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Effect of illumination intensity on the characteristics of $Cu(acac)_2$/n-Si photodiode

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ABSTRACT

Thermally evaporated copper (II) acetylacetonate $Cu(acac)_2$ thin film deposited on the n-Si wafer was used for light detection. The microstructural properties of copper (II) acetylacetonate thin film were investigated using high-resolution transmission electron microscope technique. A polycrystalline nature of $Cu(acac)_2$ film with a clearly resolved lattice fringes were obtained. The optical properties of the thin film deposited on an n-type silicon substrate were investigated using spectroscopic ellipsometry technique which suggested UV and visible light absorption of copper (II) acetylacetonate. The *I-V* characteristics of the fabricated photodiode were investigated in dark and under different light illumination intensities. The main diode parameters were determined using the Thermionic emission theory and modified Norde's method. The present architecture showed a good response to halogen lamb light, where the estimated values of rise and fall time at 80 mW/cm^2 were about 339 ms and 1046 ms, respectively. Furthermore, *C-V* measurements for the fabricated device were performed in dark at different frequencies.

1. Introduction

Today, there are significant experimental and theoretical interests focusing on the different types of organic photodiodes with response in UV or/and visible light [1–4]. Ultraviolet or/and visible light photodiodes have a wide range of applications starting from the daily used electronics such as smoke detectors, remote control and compact disc players [5]. Furthermore; there are highly sophisticated applications such as space research [5,6], optical communications [5–7] optical surveillance [8], military applications [7,9], nanoscopy imaging [10], biological and environmental research [5,8–10]. Multi-spectral photodetectors comprising a material of wide bandgap deposited on silicon substrate achieved a high spectral selectivity, low noise signal and high sensitivity [10–12].

Recently, organometal complexes have emerged as promising candidate materials in optoelectronic applications especially in photodetection. This interest is owing to their excellent optical and electrical properties and compatibility with flexible substrates [10–12]. Among all organometal complexes, there is an interesting family known as acetylacetonate complexes. Transition metal acetylacetonate complexes shined in the sky of optoelectronic applications field due to their unique properties [13]. Metal acetylacetonates are used as catalysts [13–17] and fillers in polymer industries [13,18,19]. Metal acetylacetonates often play an important role in improving the efficiency and performance of perovskite solar cells [13,20–24], polymer solar cells [13,25–27] and redox flow batteries [13,28]. Moreover; metal acetylacetonates were used in gas and organic vapor sensing [29–32]. Copper (II) acetylacetonate, Cu(acac)2, can be considered as one of the most stable transition metal complexes [13,33] with a square planar structure. Although copper (II) acetylacetonate was exploited in many photovoltaic applications [34,35], oxygen pressure sensing [36], the low-k dielectric material in ICs and microelectronics technology [37], there is no reported study on investment the wide band gap of this complex in light detection applications. According to the rapid progress in optoelectronics technology and with the emergence of new nanofabrication techniques, many forms of photodetectors were presented. The production availability of copper (II) acetylacetonate elastic single crystal [38] opens the way toward exploitation of this complex in flexible dual-band photodetection applications to follow the technological progress.

In this report, our strategy is to study the possibility of using copper (II) acetylacetonate in a heterojunction structure with the n-type silicon substrate for light detection. The performance evaluation of copper (II) acetylacetonate / n-Si heterojunction as a photodiode passed through three stages. The first stage was studying the microstructural properties of $Cu(acac)_2$ thin film using HRTEM. The second stage was evaluating

