

OPTICAL ABSORPTION IN $\text{CeO}_2\text{-V}_2\text{O}_5$ EVAPORATE THIN FILMS

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Abstract

In this work, the optical absorption near the fundamental absorption edge of co-evaporated $\text{CeO}_2\text{-V}_2\text{O}_5$ films is studied. It is found that the fundamental optical absorption in these materials is sharp more like that expected for crystals. It is also found that as the V_2O_5 content increases, the edge becomes less sharp and shifts towards higher wavelengths.

Introduction

Studying optical absorption, in particular the shape and shift of the absorption edge, is an extremely useful technique for understanding the basic mechanism of optically-induced transitions in crystalline and non-crystalline materials, as well as providing information about the band structure. The basic principle behind the technique depends on the absorption of photon with energies greater than the band-gap energy by carriers undergoing transitions from occupied states in the valence band to unoccupied states in the conduction band. Two kinds of optical transitions may occur at the fundamental edge in these materials, namely direct and indirect transitions. In a direct transition, the electron's wave vector remains unchanged and there is no phonon interactions, whereas in an indirect transition the cooperation of phonon is necessary for conserving momentum, and the electron's wave vector changes.

It has been suggested by Davis and Mott [1] that the following equation may be used for calculating the absorption coefficient in a direct transition:

$$\alpha(\omega) = B \frac{(\hbar\omega - E_{\text{opt}})^n}{\hbar\omega} \quad (1)$$

where ω is the angular frequency of the incident radiation; E_{opt} is the optical energy gap; and n is an exponent which takes values of 1/2 or 3/2, depending on whether the transitions are allowed or forbidden. A similar equation with $n = 2$ was suggested by Tauc [2] which offers the best fit to optical absorption data in many amorphous semiconductors.

Experimental Section

Thin films of $\text{CeO}_2\text{-V}_2\text{O}_5$ system with different W% of V_2O_5 were prepared by using thermal co-evaporation techniques [3] as listed in Table 1. The films were deposited at a rate of 5nm/s on Corning 7059 glass substrates held at 20°C and at a residual pressure = 1mpa. Tungsten boats were used for the evaporation since molybdenum boats reacted chemically with the evaporant, a result confirmed by x-ray photoelectron spectroscopy. The film thickness was monitored using a quartz crystal unit (Intellometrics, model IL-150) but accurately measured using an alpha-step instrument (Tencor instruments, model 200). The absorption spectra of the films were recorded with a Perkin-Elmer UV/VIS spectrophotometer (model Lambda-19).

Experimental Results

The recorded absorption spectra for all the compositions studied are shown in Figure 1. As can be seen, the fundamental absorption edge for a pure CeO_2

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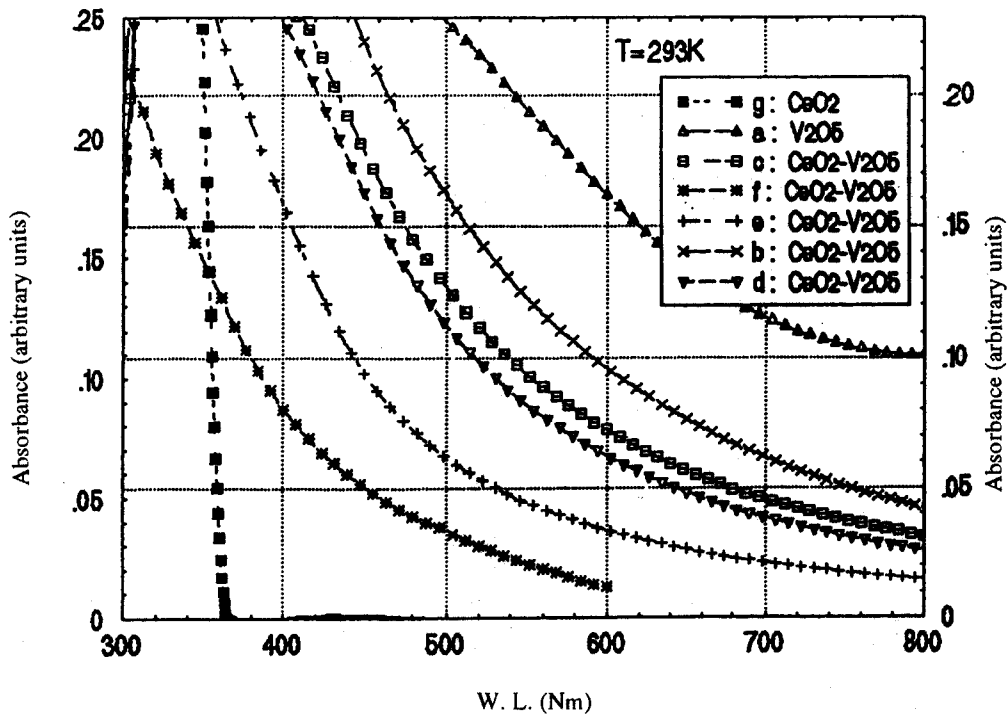


