JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 4, April 2010, p. 948 - 952

Determination and analysis of dispersive optical constants of some organic thin films

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The optical behaviour of the complexes of (2E)-3-aza-1-(hydroxyimino)-2,4-diphenylpent-2-ene (HL) was investigated by optical reflectance and transmittance measurements. The optical constants (refractive index, n; extinction coefficient, k and dielectric constant, e) of some organic thin films were determined using reflectance and transmittance spectra. The optical absorption studies show that the transition is direct with band gap energy values, which are calculated. Analysis of the basis absorption spectra was also carried out to determine optical band gap (E_g) and Urbach parameter (E_0). The analysis of the optical absorption data revealed optical direct transition with band gaps of 3.7-3.9 eV. A surface observation of these thin films was also carried out by an Atomic Force Microscope.

(Received April 7, 2010; accepted April 26, 2010)

Keywords: Optical band gaps, Urbach parameter, Atomic Force Microscope

1. Introduction

Concerning the chelating behavior of iminooximes, we have examined previously the coordination properties of some iminooximes in several transition metal complexes [1]. Iminooximes and Schiff bases are of great importance for the preparation of various pharmaceuticals and are used in many other areas of chemistry as starting materials. Recently, there has been considerable interest in the chemistry of Schiff base compounds containing oximes and their metal complexes due to their biological activities [2] and nonlinear optical properties [3]. These compounds, containing benzene, oxime and Schiff base functions in their molecules, seem to be suitable candidates for further chemical modifications and may be optical communication and optical devices. Therefore, the optical absorption spectra have proved to be very useful for elucidation of the electronic structure and optical constant of these materials. Transition metal complexes have a number of electrical properties in the dark which similar to those of classic crystalline and amorphous semiconductors and these compounds can behave like intrinsic semiconductors. Optical and electrical properties of the metal complexes have become an increasingly interesting area of semiconducting and optical materials because these materials possess great potential for device applications such as Schottky diode, solid state devices and optical sensor. The study of optical absorption of transition metal complexes, particularly the absorption edge has proved to be very useful for elucidation of the electronic structure of these materials [4]. It is possible to determine indirect and direct transition occurring in the band gap of the metal complexes by optical absorption spectra [4]. The optical constants such as refractive index, absorption index and dielectric constant can be analyzed by transmittance and reflectance spectra.

In the present work, we are to investigate optical properties of some optical thin materials-based metal complexes so that this information would be helping the researchers toward applying these materials in optical communication and optical devices.

2. Experimental

2.1 Synthesis of the complexes

Solutions of $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ (1 mmol) in 20 mL ethanol were added to a solution of the HL ligand (1,1,2,1 mmol,respectively) in 30 mL ethanol and the solutions were continuously stirred for 3 h, during which the metal complexes precipitated. The resulting precipitates were filtered, washed with cold ethanol then diethylether and dried in air. The synthesized complexes were characterized and described elsewhere [5]. The chemical structure of the complexes is given in Fig. 1.

2.2 Preparation of the films

The solution of the films was homogenized for 5 h and was rotated for homogeneous mixing. Then, the thin films deposited on glass substrates were prepared by evaporating the solvent from a solution of the compounds. The crystal structure of the films was studied by X-ray diffraction study. But, any peak is not observed in the X-ray pattern. This confirmed that the films have amorphous structure. The thicknesses of the films were determined as about 1 μm using spectroscopic ellipsometry technique.

The optical constants (refractive index, extinction coefficient, dielectric constant etc.) of the films were obtained from the method of calculation in Ref. [6]. The errors in the calculated of n, k were respectively obtained as ±1.5% and 1.1% by taking into account the experimental error in measuring the film thickness to be 1.7% and in Texp and Rexp to be ±1.1%. UV–vis spectra of the films were recorded at room temperature using a Shimadzu UV 2100 spectrophotometer. The chemical formulas of the synthesized complexes are expressed as $NiHLCl_2.2H_2O$, $[Co(L)_2Cl]_n$, $CuLClH_2O$, $ZnHLCl_2$.

