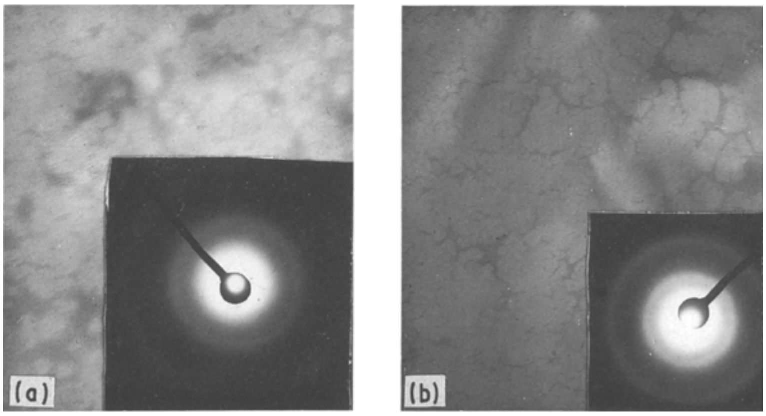

Figure 1 Electron diffraction pattern and micrograph of evaporated thin films of (a) V_2O_5 and (b) V_2O_5/B_2O_3.

itions. Michailovits *et al.* [22] reported some optical properties of evaporated V_2O_5 thin films but they did not measure the optical energy gap. Anderson and Compton [18] suggested a direct forbidden transition process for V_2O_5–P_2O_5 glasses. They also observed an increase in the optical energy gap of V_2O_5–P_2O_5 glasses with increasing P_2O_5 content.

According to our knowledge, no study on ultraviolet absorption spectra of V_2O_5/B_2O_3 films has been reported so far. We have therefore, investigated the absorption spectra of evaporated films of V_2O_5 and V_2O_5/B_2O_3, respectively, in the ultraviolet range.

2. Experimental procedure

Thin films of V_2O_5 and V_2O_5/B_2O_3 were deposited from analytical reagent grade materials on to pre-cleaned 7059 Corning glass substrates held at an elevated temperature of about 373 K in a Speedivac coating unit model 19A/122 at a pressure of the order of 10^{-6} torr (1 torr = 133.322 Pa). The co-evaporation technique used has been established and described by Hogarth and Wright [23]. Vanadium pentoxide and boric oxide were evaporated from covered molybdenum and covered tungsten boats, respectively. The evaporation parameters such as composition and thickness of the complex assembly were monitored by means of a quartz crystal monitoring system which was calibrated for each material. The total thickness of co-evaporated oxide thin films was measured by multiple beam interferometry making use of Fizeau fringes of equal thickness. The measurements of fundamental absorption edges of different samples were made using a Perkin–Elmer Lambda 9 spectrophotometer. The instrument was equipped with two beams, one used as source beam and the other as reference beam. This enabled us to obtain the transmission spectrum of co-evaporated oxide thin films by cancelling the effect of the glass substrate on placing another uncoated Corning 7059 glass substrate across the reference beam. The ultraviolet range of wavelength from 250 to 900 nm was covered. The structure of the V_2O_5 and V_2O_5/B_2O_3 thin films was studied with the help of a JEM7 electron microscope with a magnification of × 38 000. The films are amorphous as shown in Fig. 1.

3. Results

The ultraviolet transmission as a function of incident photon energy for different compositions of V_2O_5/B_2O_3 films is shown in Fig. 2. The data of Fig. 2 replotted for direct forbidden and indirect forbidden transitions are shown in Figs 3 and 4, respectively. A plot of $\ln \alpha$ against $\hbar\omega$ according to the Urbach law can be seen in Fig. 5. Fig. 1 shows the electron diffraction pattern and micrograph of V_2O_5 and V_2O_5/B_2O_3 films.