Figure 1. Absorption spectra as a function of wavelength for $\text{CeO}_2\text{-V}_2\text{O}_5$ films as listed in Table 1

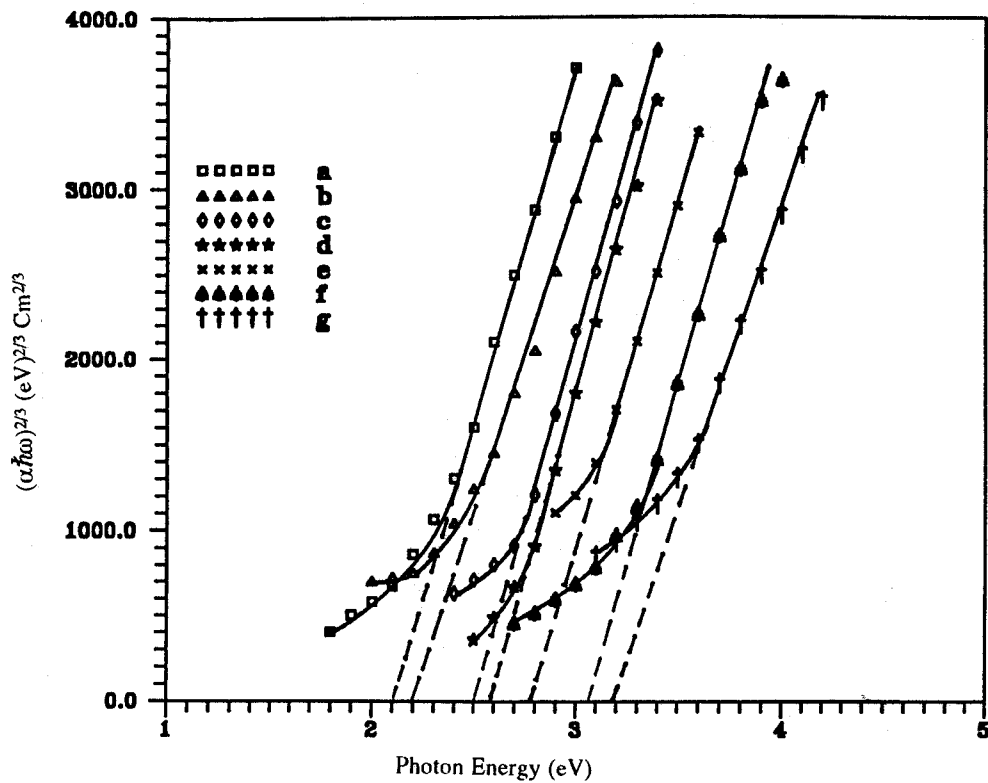


Figure 2. Variation of $(\alpha \hbar \omega)^{2/3}$ vs. photon energy for $\text{CeO}_2\text{-V}_2\text{O}_5$ film listed in Table 1