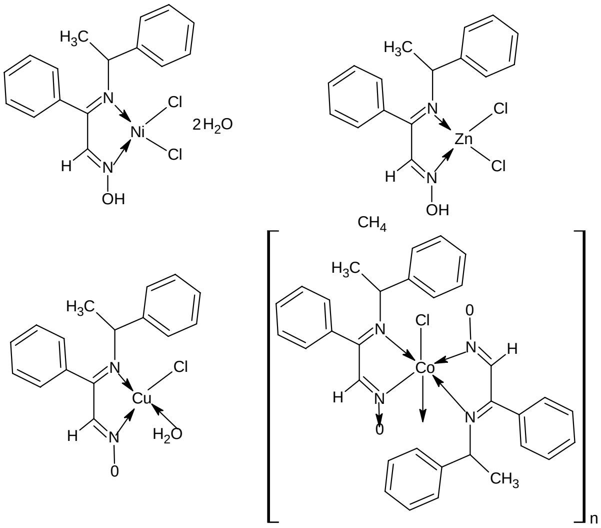

Fig. 1. The chemical structure of the compounds

2.3 Atomic Force Microscopy

Topography of the sample surface was imaged by an AFM manufactured by Nanomagnetics Instruments Co. The AFM was operated in tapping mode at the room temperature. Aluminum coated silicon probes manufactured by Nanosensors were used for tapping. The technical specifications of the silicon AFM probe were such as: resistivity, 0.01-0.02 Ωcm; resonance frequency, 204-497 kHz; thickness, 4.0 μm; length, 125 μm; width, 30 μm; force constant, 10-15 μm. The resonance frequency for imaging was 298.4 kHz.

The AFM images are typically quantified by three numbers at the microscopic scale: the mean roughness, RMS value and *z* scale. The mean roughness, R_a of an AFM image is defined as [7].

$$R_a = \frac{\sum_{i=1}^{N} \left| h_i - \bar{h} \right|}{N} \tag{1}$$

where h_i indicates the surface roughness data at the point *i*, $\bar{h}$ is the mean surface roughness, and *N* is the number of data points for the image. The simplest and most common method used for the observation of changes in surface topography is called the root mean square (RMS) roughness calculation (R_q). The image RMS, R_q is the root mean square average of the height deviations taken from the mean data plane and is expressed as [7]

$$R_q = \sqrt{\frac{\sum_{i=1}^{N} \left| h_i - \bar{h} \right|^2}{N}} \tag{2}$$

The *z* scale gives the vertical distance between the highest and the lowest point of the image.

3. Result and discussion

3.1 The refractive index and extinction coefficient of the films

Fig. 2 and 3 show the reflectance R and transmittance T spectra of the films in the UV–visible range. The optical constants (the refractive index n and extinction coefficient k) were calculated from R and T spectra of the films [8]. The complex refractive index is expressed as,

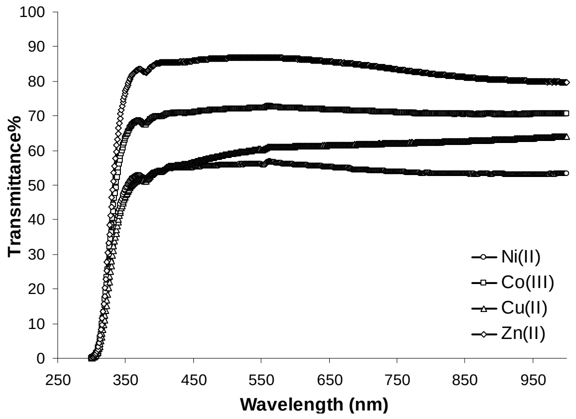

Fig. 2. The transmittance spectra of the films.

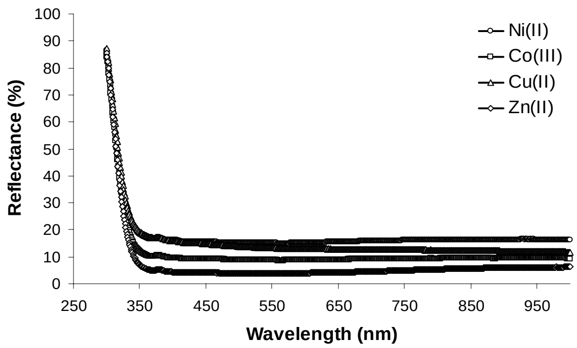

Fig. 3. The reflectance spectra of the films.

$$n^*(\lambda) = n(\lambda) + ik(\lambda) \tag{3}$$

where n is the refractive index and k is the extinction coefficient. The refractive index and extinction coefficient of the films were obtained from the method of calculation in literature [6]. The refractive index dependence of the wavelength is shown in Fig. 4. It is seen that the refractive index decreases with increasing wavelength. The spectra curves for k values are given in Fig. 5, in which k values decreases with increasing wavelength. It is evaluated that the metal coordination in the films is dominant on k values.

