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OPTICAL PROPERTIES OF POLYCRYSTALLINE ZINC FILMS

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In the present work, the complex refractive indices have been determined for thin films of zinc over the ranges from 1.55 to 4 eV and from 2.5 to 40 μm, using a transmission method. The experimental results have been compared with theoretical structure of zinc. The direct transmission spectrum of zinc thin films deposited on different substrates has been measured at 300 K. All films prepared for optical measurements, were deposited at pressure 10^{-4} Pa, with deposition rate of 2.5 nm/s. The measurements were made using a Beckman Double Beam Spectrophotometer IR-4220 and UV-5203 in the infrared and visible region, respectively.

1. Introduction

The optical properties of most metals in the visible spectrum are therefore influenced by interband transitions. The infrared properties of metals, at least for wavelengths greater than 5 μm, may be expected to obey the formula of the free electron theory. These formula have been modified by Dingle[1] to allow for the anomalous skin effect.

Little experimental work has been done on the optical properties of zinc. All of these experiments on single crystals and evaporated films were presented in Refs. 2—6. The complex refractive indices have been determined for single crystals of zinc over the range 1 to 15 μm, using a reflection method[7]. Reflectivity measurements have been performed by Rubloff[5], Lenham and Treherne[8] from 0.6 to 5.0 eV at 300 and 77 K, and by Mosteller and Wooten[4] from 2.2 to 10.8 eV at 96 K.

Theoretical calculations of the band structure have led to the development of a number of models of the energy bands of zinc[9,10]. Stark and Falicov[10] calculated the band structure using a non local pseudopotential model; Kasowski[11] calculated the interband conductivity spectrum based upon these band calculations, neglecting spin-orbit coupling. The low energy limit of data on zinc has previously been 0.6 eV, while Kasowski[11] has predicted structure in the conductivity at energies somewhat below 0.4 eV. The structure in the near-infrared and visible spectra is highly temperature dependent[6]. Since ZnO absorbs strongly above its energy gap of 3.34 eV[12], then the effect of ZnO was significant at energies greater than about 3.0 eV[5].

The aim of the present work is to investigate the optical properties of thermally deposited thin zinc films prepared under vacuum and to compare the data with those for macroscopic crystalline samples and theoretical structures of zinc.

2. *Experimental technique*

Thin zinc films of different thicknesses (20 to 190 nm) were prepared by thermal evaporation of spec. pure (99.999%) zinc under vacuum of approximately 10^{-4} Pa with evaporation rate of about 2.5 nm/s. Deposition was carried out on different substrates suitable for measuring optical transmission in the required spectrum region (KBr and mica sheet discs for IR and fused silica plates for visible region). The measurements were carried on immediately after deposition to minimize the effect of atmospheric corrosion. For optical transmission measurements a Beckman double beam spectrophotometer IR-4220 and UV-5203 was used in the infrared and visible region, respectively. The thickness of the films was determined by multiple beam interferometry techniques[13].

For scanning electron microscope observations, the films and substrate were mounted on a standard specimen stub and examined in SEMCO nanolab 7 scanning electron microscope operating at 15 kV. A thin coating ($\approx 10^{-8}$ m) of gold was deposited onto the metal film and substrate attached to the stub prior to examination in the scanning electron microscope to enhance the conductivity and secondary electron emission characteristics of the overgrowth.

3. *Results and discussion*

It is well known that with specified values of temperature and wavelength, the optical constants of a thin film of given thickness are functions of a certain number of factors: the type and the temperature of the support during evaporation, the film growth rate, the vacuum level, the type of preparation used and the nature of the residual gas. On the other hand, under well defined conditions of evaporation the optical constants have been found to vary with the thickness of the film, the temperature and the wavelengths of the radiation used in the determination of the constants.

