DENSITY OF THIN FILMS OF CADMIUM SULFIDE BY NUCLEAR BACKSCATTERING

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الخلاصة :

عُينِّتْ كثافة أغشية رقيقة من كبريتيد الكادميوم المحضرة بطريقة الترسيب البخاري باستخدام المضوائية الطيفية المدمجة مع إستطارة رذرفورد الارتدادية. حصلنا على كثافة قدرها ٠,٩٥ ± ٧٪ من قيمة كثافة كبريتيد الكادميوم في الصورة العادية. ولدى استخدام قانون لورنتس – لورينز المبني على قياسات معامل إنكسار الأغشية الرقيقة حصلنا على قيمة للكثافة قريبة من تلك المحصلة من النتائج التجريبية.

ABSTRACT

The density of thin vapor-deposited films of cadmium sulfide was determined by spectrophotometry combined with Rutherford backscattering spectrometry. The density determined was 0.95 ± 7% of the bulk value for the CdS. The Lorentz–Lorenz law, based upon the measured data on the index of refraction of the films, suggests a value of the density of the films close to the one obtained in the present work.

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1. INTRODUCTION

The II–VI compound semiconductors (such as CdS, CdSe, CdTe, ZnS, ZnSe, and ZnTe) are of interest as high-refractive-index materials [1] in multilayer optical coatings since they all have low absorption over a broad wavelength range, for example from 600 to 11 000 nm for CdS [1]. Moreover films of CdS are of interest as functional components in variety of opto-electronic devices such as solid state lasers and detectors, solar cells, and optical memories [2–4]. Generally, the density of a film is lower than that of the corresponding bulk material [1]. Densities of thin films can be accurately determined by several techniques such as (*a*) Rutherford backscattering spectrometery (RBS) combined with weighing methods [5]; (*b*) RBS combined with spectroscopic ellipsometery [6]; and (*c*) RBS combined with spectrophotometery [7, 8]. Our earlier work [8] revealed that densities of films determined by technique (*c*) are far more reliable than those determined by (*a*). However, the techniques (*b*) and (*c*) are expected to yield similar results. In the present work using technique (*c*) the density of vapor deposited thin films of CdS was determined from the RBS measurements of the energy loss of incident particles as they traverse the film, and the thickness of the film (measured by a spectrometric method), using tabulated values of the stopping cross-sections [9].

2. EXPERIMENTAL

The CdS films were deposited on fused silica substrates by physical vapor deposition technique (PVD) in a Leybold model L560 box coater evacuated by a turbomolecular pump. Physical vapor deposition techniques have been among the most commonly used deposition technologies for thin film preparation [10]. The system was pumped to a base pressure of less than 10^{-4} Pa. During film deposition the chamber pressure remained nearly unchanged. Source material (CdS) of purity 99.999%, supplied by Balzers, was evaporated from a molybdenum boat by thermal heating. Substrates were rotated during the deposition process. Substrates were not heated. A quartz crystal thickness monitor/rate controller controlled the rate of evaporation (0.7 nm/s). The source to substrate distance was about 40 cm. Films which varied in thicknesses from about 150 to 500 nm were deposited under similar evaporation conditions. After deposition, the film-coated substrates were removed from the coating chamber and exposed to the ambient atmosphere, prior to optical and RBS measurements.

Transmittance measurements at normal incidence on the CdS films were made over a 700–2500 nm wavelength range using a Cary 2390 spectrophotometer. The RBS analysis was carried out with 2 MeV He^{2+}. The system has been described elsewhere [11]. Briefly, a beam of helium ions strikes the sample surface at normal incidence. A solid state detector (Tennelec model PD-50-100-14-CB) was placed in the chamber at a scattering angle of 164°, with an effective solid angle of 1.75 msr. The system resolution for the used He^{2+} beam, including detector resolution, straggling, and electronics set up was 17 keV [11]. The collected RBS spectra were then fitted by the code RUMP [12] to find the relative concentrations of the two elements in the CdS films. For all the films it was found that the films were stoichiometric within experimental uncertainty, *i.e.* ±3%. Energy straggling has been accounted for using the simple Bohr straggling model (RUMP [12]).