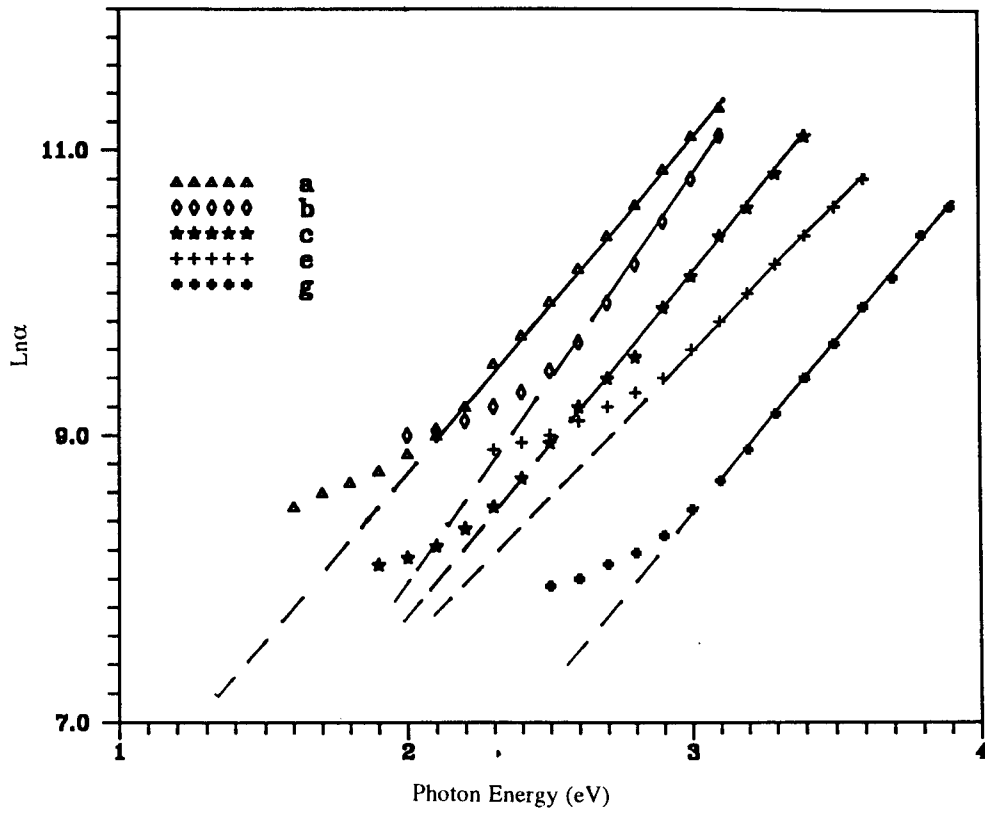


Figure 3. Variation of $\text{Ln } \alpha$ vs. photon energy ($\hbar\omega$) for $\text{CeO}_2\text{-V}_2\text{O}_5$ films given in Table 1

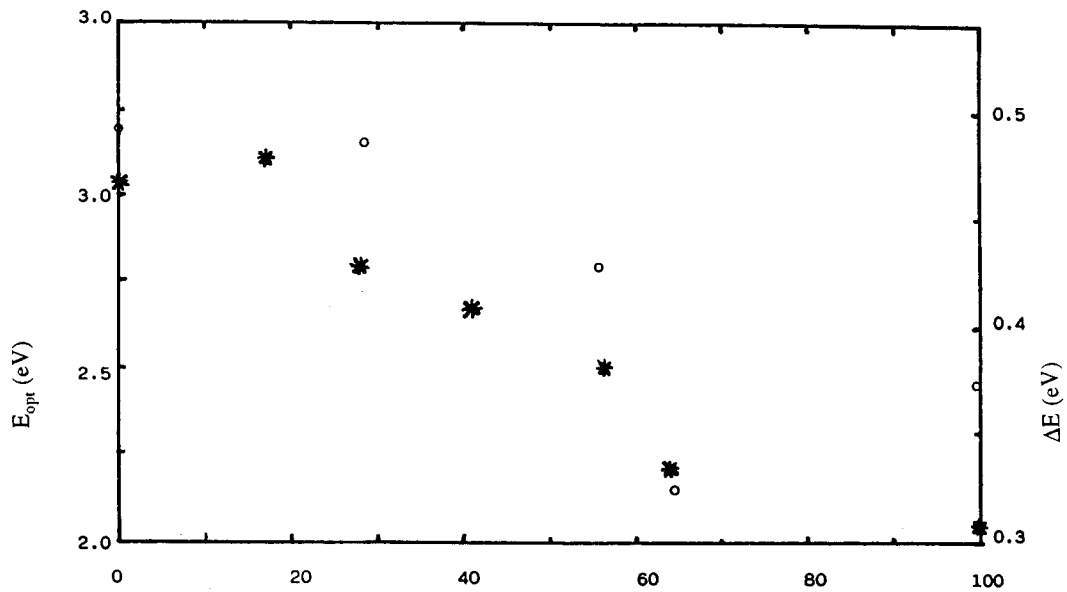


Figure 4. Variation of E_{opt} (*) and ΔE (o) with composition for $\text{V}_2\text{O}_5\text{-CeO}_2$ system

