Surface characterization and optical properties of the complexes of oxi-imino alcohol ligand

A. ASLI KAYA*
Department of Physics, Arts and Sciences Faculty, Uludag University, 16059 Gorukle-Bursa, Turkey

The optical constants (refractive index, n; extinction coefficient, k and dielectric constant, ε) of the complexes of oxi-imino alcohol ligand are determined using reflectance and transmittance spectra. Analysis of the basis absorption spectra is also carried out to determine optical band gap (E_g) and Urbach parameter (E_0). The optical absorption studies reveal that the transition is direct with band gap energy values are calculated. The optical band gaps, film thickness and Urbach parameters are approximately found 3.9 - 4.0 eV, 1μm and the range of 0.210-0.657 eV, respectively.

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1. Introduction

Recently, there has been an increasing interest in organic thin film materials according to their extensive applications in the fields of mechanics, flexible electronics and optics [1, 2]. Optoelectronics is the area in which organic films and organic-inorganic nanostructures have found their main applications in the last decade. Organic-inorganic composites represent a very interesting class of materials with great potential in optoelectronics applications. The unique features of these materials related to the phase interpenetration can be used in electronic and optoelectronic devices [3]. These organic thin films have been also used in a wide variety of applications such as Schottky diodes, solid state devices and optical sensors. There has been considerable concern with the chemistry of Schiff base compounds containing oxime and alcohol and their metal complexes due to their biological activities [4].

A Schiff base (or azomethine), named after Hugo Schiff, is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, but not hydrogen [5]. The study of optical properties such as absorption of metal complexes has proved to be very beneficial for explanation of the structure of these materials. The data transmittance and reflectance can be analyzed to determine optical constants such as refractive index, absorption index and dielectric constant [6].

This paper is concentrated on the preparation of a oxi-imino alcohol ligand and its Cu(II), Zn(II), Co(II) and Ni(II) complexes, and also their optical band gap, the optical constants such as refractive index, extinction coefficient and dielectric constant are investigated.

2. Experimental measurements

2.1. Synthesis of the complexes

All of the complexes were prepared by the reported procedure [7]. The chemical structures of the complexes are given in Fig. 1.

2.2. Preparation of the films

The solution of the films was homogenized for 5 h and 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 etc.) of the films were obtained from the method of calculation in Ref. [6, 11-13]. UV-Vis spectra were recorded between 190 and 900 nm wavelength using Ati-Unicam UV2 UV-Vis spectrophotometer at room temperature.

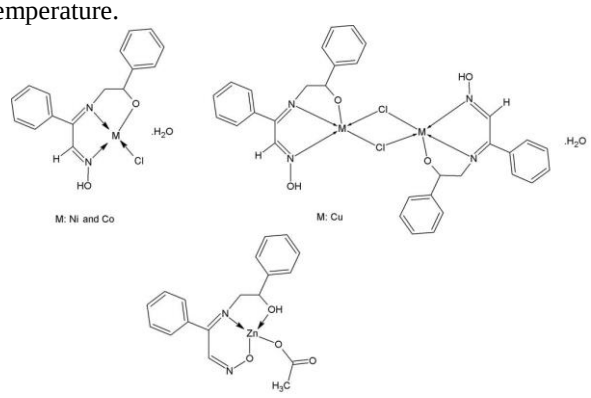


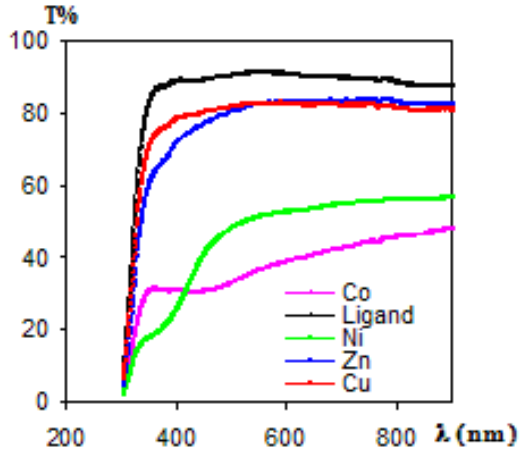
Fig. 1. The chemical structure of the compounds.

3. Result and discussion

The optical transmission and optical reflection values were obtained from Fig. 2. The measured transmittance (T) was used to calculate approximately the absorption coefficient (α) using the relation;

$$A = \frac{1}{d}\ln(\frac{1}{T}) \quad (1)$$

where d is the thickness of the sample.