3. RESULTS AND DISCUSSION

In the present work, the method described elsewhere [13] in which refractive index (n_f) and thickness (t_f) of a transparent film are simultaneously determined from the measurement of transmittance at normal incidence, was used. In this method the dispersion curve (n_f *versus* wavelength) may be calculated from measured transmittance beginning with an approximate thickness that may be obtained from the spectral position of the consecutive maxima and minima of the transmittance *versus* wavelength curve, and then the thickness may be adjusted in an attempt to obtain a continuous dispersion curve [13]. It was shown in reference [13] that a continuous dispersion curve cannot be obtained when the film thickness is overestimated or underestimated. Moreover, the characteristics of the dispersion curves corresponding to an overestimate and underestimate of the thickness are easily distinguishable, such that the appropriate adjustment of the thickness becomes a simple method [13]. The estimated uncertainties in the n_f and t_f determined by this method are less than ±1% [13].

In the wavelength region from 700 to 2500 nm (of concern in the present work), CdS films are known to be transparent [1]. An average dispersion (n_f *versus* wavelength, λ) curve from different CdS films is shown in Figure 1. Variations in n_f from film to film were less than 1%. The present results are also compared with those reported [14] for bulk crystalline CdS measured for ordinary (n_o) and extraordinary (n_e) rays. The bulk CdS (having hexagonal structure) is a birefringent material, so named because it has two different indices of refraction, n_o and n_e, as measured for the incident beam parallel and perpendicular to the optical axis of crystalline CdS. A bulk birefringent crystal can be cut and polished to produce an element in which the optical axis may have any desired orientation relative to the incident light. However, for a CdS film deposited on a substrate this option is not available. Therefore, separate measurement of the two refractive indices (*i.e.* n_o and n_e) in the case of films is not possible. The CdS films grown on fused silica substrates are known to have a polycrystalline structure. Thus, the measured refractive index of a CdS film will have contributions from both ordinary and extraordinary rays, and therefore its value should lie between n_o and n_e, provided the film has the same density as that of the bulk CdS. In the spectral region covered by n_f and n_e (or n_o) curves (Figure 1), it was found that the refractive index of the film was smaller than that of the bulk material. Generally, the density of a film is lower than the corresponding bulk material and consequence of this is that the refractive index is lower in the film than in the bulk [1].

A typical RBS spectrum from a film of thickness of 471 nm is shown in Figure 2. The high-energy edges of the peaks corresponding to cadmium and sulfur (in thin CdS films) and Si (in fused silica substrate) are used in Figure 2. The collected RBS spectrum (data represented as dots) were then fitted (full curve) by code RUMP [12]. Reasonably good fit to the data was obtained on the assumption that the sample was a stoichiometric film of CdS on a silica substrate. Similar spectra were obtained for other films. The energy width *i.e.* energy loss ΔE (ΔE_{Cd} for cadmium and ΔE_s for sulfur peaks