Plate 1 (a, b) shows a scanning electron micrograph of a thin film of zinc deposited on both amorphous and crystalline substrates, respectively. It is well known that the substrates of amorphous structure have been considered as neutral substrates. They have practically no effect on the formation, growth and orientation of the film condensed on them. But, in case of crystalline substrate, the deposition will be governed by the relation between the intra-atomic spacing of the network of both the substrate and zinc, and by the substrate surface features. Hence, the deposition with mainly occur at certain preferred sites.

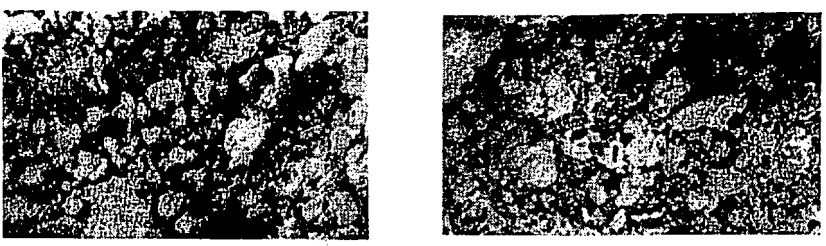

Plate 1 (a, b) — Scanning electron micrographs of a freshly deposited zinc film on KBr and mica substrates, respectively (d = 182 nm).

For graphical presentation of the results of the polyvalent metals, the optical conductivity $\sigma_1(\omega)$ is more convenient than the dielectric constant. They are related by:

$$\sigma_1(\omega) = \varepsilon_2(\omega) \cdot \omega/4\pi. \tag{1}$$

The detailed variation of $\sigma_1(\omega)$ with wavelength, for the samples of different thicknesses deposited on different substrates is shown in Fig. 1. It can be seen that well defined peaks are shown at 0.413 eV and 0.335 eV, and also shoulder at 0.155 eV for the layers deposited on KBr substrate only.

These values are in good agreement with the data of Weaver et al.[6] and Kasowski[11]. Kasowski used the band structure of Stark and Falicov[10] to calculate the interband conductivity (σ_1) spectrum. He found sharp peak at about 0.15 eV and small shoulder in absorptivity curve at about 0.4 eV. The low-energy interband transition was attributed to transitions near the point K in the Brillouion zone[9]. The calculated low-energy peak was broader and was centered at a higher energy. The discrepancy probably arises from »noise« in the calculations of low-energy structure.

As Lettington[2] has already pointed out both polarization should lead to transition $L_1 \rightarrow L_1$, $S_1 \rightarrow S_2$ involving the (101) Brillouin zone face, while C-axis polarization should in addition lead to $\Sigma_1 \rightarrow \Sigma_3$ and $\Gamma_1^+ \rightarrow \Gamma_3^+$ transitions involving the (002) face. Harrison's pseudopotential calculation[14] give energy gaps for the (002) faces of 0.36 eV.

On the basis of the energy band diagram (Fig. 2) for Γ to K direction in zinc and the Fermi-surface models for Cd and Zn[15,16], Lenham and Treherne[8] consider the absorption peaks to arise from transitions across the Fermi-level from band 1 to bands 2 and 4. In the case of zinc the energy difference between bands 2 and 4 for vertical transitions in the (E, K) diagram at the transition levels is

