Synthesis of Copper(II) Schiff Base Complex and Its Mixed Thin Layer with ZnO Nanoparticles

Charles, A.
Research and Development Centre, Bharathiar University, Coimbatore-641 046, Tamil Nadu, INDIA

Sivaraj, K.*[+]
Department of Chemistry, Tamilavel Umamaheswaranar Karanthai Arts College, Thanjavur-613002, Tamil Nadu, INDIA

Krishnaraj, S.
Department of Physics, National Institute of Technology Tiruchirappalli - 620 015, Tamil Nadu, INDIA

ABSTRACT: *Cu(II) complex derived from Synthesis of N-((1H-pyrrol-2-yl)methylene)-4-methoxyaniline Schiff base(PMMA) was studied by UV-Vis, IR spectra, and EDAX. Zinc oxide was synthesized using a simple homogeneous precipitation method with zinc acetate as a starting material. The thin layer of the studied Cu(II) complex was deposited on ZnO/Si(111) substrates by a spin coating method and characterized with scanning electron microscopy (SEM), atomic force microscopy (AFM), and photoluminescence spectroscopy. The SEM images revealed that silicon surfaces are uniformly covered by the Cu(II) complex. AFM micrographs reveal that films are closely packed and granular in nature; the signature of agglomeration of grains is almost absent. For Cu(II) complex/ZnO/Si layer the most intensive fluorescence bands due to intra-ligand transitions were observed between 498 and 520 nm, the quenching of the emission band from ZnO at 360 nm (λex =320 nm) associated with various intrinsic or extrinsic lattice defects was noted.*

KEYWORDS: *Thin layer; ZnO nanoparticles; copper complexes; AFM; SEM.*

INTRODUCTION

Thin organic and organometallic films have attracted research interest due to their technologically important optical and electronic properties [1]. These materials exhibit luminescence; they are used as conductors, semiconductors, Organic Light-Emitting Diodes (OLED), and drug transporters [2,3]. Also many thin films of metal complexes, such as Zn(II), Pt(II), Cu(II), or Ag(I) with Schiff bases were synthesised and their luminescence properties have been employed in organic optoelectronics [4-8]. Some of those films were spin coated or vacuum deposited [9]. ZnO is a candidate photoelectrical nanomaterial for the photocatalysis and degradation of various organic pollutants due to its high sensitivity, high stability, wide bandgap, and environmental friendliness.

** To whom correspondence should be addressed.*
+ E-mail: sivaa25@gmail.com
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Nanomaterials with unique features such as quantum effect and optical behavior render them suitable for biomedical applications [10,11] . In this article, report made how a simple and efficient method as spin coating can be utilized to produce composite films using both nanoparticle dispersions and complex solution. Moreover, the aim of the study was to investigate the microstructural and spectroscopic properties of obtained layer. Therefore, the new copper(II) complex was used as precursor of thin layer in the spin coating technique. In addition, the zinc oxide and the Cu(II) complex layer doped with ZnO nanopowder was obtained. Thin film of synthesized copper complex produced on Si (111) covered with ZnO. Thin film was deposited on Si wafers (8X8 mm) covered with 2 nm thickness of ZnO nanoparticles using spin coating. The morphology and homogeneity of the layers were analyzed by AFM and SEM microscopy, and the photoluminescence and electrical properties of the layers were studied.

EXPERIMENTAL SECTION

Materials and methods

All the chemicals purchased from Merck Chemical Co. and used without further purification.

Preparation of the Copper Complex $[Cu(PMMA)_2]Cl_2.2H_2O$

The complex was produced using the reported procedure [12]. Briefly, an equimolar of pyrrole-2-carbaldehyde (0.01mol) was added into 4-methoxy aniline (0.01mol) in methanol followed by the addition of copper chloride (0.005 mol) in methanol into a 100 mL flask. The mixture was refluxed a temperature of 50°C for 3h. The formed precipitate was then filtered, washed three times with acetone, and dried in a desiccator. The synthesis process shown in Scheme I.

Synthesis of ZnO nanoparticles

In a typical synthesis procedure, $Zn(OOCCH_3)_2 \cdot 2H_2O$ (0.649g, 3mmol) and urea (0.995g, 9mmol) were added to water/EG solution(1:8v/v,75mL)and kept under stirring solutions at 25 ◦C until a homogeneous solution was obtained. The resultant solution was heated to 90 ◦C. The conditions were kept for 1.5 h and then the mixture was cooled to room temperature. The resulting white precipitate was washed and centrifuged at 9000 rpm with water, acetone and ethanol. The film was deposited on Si wafers [3]. Thin film of newly synthesized copper complex produced on Si (111) covered with ZnO. Thin film was deposited on Si wafers (8X8 mm) covered with 2 nm thickness of ZnO nanoparticles using spin coating [3]. For this purpose copper complex was dissolved in DMSO.