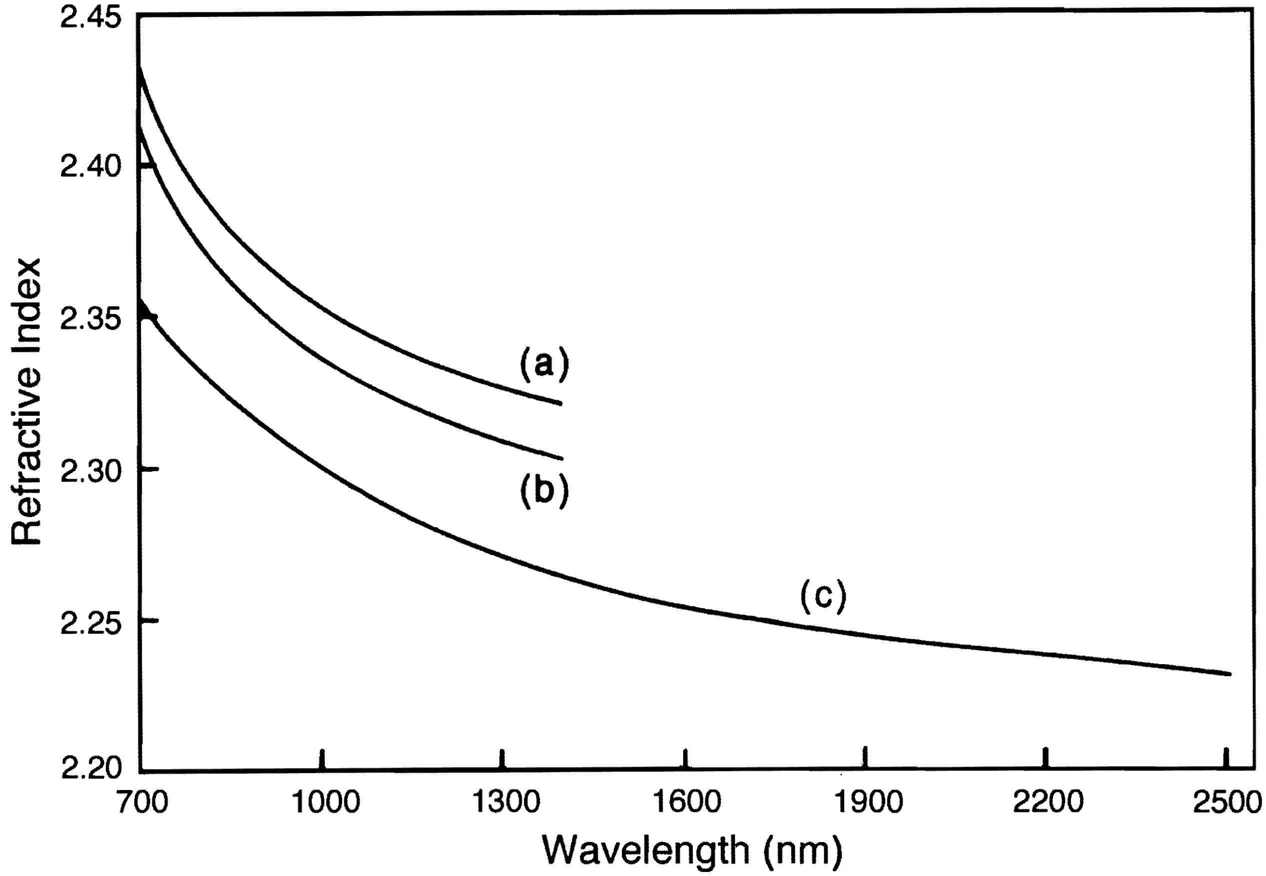

Figure 1. Dispersion Curves: (a) $n_e - \lambda$, *for bulk crystalline CdS for the extraordinary ray [5],* (b) $n_o - \lambda$, *for bulk crystalline CdS for the ordinary ray [5], and* (c) $n_f - \lambda$, *for thin films of CdS, present work.*

in Figure 2), of the He^{2+} beam between the surface and the interface (film-substrate) is related to the CdS film thickness (t_f) through [15]:

$$\Delta E = S\, t_f \,. \tag{1}$$

Where S is the backscattering energy loss factor, given by surface energy approximation [15]:

$$S = (N_A\, \rho_f / M)\, [K\varepsilon_{mol}(E_o) + \varepsilon_{mol}(KE_o) / |\cos\theta|] \,. \tag{2}$$

K is the kinematic factor, $\varepsilon_{mol}(E_o)$ is the molecular (CdS) stopping cross-section at energy $E_o = 2.0$ MeV (incident beam energy), $\theta = 164°$ is the scattering angle, N_A is the Avogadro's number, ρ_f is the density of the film, and M is the molecular mass of CdS. The kinematic factor, K, is defined as the ratio of the projectile energy after the elastic collision to that before the collision. The factor depends only on the ratio of the projectile (He^{2+}) to the target masses and on the scattering angle ($K_{Cd} = 0.870$ for cadmium and $K_S = 0.611$ for sulfur atoms [9]). According to Bragg's Rule [9] molecular stopping cross-section may be written in terms of atomic cross-sections, as in the present case:

$$\varepsilon_{mol} = \varepsilon_{Cd} + \varepsilon_S \,. \tag{3}$$

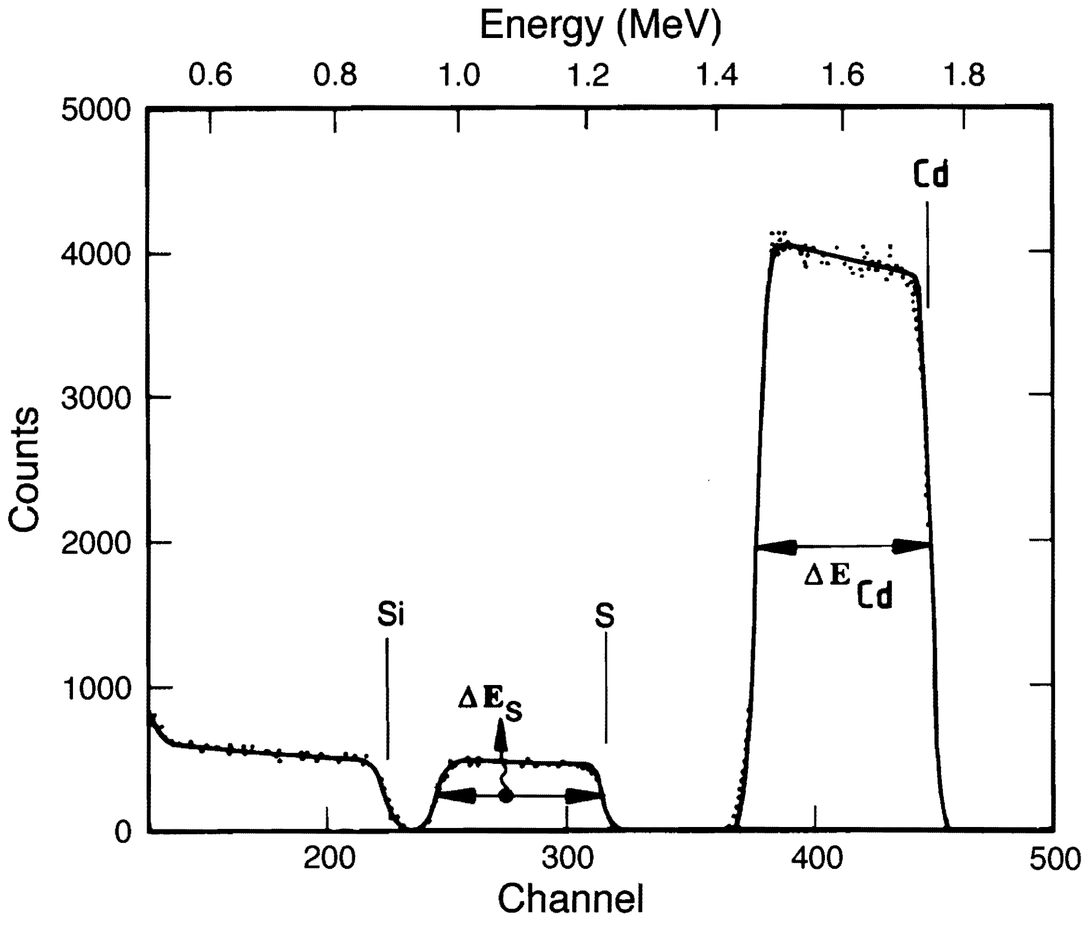

Figure 2. The RBS spectrum (2 MeV He^{2+} analysis) from a 471 nm thick film of CdS on a fused silica substrate (······), overlaid with the corresponding theoretical fit (——) generated by the code RUMP [12].

Where ε_{Cd} and ε_S are stopping cross-sections of cadmium and sulfur atoms, respectively. In the present work, the values of ε_{Cd} and ε_S at different energies were taken from reference [16]. It follows from the above that:

$$\Delta E_s/\Delta E_{Cd} = [K_S\varepsilon_{mol}(E_o) + \varepsilon_{mol}(K_SE_o)/|\cos\theta|] \,/\, [K_{Cd}\varepsilon_{mol}(E_o) + \varepsilon_{mol}(K_{Cd}E_o)/|\cos\theta|] = 0.94.$$

The measured values of the above ratio (see Figure 2) for different films were found to lie in the range 0.95 ± 0.02. A close agreement between the measured and calculated values of the ratio justifies the use of Bragg's rule in the present case. In Figure 3, ΔE_{Cd} (as measured through RBS spectra, such as in Figure 2) is plotted as a function of film thickness (t_f, as measured through the spectrophotometric method [13]) for CdS films. Uncertainties in the measurements of ΔE_{Cd} and t_f are 17 keV and 1%, respectively. The straight line is the result of a least-squares linear fit to the data. The slope of the straight line in Figure 3, was found to be $(5.82 \pm 0.41) \times 10^9$ eV/cm. Using this value of the slope, M = 144 g.mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1} and the other parameters as $K_{Cd} = 0.870$ [9], $\varepsilon_{mol}(E_o) = 154 \times 10^{-15}$ eV.cm^2 [16] , and $\varepsilon_{mol}(K_{Cd}E_o) = 163 \times 10^{-15}$ eV.cm^2 [16], we obtain from Equation (2) the density $\rho_f = 4.60 \pm 0.32$ g.cm^{-3}. Bragg's rule (Equation (3)) was used in calculating the molecular stopping cross-sections from the given [16] atomic cross-sections. This value is (95 ± 6.7)% of 4.82 g.cm^{-3}, the density for the bulk crystalline CdS.