film is quite sharp, resembling that found in the crystalline materials [9], but as the V_2O_5 content increases, the fundamental edge becomes less sharp and shifts towards higher wavelengths. These results suggest that the ratio: V^{4+}/V^{5+} could be responsible for the conduction mechanism. We suggest that it will be necessary to conduct thermoelectric power and electron spin resonance (ESR) to verify this tentative conclusion. In order to examine the equation (1) and to evaluate the exponent n , graphs of $(\alpha\hbar\omega)^{1/n}$ vs $\hbar\omega$ were plotted with different values of n [1]. $\alpha(\omega)$ was calculated from the relation

$$\alpha(\omega) = (1/d) \ln(I_0/I_t) \quad (2)$$

where I_0 and I_t are the intensities of the incident and transmitted beams, respectively, and d is the film thickness. It was found that $n=3/2$ gave the best linear fit in the higher absorption region. Figure 2 depicts the variation of $(\alpha\hbar\omega)^{2/3}$ with $\hbar\omega$ for films 730nm thick; E_{opt} is obtained by extrapolating the linear portion in Figure 2 onto the $\hbar\omega$ axis.

E_{opt} varies between 2.1 and 3.05 eV as the V_2O_5 content increases [see Fig. 3 and Table 1]. Values of B in equation (1) can be obtained from the gradient of the curve of Figure 2; they are also given in Table 1.

Table 1. Optical data for V_2O_5 - CeO_2 thin films of various compositions prepared and measured at room temperature

V_2O_5 composition/wt%	E_{opt}/eV	$\Delta E/eV$	$B/10^4 eV^{-1}cm^{-1}$
100 (a)	2.1	0.42	2.5
64 (b)	2.2	0.33	2.2
56 (c)	2.5	0.43	2.35
41 (d)	2.6		2.3
28 (e)	2.8	0.50	2.5
17 (f)	3.2		2.85
0 (g)	3.1	0.50	2.35

Letters (a)-(g) are used in Figs. 1-3.

Conclusion

The experimentally-deduced values are in good agreement with the theoretical values. It should be noted that the absorption edge for films with a V_2O_5 content of less than 20 wt% lies at higher photon energies than for pure CeO_2 whereas films with greater than 20 wt% V_2O_5 lie at lower photon

energies. This result suggests that the Ce^{4+} ion dominates the optical absorption process for films with a V_2O_5 content of less than 20 wt%. X-ray photoelectron spectroscopy (XPS) analysis of cerium compounds indicates the existence of Ce^{4+} and Ce^{3+} ions, the exact proportion depends on the method of preparation [4]. Also, V_2O_5 in compounds tends to decompose irreversibly [5]. The consequential loss of oxygen results in a non-stoichiometric oxide in which some of the vanadium ions are reduced to a lower valence state; these are mostly V^{4+} ions which have the 3d configuration.

The results in Figure 1 also follow the Urbach law [6], viz.

$$\alpha(\omega) = C \exp(\hbar\omega/\Delta E) \quad (3)$$

where ΔE is the extent of band-tailing due to the presence of localized states, arising from lack of long-range order.

Figure 4 shows that graphs of $\ln\alpha(\omega)$ vs $\hbar\omega$ are linear. There have been a number of different interpretations of the origin of the exponential dependence of α on photon energy. One is based on the presence of strong internal electric fields due to structural disorder [7] whilst another says that it is due to electric transitions between localized states in the band edge tails, the density of which falls off exponentially with energy. Mott and Davis [9] rejected the latter interpretation because the slopes of the exponential absorption edges are much the same in a variety of materials. Data showing the variation of E with compositions are included in Table 1.

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