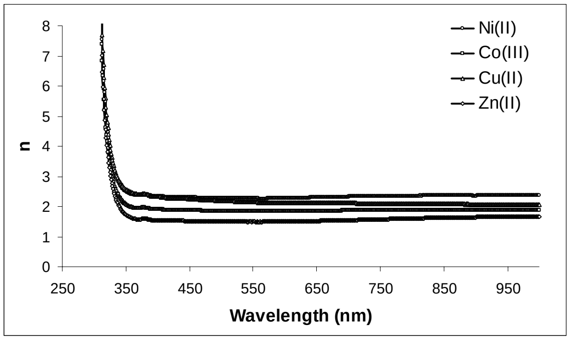

Fig. 4. The variation of refractive index with wavelength.

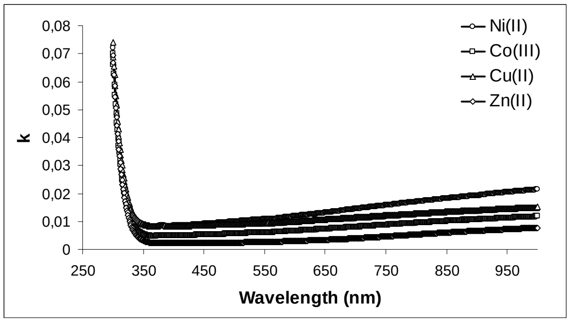

Fig. 5. The variation of extinction coefficient with wavelength.

3.2 Dielectric function of the films

It is well known that polarizabiltiy of any solid is proportional to its dielectric constant. The real and imaginary parts of the complex dielectric constant are expressed as [9],

$$\varepsilon_1 = n^2 - k^2, \varepsilon_2 = 2nk \tag{4}$$

where ε_1 is the real part and ε_2 is the imaginary part ofthe dielectric constant. The real and imaginary parts of the dielectric constant were calculated by using n and k values calculated via Eq. (4) and are shown in Fig. 6 (a) and (b). The dielectric properties of the films change with refractive index. ε_1 is characterized by a sharp increase associated with the valence band to conduction band transition.

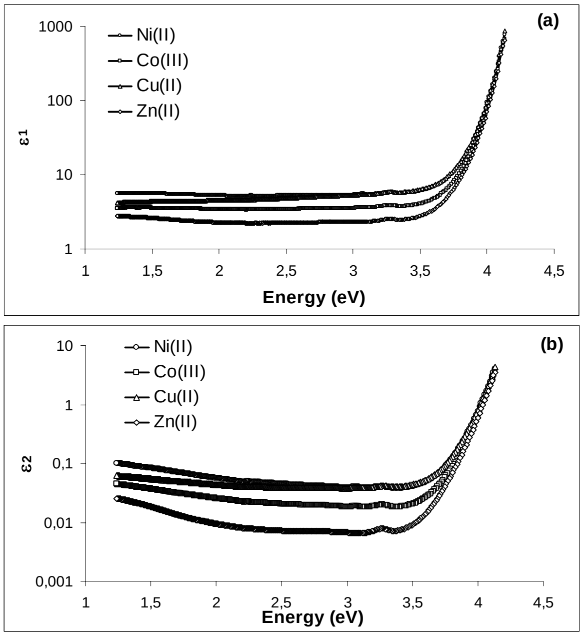

Fig. 6. The variation of real and imaginary parts of the dielectric constant with energy.

3.3 Absorption edge of the films

As known, the valuable information about optical band gap is provided by study of fundamental absorption edge. In the absorption process, a photon excites an electron from a lower to a higher energy state which is called an absorption edge. The absorption coefficient was obtained from the transmittance and reflectance spectra of the films (Fig. 2 and 3) using relationship [9],

$$\alpha = \frac{1}{t}\ln\frac{T}{(1-R)^2} \tag{5}$$

where t is thickness of the film. Absorption in these films occurs by excitation of electrons from the filled states to empty ones. The optical absorption edge was analyzed by the following relationship [10],

$$\alpha h\nu = A(h\nu - E_g)^m \tag{6}$$

where A is a constant, m value is respectively 1/2 and 2 for direct and indirect transitions and E_g is the optical band gap. In order to determine optical band gap of the films, we applied the models for both direct and indirect transitions. For this, the $(\alpha h\nu)^2$ (direct transitions) and $(\alpha h\nu)^{1/2}$ (indirect transitions) vs hν were plotted. From these results, it was concluded that the absorption in the films corresponds to a direct energy gap. The plots for direct transitions are shown in Fig. 7(a)–(d). The linear portion of the plots at the absorption edge confirms that the thin film has a direct optical band gap. The E_g values were obtained by extrapolating the linear portions of the plots to intercept the photon energy axis and calculated E_g values are given in Table 1.