One naturally speculates that the density of a sample may be related to other physical properties, such as electrical conductivity, optical properties, electron spin resonance, and small angle scattering, which also show some variations from sample to sample [16]. The variation of the refractive index with density as given by the Lorentz–Lorenz law appears to be a good prospect [8]. From the Lorentz–Lorenz law, the ratio of the densities of film (ρ_f) and bulk material (ρ_b) in terms of their refractive indices (n_f-film and n_b-bulk) is [1]:

$$\rho_f / \rho_b = [(n_f^2 - 1)(n_b^2 + 2)] \,/\, [(n_f^2 + 2)(n_b^2 - 1)].$$

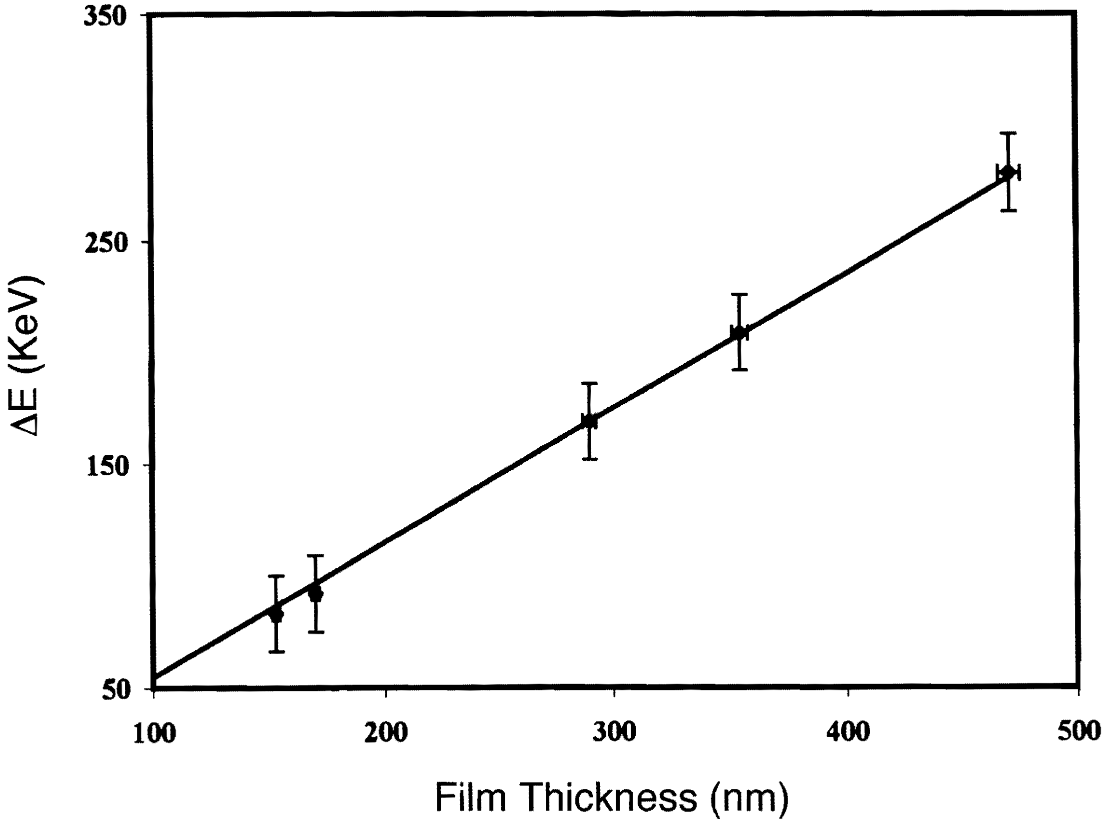

Figure 3. Energy loss, ΔE_{Cd}, in the CdS films as obtained from backscattering spectra (see Figure 2) plotted as a function of the film thickness, t_f, which was obtained from spectrophotometric method. The open circles represent data. The straight line is the least-squares linear fit to the data.

In case of a bulk birefringent crystal (such as CdS), measurement of the refractive index made for an incident ray in any direction with respect to the optical axis of CdS, will yield a refractive index that lies between n_o and n_e. Thus, n_b can have a value that lies in the range n_o and n_e. It was found (Figure 1) that $0.97\, n_e \leq n_f \leq 0.98\, n_o$. For $n_f = 0.97\, n_e$ and taking the values of $n_b = n_e$ from Figure1, we find from the above relation that $\rho_f = 0.97\, \rho_b$. Similarly, for $n_f = 0.98\, n_o$, it was found that $\rho_f = 0.98\, \rho_b$. Thus, the Lorentz–Lorenz law suggests that the film density may lie within 97 to 98% of the value of the bulk density for CdS. Indeed, these values are close to the one measured in the present work.

CONCLUSION

The density of thin films of CdS has been determined. This value is close to the one obtained by the Lorentz–Lorenz law.

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