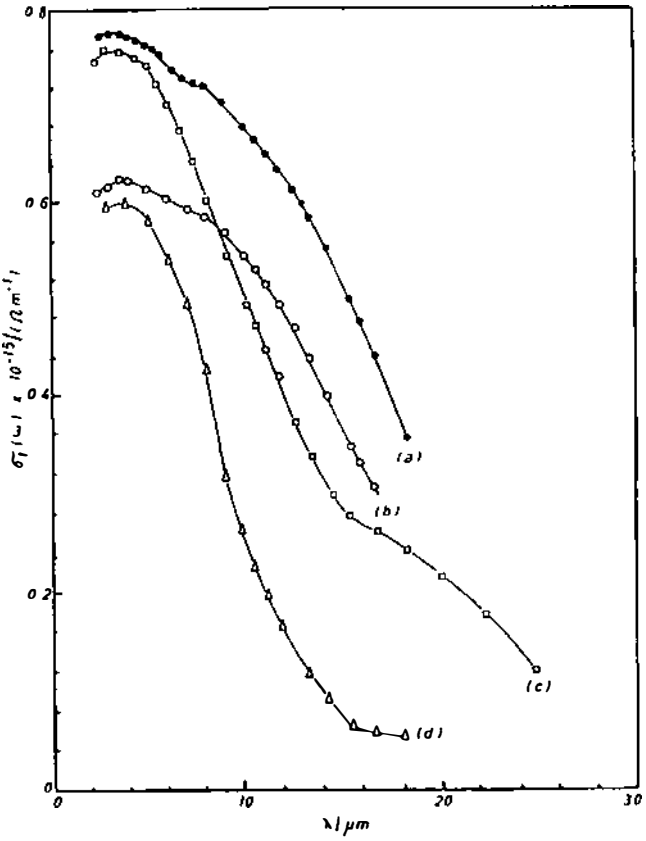

Fig. 1. Dependence of the optical conductivity $\sigma_1(\omega)$ on wavelength.
(a) $d = 182$ nm, (b) $d = 160$ nm (on KBr disc)
(c) $d = 182$ nm, (d) $d = 160$ nm (on Mica sheet).

small and the observed peak, in each direction, could be a summation of two transitions[9].

Fig. 3 shows the dependence of the optical conductivity $\sigma_1(\omega)$ on the photon energy for a film of 30 nm thickness[17]. The results are compared with the data of Graves and Lenham[3] for a hand-polished crystalline zinc, using a modified Drude technique for oblique incidence reflectance, the data of Lettington[2] on electropolished samples and the data of Rubloff[5] on electrolytically polished single crystal samples. Generally, the curves differ from each other, however, the position of the absorption peak for the 30 nm thickness film is close to the absorption peak observed by Rubloff[5] for electropolytically polished crystalline zinc using polarized radiation in the direction $\vec{E} \perp \vec{C}$.

The differences between the curves can be attributed to the quality of the surface of the samples, since mechanical polishing affects the surface and produces a cold-worked face layer of different structure, while thin films have a structure