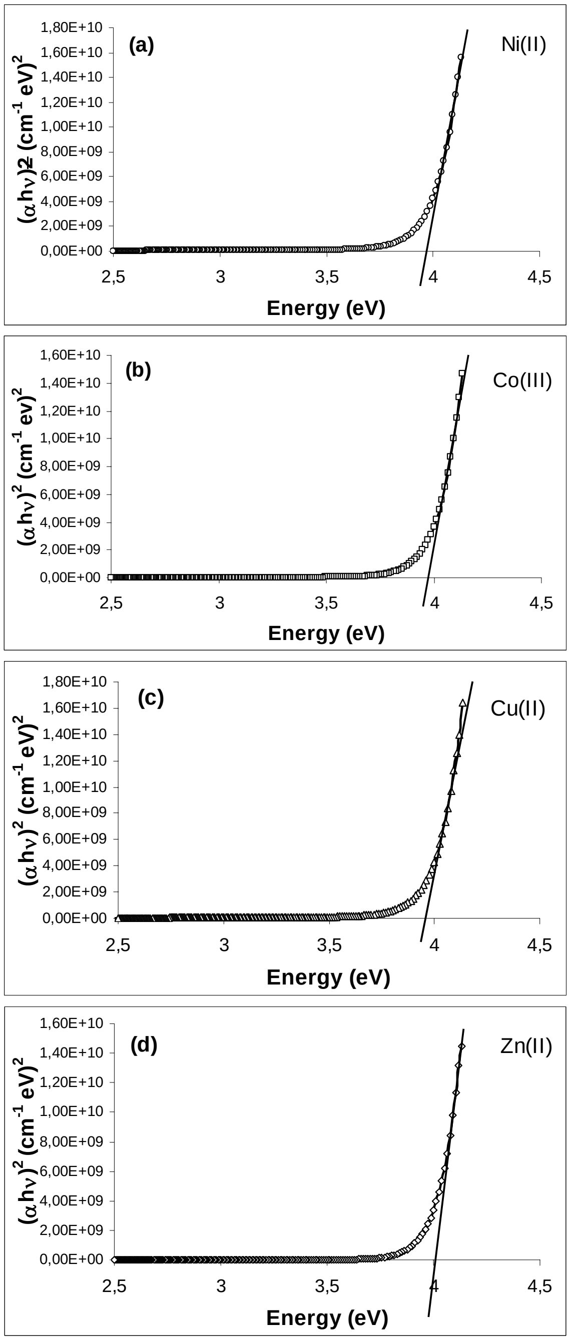

Fig. 7. The $(\alpha h\nu)^2$ vs photon energy plots of the films: (a) $NiHLCl_2.2H_2O$, (b) $[Co(L)_2Cl]_n$, (c) $CuLClH_2O$ and (d) $ZnHLCl_2$.

Table 1. The optical parameters of the films

Film	E_g (eV)	E_0 (meV)
$NiHLCl_2.2H_2O$	3.88	242
$[Co(L)_2Cl]_n$	3.91	193
$CuLClH_2O$	3.86	232
$ZnHLCl_2$	4.00	164

3.4 Urbach spectral tail in the films

The absorption tail of the complexes was investigated in the energy range studied. The spectral dependence of the absorption coefficient α was studied at photon energies less than the energy gap of the complexes i.e. in the region of the so-called Urbach spectral tail, where the absorption coefficient a falls off exponentially for decreasing photon energy E, and it is expressed as [11],

$$\alpha = \alpha_0 \exp(E/E_0) \tag{7}$$

where E_u is the Urbach energy. The Urbach parameter value was also calculated from the slopes of the linear relationship lnα against hν, using eq. (8) [12]

$$E_0 = [\frac{d(\ln\alpha)}{d(h\nu)}]^{-1} = \frac{1}{tg\alpha} \tag{8}$$

The ln(α) vs. hm plots of the films are shown in Fig. 8. Urbach energy was calculated from the reciprocal gradient of the linear portion of these curves and is given in Table 1.