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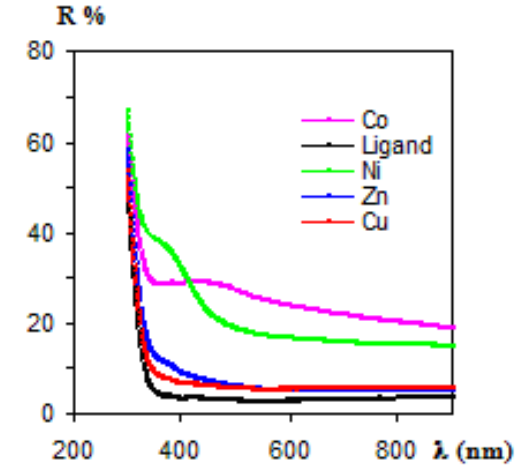

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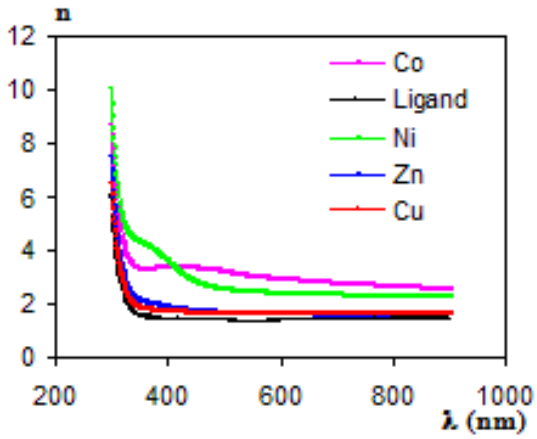
Fig. 2. (a) The transmittance and (b) reflectance spectra of the films.

These films have normally high transmission (%70-90) and low reflection (%5-30) in visible region. Since Ni(II) and Co(II) complexes of the films have high thickness and smooth surface, these values are obtained different from expected values and they are %45 and %35, respectively.

The dispersion plays an important role in the research for optical materials due to a significant factor in optical communication and in designing devices for spectral dispersion. The refractiveness wavelength (n-λ) spectrums for the films are shown in Fig. 3a. It is seen that the refractive index decreases with increasing wavelength. The spectra curves for k values are given in Fig. 3b, in which k values decreases with increasing wavelength. It is evaluated that the metal coordination in the films is dominant on k values. It is shown that these films have also high refractiveness in visible region.



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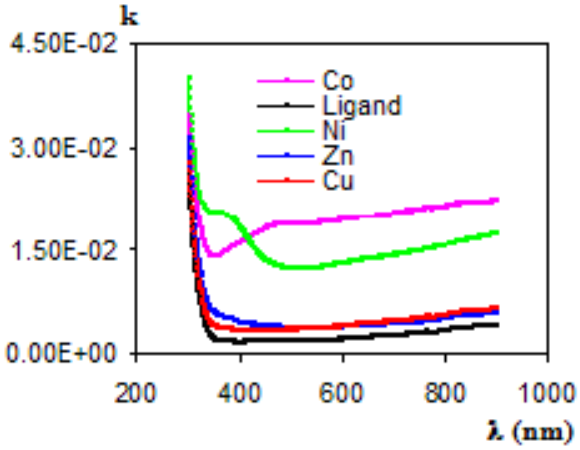

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Fig. 3. The variation of (a) real and (b) imaginary parts of the refractive index with wavelength.

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) versus $h\nu$ were plotted. From these results, it is concluded that the absorption in the films corresponds to a direct energy gap. The plots for direct transitions are shown in Fig. 4. 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 are 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.

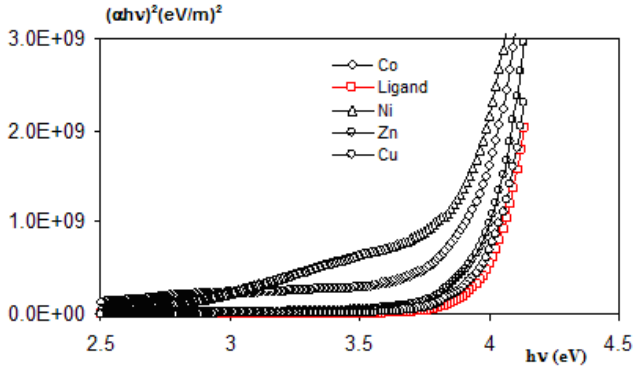


Fig. 4. The basis absorption spectrum of the films.

Table 1. Optical parameters of the films.

Film	E_g (eV)	E_0 (eV)
Ligand	4.030	0.210
Cu (II)	3.980	0.264
Zn (II)	3.950	0.297
Co (II)	3.930	0.497
Ni (II)	3.900	0.657

Fig. 5 shows the $\ln\alpha$ versus $h\nu$ variations for the films. Urbach energy is calculated from the reciprocal gradient of the linear portion of these curves and is given in Table 1. The Urbach parameter value is also calculated from the slopes of the linear relationship $\ln\alpha$ against $h\nu$ using (1) [8-10].

$$E_0 = \left[\frac{d(\ln\alpha)}{d(h\nu)}\right]^{-1} = \frac{1}{tg\alpha} \quad (2)$$