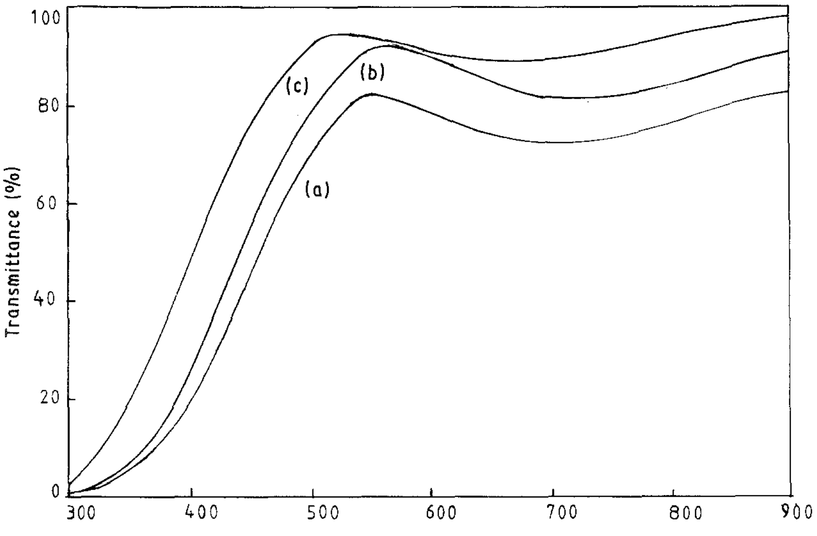

Figure 2 The transmission spectra of different compositions of V_2O_5/B_2O_3 (300 nm) thin films, (a) 100% V_2O_5, (b) 85% V_2O_5, (c) 65% V_2O_5.

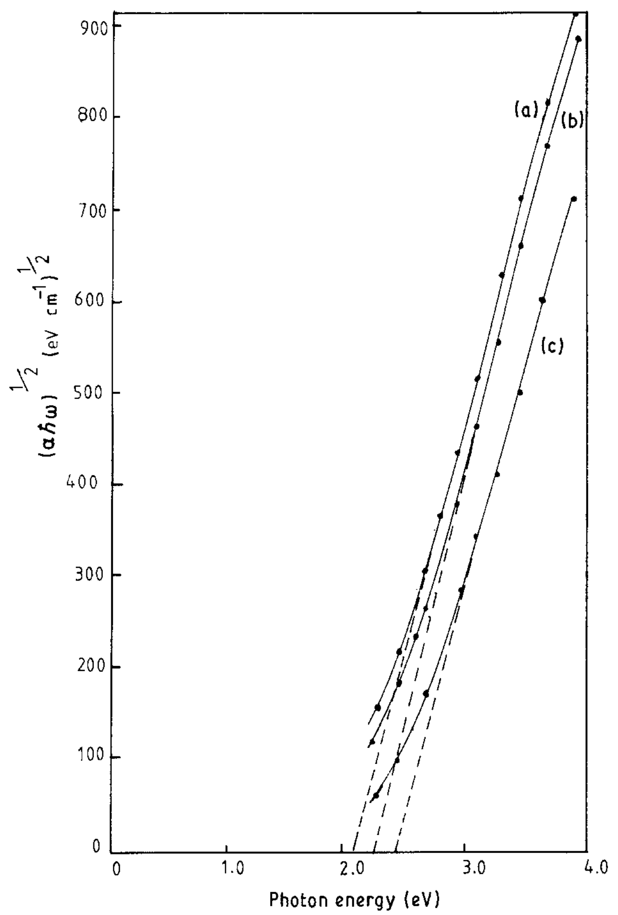

Figure 3 Data of Fig. 2 replotted for the indirect forbidden transitions.