Infrared Spectrophotometric Measurement*:* The infrared spectra were recorded in KBr disc on a Shimadzu double beam infrared spectrophotometer and measuring the relative intensity of transmitted light energy versus wave number in the region of 4000-400 cm^{-1}.

The X-ray diffraction (XRD*)* pattern was carried out by a X-ray diffractometer (PANalytical PW 340/60 X'pert PRO) which was operated with Cu Kα (λ = 1.5406 A^0) radiation.

Photoluminescence spectra were recorded using Spectro Fluorometer (Jobin Yvon-FLUROLOG-FL3-11) with Xenon Lamp (450W) as the excitation source of wavelength of 325nm at room temperature.

Scanning Electron Microscope: The synthesized products were characterized using a VEGA3 TESCAN (Czech Republic) Scanning Electron Microscope (SEM) and AFM images were obtained using atomic force microscope (Veeco-di CPII).

RESULTS AND DISCUSSION

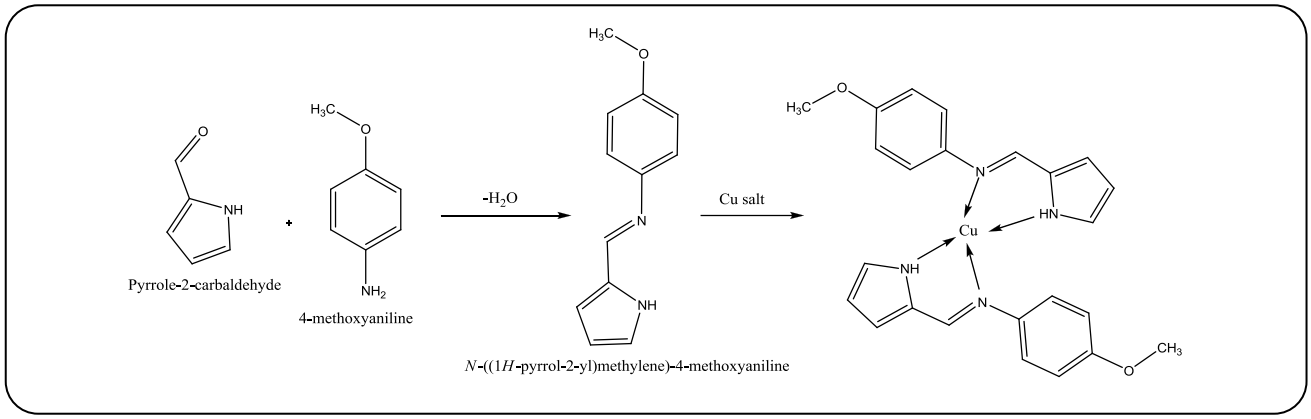
Infrared spectroscopy

The band from stretching vibrations of the -C=N- group, characteristic of the Schiff base, appeared in 1616 cm^{-1} (Fig.1). Significant FTIR bands for copper complex: υ (C=N):1585 cm^{-1}, υ (Cu-N): 441cm^{-1}.The band of ν(C=N) vibrations are shifted to 1585 cm^{-1} (Fig.2) in the spectra of copper(II) complex towards lower frequency, as a result of Cu(II) coordination with the ligand *via* the azomethine group [13].

The copper complex was subjected to energy dispersive X-ray spectroscopy (EDX) analysis to confirm the composition of the complex. The results by EDX have indicated that there were chloride, carbon, oxygen and copper peaks. The EDX spectra (Fig.3) confirm the elemental composition of copper and carbon. Table 1 shows EDX analysis of copper complex.

XRD

Fig.4 shows the diffraction pattern of the film. The x-axis 2 theta corresponds to the angular position of the detector that rotates around the sample. The peaks occur at



Scheme I : Synthesis of N-((1H-pyrrol-2-yl)methylene)-4-methoxyaniline Schiff base(PMMA) and its copper complex $[Cu(PMMA)_2]Cl_2.2H_2O$.