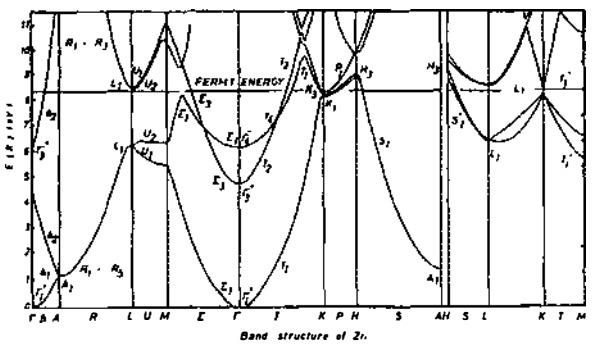

Fig. 2. Band structure of zinc

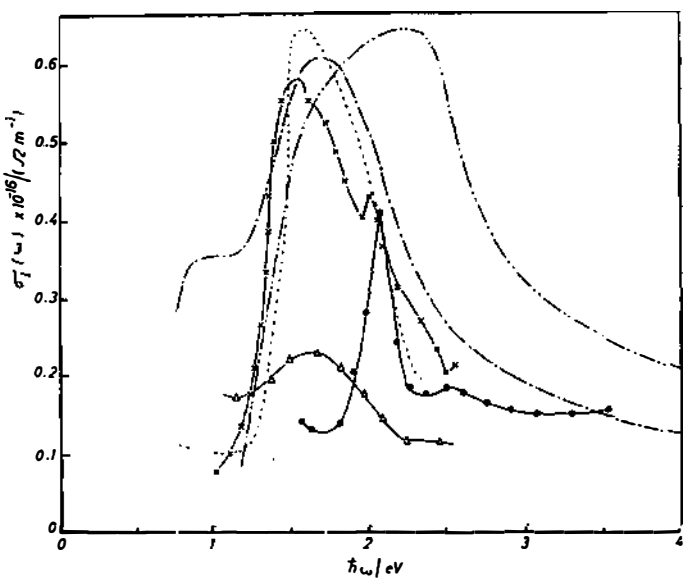

Fig. 3. The dependence of the optical conductivity $\sigma_1(\omega)$ on the photon energy. —··—··— Rubloff[5] E ⊥ C; —·—·— Rubloff[5] E∥C; – – – – – Graves and Lenham[3]: —x—x—x Lettington[2], Basal plane; —Δ—Δ—Δ— Lettington[2], C-axis; —Θ—Θ—Θ present work (30 nm film).

different from bulk samples. Internal stresses may appear in thin films because of the difference between the thermal expansion coefficients of the film and the substrate. Deformation due to such internal stresses alters the absorption and the band structure[18] and could give rise to a decrease in the absorption. Moreover, the structure of zinc at the interface with the substrate is not the same as the bulk material. Strains at the interface may alter the atomic spacing in the layer and, therefore, affect the optical properties. If the volume of the crystal is changed by about 1%, the value of the energy gap will shift by about 0.1 eV. Such a change in energy gap will have a direct effect on the optical absorption[19]. Some work was

done on thin layer of germanium, the theoretical analysis yielded a shift in the conduction band minimum by about 5×10^{-6} eV kg^{-1} cm^2. A coefficient of 12×10^{-6} eV kg^{-1} cm^2 was obtained by measuring the shift in the absorption for the transition $\Gamma_{2'} - \Gamma_{2s'}$. This may explain the decrease of the absorption at lower energies.

The optical conductivity curve represents the summation of the interband and intraband absorptions. Mosteller and Wooten[4] have shown that the dielectric function of clean vacuum-cleaved zinc can be calculated from the free electron functions

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{(\omega^2 + 1/\tau^2)} \tag{2}$$

$$\varepsilon_2(\omega) = \frac{\omega_p^2}{\omega\tau(\omega^2 + 1/\tau^2)} \tag{3}$$

where $\hbar\omega = 10.1$ eV is the plasma energy and τ is the relaxation time $\tau = 2 \times \times 10^{-15}$ s. Eq. (3) represents the intraband or free carrier contribution to ε_2, and the optical conductivity due to free carriers is proportional to $1/\omega^2$. Rubloff[5] had shown that the free carrier contribution in crystalline zinc is predominant below 0.5 eV, and falls rapidly to minimum value at 0.5 eV, and the structure observed near 2.0 eV is considered essentially as interband absorption.

An indication of the accuracy of the magnitudes of the optical constants is obtained from calculating the sum rule for the imaginary part of the dielectric constant ε_2

$$\int_0^\infty \omega\,\varepsilon_2(\omega)\,\mathrm{d}\omega = \pi\omega_p^2/2, \tag{4}$$

where $\omega_p^2 = 4\pi N n_{eff} e^2/m_0$, N is the density of atoms per unit volume, n_{eff} is the effective number of electrons per atom, e and m_0 are the charge and mass of the electron, respectively. For zinc, n_{eff} should saturate at $n_{eff} = 2.0$, when the oscillator strength of the two outer s electrons of the atoms is exhausted. Eq. (4) can be rewritten as

$$n_{eff}(\hbar\omega) = \frac{m_0 c}{\pi N e^2 \hbar} \int_0^{\hbar\omega} \frac{\varepsilon_2(\hbar\omega)}{\lambda}\,\mathrm{d}(\hbar\omega). \tag{5}$$

This function is plotted in Fig. 4 for a zinc film of 30 nm thickness[17]. In the same figure the data of Rubloff[5] for zinc single crystal bulk samples are represented. The values of n_{eff} for the thin film are somewhat lower than that for bulk samples, however, at higher energies just above the plasma energy for the two s electrons ($\simeq$ 10 eV), n_{eff} asymptotically approaches $n_{eff} = 1.9$, which can be considered as a reasonable value for the thin film.