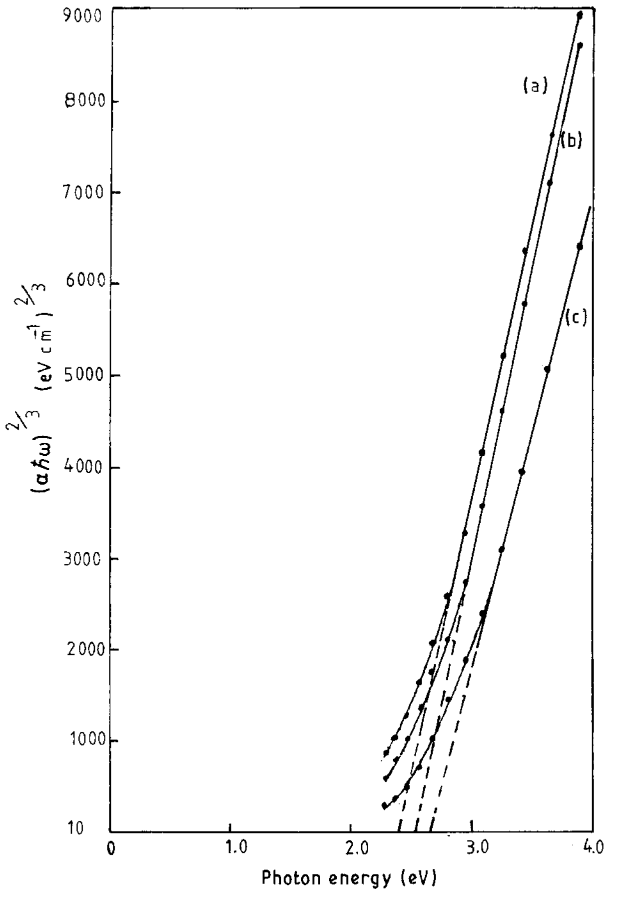

Figure 4 Data of Fig. 2 replotted for the direct forbidden transitions.

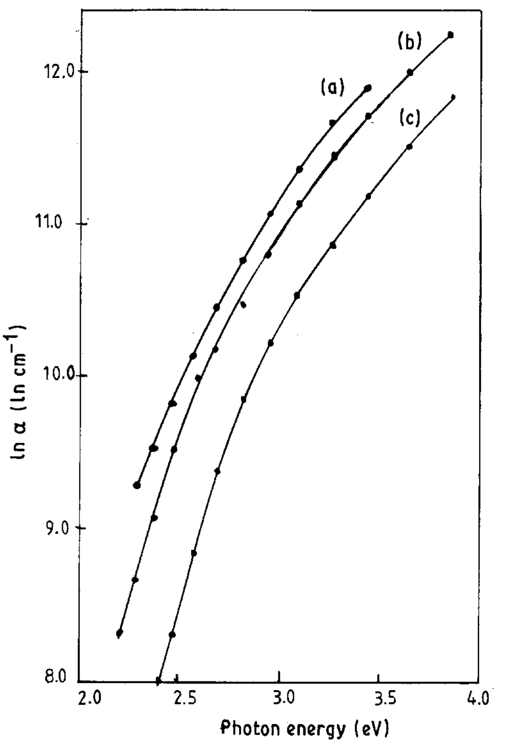

Figure 5 Data of Fig. 2 replotted as ln α versus $\hbar\omega$.

4. Discussion

The optical absorption of evaporated V_2O_5 and V_2O_5/B_2O_3 films has been calculated from the transmission spectra of the films (Fig. 2) using the relationship

$$\alpha(\omega) = 2.303A/d \qquad (3)$$

where $A = \ln(I_0/I_t)$ is the absorbance and I_0 and I_t are the intensities of the incident and transmitted radiation and d is the thickness of films. In order to calculate the optical energy gap, the values of $(\alpha\hbar\omega)^{1/2}$ and $(\alpha\hbar\omega)^{2/3}$ corresponding to different compositions have been plotted against $\hbar\omega$ for indirect allowed and direct forbidden transitions, respectively. It is observed that for the higher photon energies, the absorption spectra show a better fit to the direct forbidden transition (Fig. 4) as compared to that for indirect allowed transitions (Fig. 3). The value of optical energy corresponding to these two different processes for different compositions has been calculated by extrapolating the straight parts of the curves in Figs 3 and 4 to $(\alpha\hbar\omega)^{1/2} = 0$ and $(\alpha\hbar\omega)^{2/3} = 0$, respectively.

The value of optical band gap for V_2O_5 for indirect allowed and direct forbidden transitions is found to be 2.1 and 2.4 eV, respectively. Bullot *et al.* [24] have also obtained good straight lines for direct forbidden transitions for the V_2O_5 layers deposited from gels. It is suggested that in V_2O_4 the conduction band formed by vanadium 3d bands is separated by a band gap of 2.5 eV from the valence band formed by the oxygen 2p bands [25]. Similarly, Mokerov and Rakov [26] reported that in V_2O_5, the valence band is the 2p band of oxygen and the conduction band is the 3d band of vanadium. Koffyberg and Koziol [27] suggested that the absorption edge analogous to the band gap absorption in crystalline V_2O_5 at 2.35 eV, is due to the transition from a mainly oxygen p-type wave function to mainly 3d-type vanadium wave functions. Janakirama-Rao [16] proposed that the fundamental absorption edge in vanadium glasses in general is the same as that of crystalline V_2O_5 and it occurs at about 2.5 eV or higher energies in oxide glasses containing vanadium impurities. Sanchez *et al.* [19] suggested that for the V_2O_5 layers deposited from gels, a strong absorption in the ultraviolet region arose from the charge transfer from the O 2p valence band to the empty V 3d conduction band.