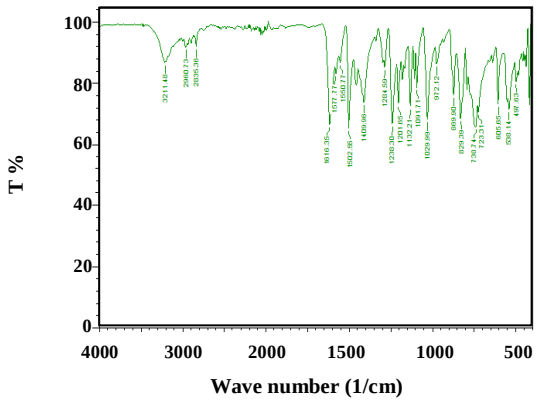


Fig. 1: IR spectrum of N-((1H-pyrrol-2-yl)methylene)-4-methoxyaniline(PMMA) Schiff base.

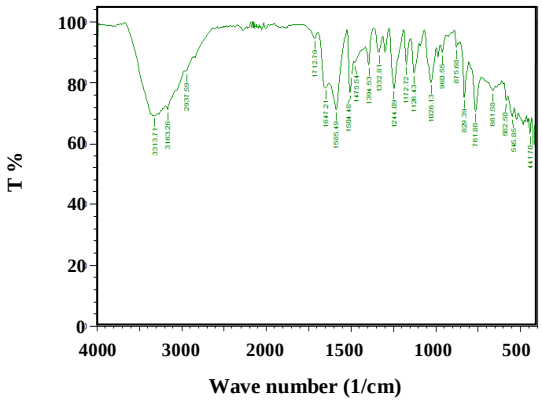


Fig. 2: IR spectrum of copper complex $[Cu(PMMA)_2]Cl_2.2H_2O$.

2θ=34.42° and 36.7° which are attributed to the (002) and (101) planes, respectively, and it is compared with the JCPDS standard value 34.42º, indicating a wurtzite structure of thin film , which belong to the hexagonal.

Experimentally obtained diffraction pattern of the sample is compared with 'Joint Council Powder Diffraction (JCPDS)' data for Standards. This gives information of different crystallographic phases, the relative abundance and preferred orientations. The profiles of the XRD structure reveal that the growth of the film is along the c-axis oriented with hexagonal wurtzite structure. In associated with the ZnO (002) plane structure other peaks (101) were present. The Texture Coefficient (TC) of the doped ZnO thin film corresponding to the preferential oriented plane (002) is calculated using the following Equation.

$$TC_{(hkl)} = \frac{I_{(002)} / I_{o(002)}}{1/N\left[\sum_{N} I_{(hkl)} / I_{o(hkl)}\right]}$$

Where I(002) and I_o(002) are the measured and the standard relative intensity (JCPDS: 36-1451) values of the (002) plane, I(hkl) and I_o(hkl) are the measured relative intensity and standard relative intensity of the hkl plane respectively and N is the number of the diffraction peaks. TC value suggesting a monotonically degradation in the crystalline quality of the film due to doping.

SEM

The SEM images revealed that silicon surfaces are uniformly covered by the Cu(II) complex. The layers were amorphous, but small crystallites appeared in some places due to incomplete solidification of the complex solution

Table 1: Energy dispersive X-ray spectroscopy (EDX) analysis of copper complex.

Element	Weight %	Atomic %	Error %
C K	46.23	60.06	8.74
O K	35.61	34.73	9.82
Cu L	14.3	3.51	7.78
Cl K	3.86	1.7	19.54

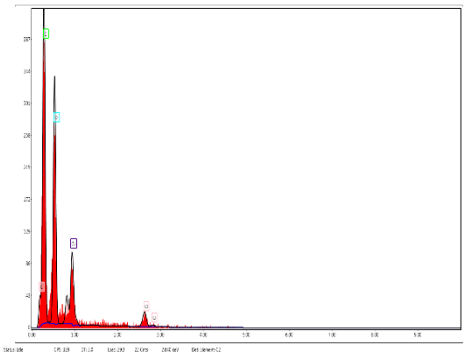


Fig. 3: EDX spectrum of copper complex [Cu(PMMA)$_2$]Cl$_2$.2H$_2$O.

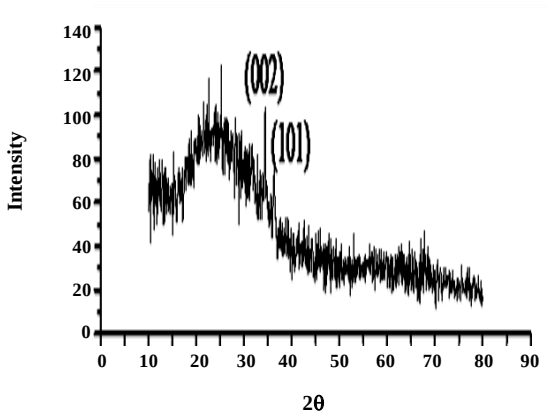


Fig. 4: XRD pattern of mixed thin film.

during the spin coating process, The layers are amorphous, but sporadically crystalline structures appeared. The dimensions of these crystallites ranged from 0.07 to 0.19 μm (Fig.5).