It is well known that the conductivity of thin films depends strongly on film thickness and substrate. The value of the conductivity is reduced by few order of magnitude for thin films compared with the corresponding values for bulk mate-

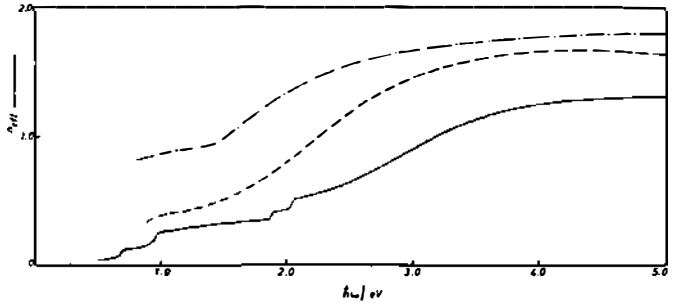

Fig. 4. The dependence of the effective number of electrons on the photon energy.
— · · — Rubloff[5] E||C; — — — Present work ($d = 30$ nm); ——— theoretical[11], interband values.

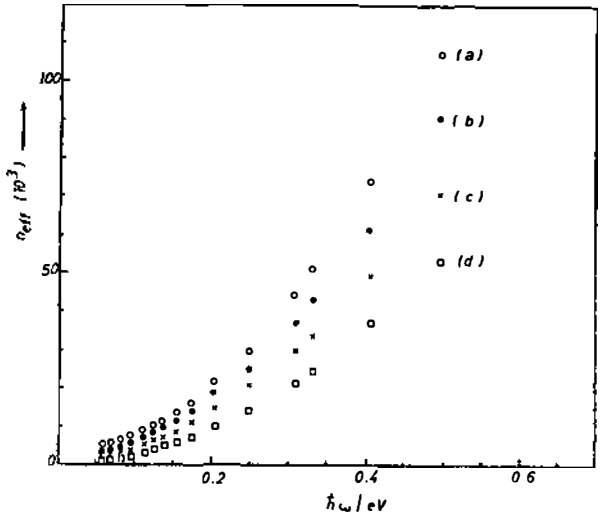

Fig. 5. The dependence of the effective number of electrons on the photon energy.
(a) $d = 182$ nm on KBr (b) $d = 170$ nm on KBr
(c) $d = 160$ nm on KBr (d) $d = 182$ nm on mica sheet.

rials. These phenomena are known as the size effect, which introduces the effect of film thickness as shown in Fig. 1. The effect of these parameter is shown in Fig. 5 which also represents the above function in the infrared region for a family of zinc films of different thicknesses deposited on different substrates. It is clear that the effective concentration of carriers increases with film thickness on both substrates. As well, films deposited on KBr contribute more effective carriers which is conformed with the classical size effect. Few publications have been presented by the author in this field[21-23]. The concentration of lattice defects and the migration routs are behind the variation of the optical conductivity of zinc films deposited on both substrates.

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OPTIČKA SVOJSTVA POLIKRISTALINIČNIH FILMOVA CINKA

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Rad je posvećen određivanju kompleksnog indeksa loma tankih filmova cinka u intervalu od 1,55—4 eV, od 2,5—40 μm, upotrebom optičkih transmisionih metoda. Eksperimentalni rezultati uspoređeni su sa teorijskom strukturom cinka. Transmisioni spektar tankih filmova Zn deponiranih na različite podloge mjeren je na 300 K. Filmovi Zn priređeni za optička mjerenja, deponirani su na pritisku od 10^{-4} Pa, sa brzinom depozicije od 2,5 nm/s. Mjerenja su izvršena pomoću Beckman Double Beam Spektrometra IR-4220 i UV-5203, u IC i vidljivom području spektra.