From the infrared [16, 18] and ESR [28, 29] studies, it has been reported that the site symmetry of vanadium cations in amorphous V_2O_5 is similar to that in crystalline V_2O_5. We propose that our evaporated amorphous V_2O_5 films also behave in a similar way. The fundamental absorption in our samples occurs due to the transfer of electronic charge from oxygen 2p to vanadium 3d band following a process of direct forbidden transitions. This is consistent with the findings of some other authors [9, 17, 18, 19]. The value of optical energy gap corresponding to direct forbidden transitions in the present studies is in agreement with those measured for crystalline [9, 17–27] as well as amorphous V_2O_5 [18]. It is also in excellent agreement with the band structure of V_2O_5 reported by Fiermans and Vennik [30] through the X-ray photoelectron spectroscopic studies.

The effect on the optical absorption of increasing V_2O_5 content in composite V_2O_5/B_2O_3 films can be explained in the following way. On increasing the B_2O_3 content, the concentration of charged non-bridging oxygens will go on decreasing due to the increase in the V^{4+} content. Thus the valence band will go on contracting because an uncharged bridging oxygen in a V_2O_5-like network would introduce energy levels lower than those of a non-bridging charged oxygen ion. In this way the optical band gap will increase with increasing B_2O_3 content of the composite V_2O_5/B_2O_3 films. This is again consistent with the decrease in the optical band gap of V_2O_5–P_2O_5 glasses with the increase in the P_2O_5 content as reported by Anderson and Compton [18]. The variation of optical energy gap of V_2O_5/B_2O_3 films with the change in B_2O_3 content is shown in Table I. The V_2O_5/B_2O_3 films with B_2O_3 molar content higher than 40% were unstable because of their hygroscopic nature, so we could not exceed that limit.

TABLE I Optical energy gaps corresponding to different compositions of evaporated V_2O_5/B_2O_3 (330 nm) thin films estimated for indirect forbidden and direct forbidden transitions. The last column shows Urbach energies corresponding different compositions

Composition	E_{opt} for forbidden indirect transitions (eV)	E_{opt} for forbidden direct transitions (eV)	Urbach energy (eV)
100% V_2O_5	2.10	2.40	0.44
85% V_2O_5	2.25	2.50	0.31
65% V_2O_5	2.40	2.65	0.28

It can be seen from Fig. 5, that our evaporated thin films of V_2O_5/B_2O_3 of different compositions show an exponential tail for the low-energy incident photons. Because of a large separation between oxygen 2p and vanadium 3d levels and the low value of the incident photon, the 2p states cannot take part in such an absorption process. Owing to disorder, some of the d states corresponding to V^{4+} ions may penetrate to some extent into the band gap. The absorption tail in the optical spectra of V_2O_5 and V_2O_5/B_2O_3 films may be related to the electronic transitions among such tailed-off d–d type states. A similar argument has been given by Anderson and Compton [18] and Anderson [31] for vanadium phosphate glasses. The value of Urbach energy corresponding to different compositions of V_2O_5/B_2O_3 films decreases with the increase in B_2O_3 content as shown in Table I.

5. Conclusion

In both types of evaporated (V_2O_5 and V_2O_5/B_2O_3) films, the optical absorption process is observed to be governed by the direct forbidden transitions from the valence band (oxygen 2p band) to the conduction band (3d vanadium band). The optical energy gap (2.4 eV) for amorphous V_2O_5 films is comparable to that of crystalline V_2O_5. The exponential tail is attributed to the electronic transitions among the tailed-off p–p states into the band gap. With the increase in V_2O_5 content, the optical band gap of V_2O_5/B_2O_3 films increases as a result of decrease in the concentration of non-bridging oxygen in the composite films.

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