Photoluminescence

Photoluminescence spectroscopy is an important tool to study the optical properties of semiconducting materials. It is known that ZnO nanoparticles and the Schiff bases exhibit photoluminescence (PL) [15,16] and have varied optical applications [17]. In the PL spectrum, typically there are emission bands in the UV and Visible regions [18]. Fig.6 shows the photoluminescence spectra of the thin layer deposited at a temperature of 250^{o}C recorded at room temperature with an excitation wavelength of 325nm. The PL spectrum of thin film excited at 325 nm showed two UV emission bands at 360nm and 380nm (Fig. 6). The emission peak at 360nm may be attributed to the band gap luminescence as it is blue shifted compared to the optical absorption. The near-band edge (NBE) emission peak at 380nm is assigned to the recombination of free excitants [19]. A blue band nearly 498nm were observed, and a peak around 520 nm was also observed no exact green emission was detected (Fig.6), which shows the stoichiometrical nature of obtained film. It is accepted generally that the near UV emission of ZnO film is closely related to the exciton transition from the localized level below the conduction band to the valence band. The formation of this localized level is related to the breaking of lattice periodicity, which often originated from the free impurity atoms, various defects, surface and interface.

The broad blue emission band at 498 nm is generally attributed to the radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy. It is known that the PL emission is caused by the recombination of excited electrons and holes, and the lower PL intensity may indicate the lower recombination rate of electrons and holes under light irradiation. The PL intensity is highest, indicating the highest recombination of electrons and holes [20,21].

The band gap is identified as being of charge-transfer origin rather than arising from $d \rightarrow d$ transitions [11]. The energy band gap can be determined from the photoluminescence spectrum. The E_g for the ZnO thin film is calculated by using the following relation

$$E_g = \frac{1240}{\lambda\,(nm)}$$

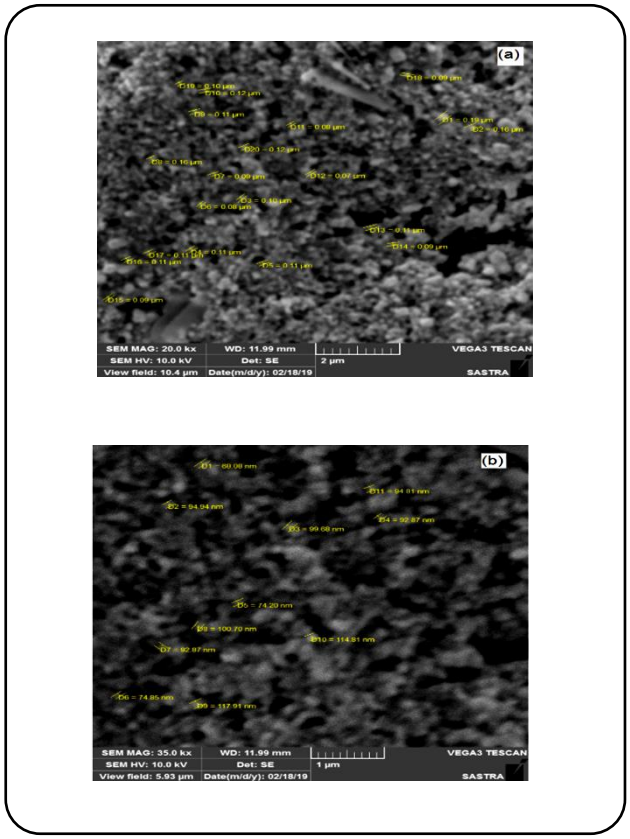


Fig. 5: SEM images of mixed thin film at different magnifications (a) 2 µm (b) 1 µm.

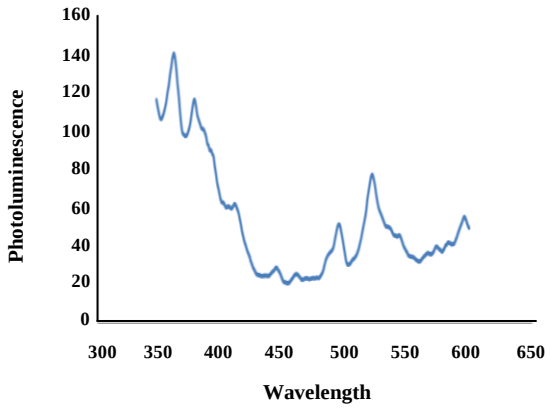


Fig. 6: Photoluminescence spectra of mixed thin film.