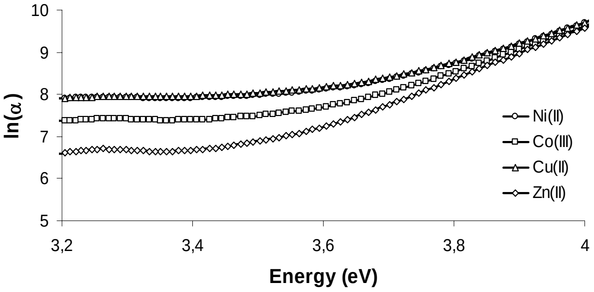

Fig. 8. The ln(α) vs energy plot of the films

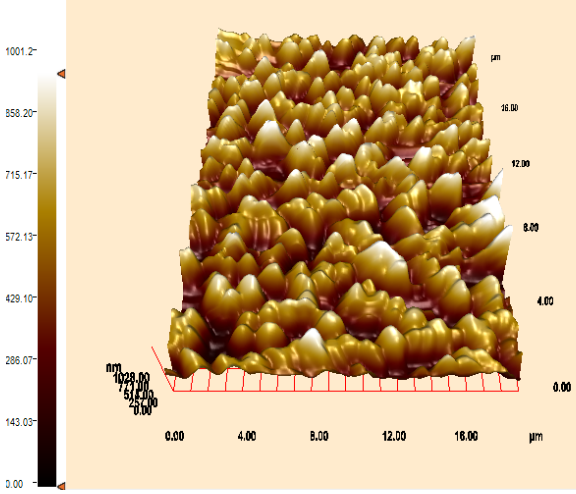

Fig. 9. 3D AFM image of organic thin film.

Fig. 9 shows a 3D AFM topography image for organic sample from an area of 20x20 µm^2. The following conclusions can be drawn from AFM study: AFM image has revealed coating is homogeneous. The big and small pieces have been observed on the surface. The RMS roughness, R_q, is 237.8, while the mean roughness, R_a, of the sample is measured as 195.5 within the area of 20x20 µm^2. The z scale value is found to be 1028. These roughness values have clearly shown the coating process to be successful.

4. Conclusions

The optical constants (refractive index n, extinction coefficient k and dielectric constant) of the complexes were analyzed from the transmittance and reflectance spectra. The spectral dependence of the optical constants indicate that both refractive index and extinction coefficient increases with photon energy. The optical band gaps which turned out to depend significantly on the metal coordination were calculated by optical absorption method. Type of optical transition responsible for optical absorption was direct transitions. It is observed that E_g values do not show any certain trend according to atomic number of the metal ion, in which the atomic number follows order of Co(II) < Ni(II) < Cu(II) < Zn(II).

Acknowledgement

This work was supported by the Research Fund of the Uludag University Project number: F-2009/44. The authors would like to thank for this support.

References

[1] A. Cukurovali, I. Yilmaz, Polish J. Chem., **74**(1), 147 (2000).
[2] A.E. Liberta, D.X. West, Biometals **5**(2), 121 (1992).
[3] L. Coghi, A.M. Lanfredi, A. Tiripicchio, J. Chem. Soc. Perk. Trans. 2 (15) (1976) 1808.
[4] F. Yakuphanoglu, Ph.D. Thesis, Firat University, Elazig, Turkey, 2002.
[5] Y. Kaya, G.Irez and H.Mutlu, Assian Journal of Chemistry, 2009, in pres.
[6] J. Rodriguez, M. Gomez, J. Ederth, G. A. Niklason, C.G. Granqvist, Thin Solid Films **365**, 119 (2000).
[7] Digital Instruments, Command Reference Manual, 2001.
[8] T. S. Moss, Semiconductor Optoelectronics, Butterworths, London, 1973.
[9] N. Chopra, A. Mansingh, G. K. Chadha, J. NonCryst. Solids **126**, 194 (1999).
[10] N. F. Mott, E. A. Davis, Electronic Process in Non-Crystalline Materials, Calendron Press, Oxford, 1979.
[11] F. Urbach, Phys. Rev. **92**, 1324 (1953).
[12] A. A. Taysioglu, K. Erturk, M. C. Haciismailoglu, N. Derebasi, J. Optoelectron. Adv. Mater. **10**, 356 (2008).

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