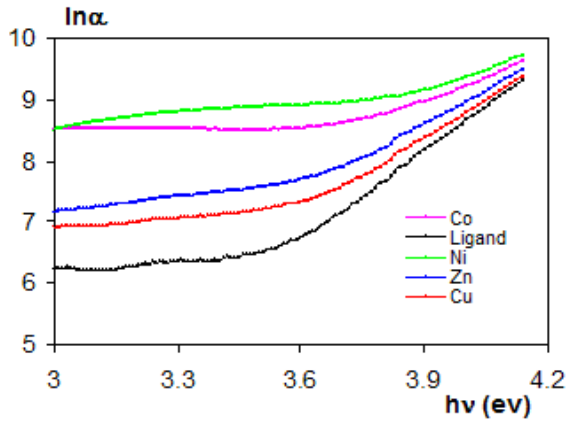
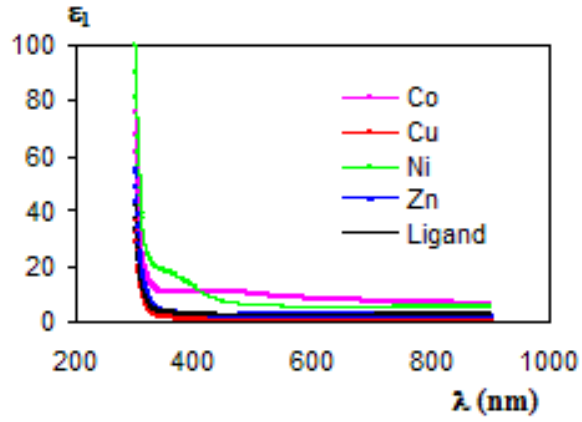


Fig. 5. The variation of $\ln\alpha$ as a function of $h\nu$.

The increasing values of E_0 reveals with the increasing width of the localized states in the optical band gap. The decrease in the band gap can be explained based on the density of states model. The optical band gap decreases with increasing width of the localized states in the optical band gap, i.e., E_g values decrease with increasing E_0. It can be evaluated that when the metal complex is synthesized, the localized energy levels are converted from conduction band to energy band gap or from valence band to energy gap. After formation of the complex, the chemical structure of the complex is changed, the width of the localized levels is expanded and in turn [6].



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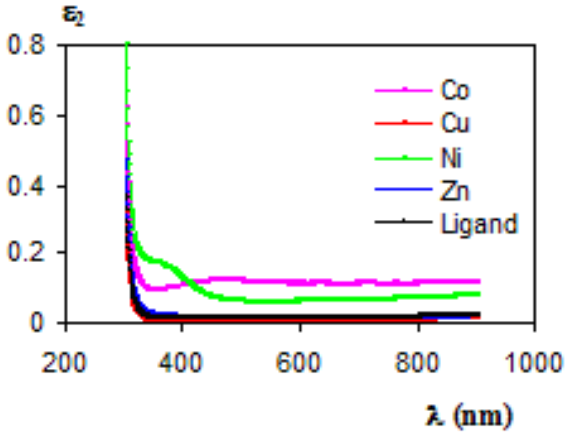

b

Fig. 6. The variation of (a) real and (b) imaginary parts of the dielectric constant with wavelength.

The real and imaginary parts of the dielectric constant of the films are respectively shown in Fig. 6 a and b. It is seen that both ε_1 and ε_2 decreases with increasing wavelength. The real and imaginary parts follow the same pattern and the values of real part are higher than imaginary parts. It is seen from Fig. 6b that there is an additional peak on the spectrum of Ni and Co complexes at about 350 and 450 nm, respectively, however this peak does not exist on the other spectrums. These peaks are associated with the charge transfer between oxi-imino alcohol ligand and complex structure.

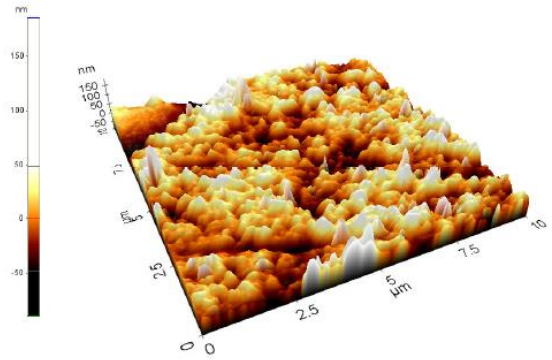

Fig. 7. 3D AFM image of organic thin film of Ni(II) complex.

Fig. 7 shows a 3D AFM topography image for organic sample from an area of 10×10 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. White regions in this figure represent the formation of agglomerated grains one on the top of the other. For these white regions, we think that neighboring grains come together forming large clusters. So, grains in the white regions are larger in size as compared to others. From all of these interpretations, film growth mechanism is thought to be formed firstly layer by layer and then island growth type (mixed growth). Smooth surfaces are very important optical device applications. 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 10×10 μm^2. The *z* scale value is found to be 1028. The rough surfaces are thought to encourage reduction in reflection and trapping of photons within the film due to scattering at the surface [14]. These roughness values have also clearly shown the coating process to be successful.

4. Conclusion

A new oxi-imino alcohol ligand and its complexes (Cu(II), Zn(II), Co(II) and Ni(II)) were synthesized and characterized by optical absorption studies. The optical absorption spectra of the thin films show that the absorption spectra mechanism is direct transition. The complexes of compounds with Cu(II), Zn(II), Co(II) and N (II) cause to decrease on the optical band gap E_g. The optical constants (transmission and refractive indexes, dielectric constant and extinction coefficient) and Urbach energy E_0 are also calculated for the organic thin films.

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*Corresponding author: aslitay@uludag.edu.tr