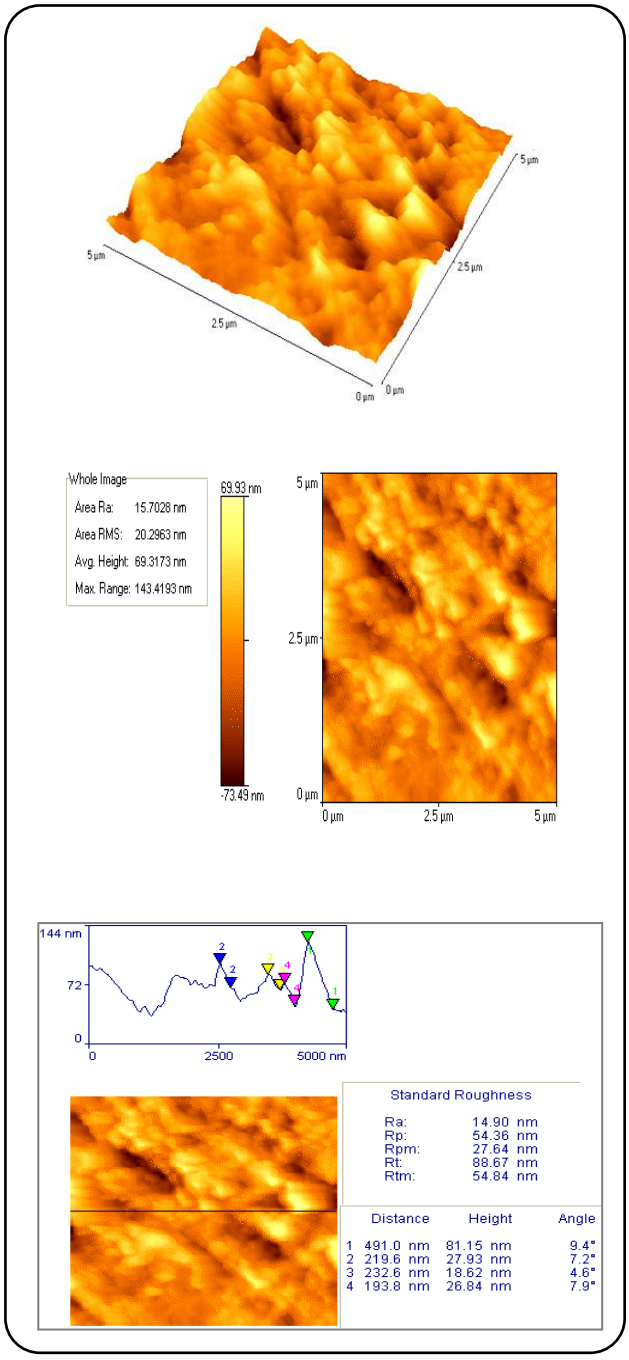


Fig.7: AFM images of Cu complex/ZnO/Si film (5 × 5µm) (a) 3D images, (b) 2D images (c) Section analysis.

The energy gap for the wavelengths 360 nm and 520 nm of the PL spectrum are found to be 3.44eV and 2.38eV respectively.

Atomic Force Microscopy

AFM measurement performed to study the surface morphology of the copper complex ZnO/Si layer. Fig 7 shows the 2D & 3D AFM images of the film for (5µm × 5µm). Micrographs reveal that films are closely packed and granular in nature; signature of agglomeration of grains is almost absent. AFM images have also been utilized to estimate the grain size of the samples. Uniform brightness contrast exhibits absence of impurities or clusters .

It is found that the average roughness of the film is 14.90 nm and the maximum profile peak height is 54.36 nm.

Electrical properties

Electrical measurement was carried out for Cu/ZnO/Si thin film using the four-probe method. The Electrical sheet resistance (R_{sh}) and Resistivity of the thin film was calculated. The sheet resistance (R_{sh}) and resistivity (ρ) of the film are 231.58×10^{2}(Ω/Cm) and 440×10^{-4}(ΩCm) and respectively.

CONCLUSIONS

The characterization studies include X-Ray Diffraction (XRD), optical studies, and Atomic Force Microscopy (AFM). The result of XRD clearly reveals polycrystalline nature of ZnO film with hexagonal wurtizite structure and (002) preferential orientation. The grain size was computed to be in the nm range. The developed films have a direct bandgap value of 3.2eV which is close to the reported value 3.37eV from the literature. The characterization studies confirm the suitability of deposited ZnO thin films for using them in optoelectronic devices and solar cells.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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