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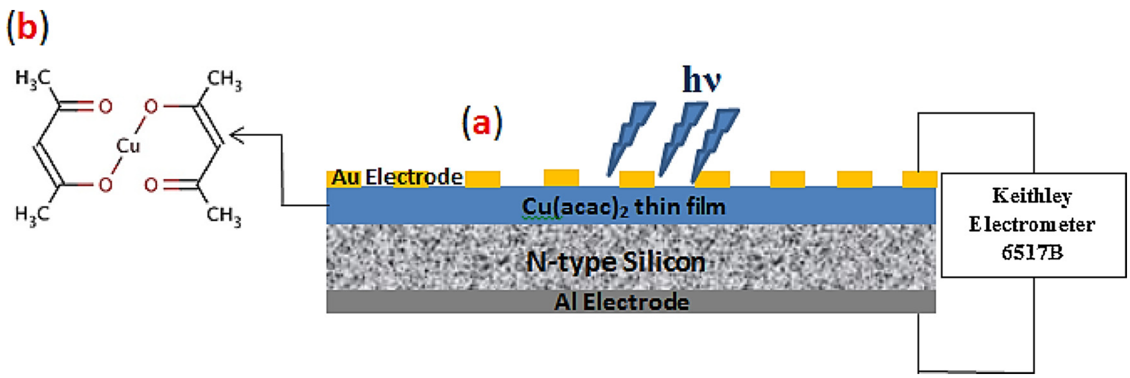

Fig. 1. **(a)** Schematic diagram of the fabricated device and (**b**) molecular structure of $Cu(acac)_2$.

the optical properties of $Cu(acac)_2$ thin film on an n-Si substrate using spectrometric ellipsometry. Finally, the electrical characteristics of the prepared prototype were investigated under white light illumination.

2. Experimental procedures

2.1. Device manufacture

Copper (II) acetylacetonate ($C_{10}H_{14}CuO_4$) of a chemical structure shown in Fig.1 is our raw material. Cu $(acac)_2$ is a blue powder of molecular weight 261.76 g/mol and purity 99.9% purchased from Sigma-Aldrich Company. A thin film of $Cu(acac)_2$ with 200 nm thickness was deposited through thermal vapor deposition technique using a coating unit model (Edwards, E-306 A, England). The deposition process was performed at vacuum pressure 1×10^{-5} mbar and room temperature. The $Cu(acac)_2$ thin film was deposited on chemically pre-etched n-type silicon substrates of orientation [111] and resistivity (8–13 Ω.cm). The deposited film thickness was controlled using the quartz crystal monitor Edward FTM6 model.

The etching process was performed using a CP4 etching solution (1HF: $6HNO_3$:1 CH_3COOH) for 10 s followed by immersion of Si substrates in water and alcohol for 3 min. Hence, a 50 nm-thick gold top electrode was deposited on $Cu(acac)_2$ thin film using a shadow mask in the form of a mesh. Finally, a thick aluminum rear electrode of thickness 400 nm was deposited on the back side of Si. Fig.1 shows the schematic diagram of the fabricated device.

2.2. Characterization techniques

The microstructural properties of $Cu(acac)_2$ thin film were investigated by using a high-resolution transmission electron microscope, HRTEM; model JEOL-JEM-HR-2100 with accelerating voltage 200 KV. The films deposited on a carbon grid to be suitable for TEM observation without any further thinning procedure. The plane view of all films was recorded at different magnifications. The obtained TEM images were in DM3 format and were analyzed using *Image.J* software. The optical properties of $Cu(acac)_2$ thermally evaporated thin film deposited on an n-type silicon substrate were investigated using spectroscopic ellipsometry. Spectroscopic ellipsometry (SE) measurements were performed using J.A. Woollam variable angle spectroscopic ellipsometer (VASE) M-2000. The measurement process was carried out at room temperature and atmospheric pressure at multi-incidence angle 50°, 55° and 60° over wavelength ranges from 190 nm to 1690 nm. The measured values of the relative amplitude and phase angle were analyzed using *Complete EASE Data Analysis* Software version 4.29 by *J. A. Woollam Co., Inc.*

The Photoelectrical properties of the fabricated Au/$Cu(acac)_2$/n-Si/Al diode were investigated by measuring the *I-V* characteristic curve using a Keithley electrometer model 6517B. The measurement process was performed at room temperature from -3.5 Vs to + 3.5 Vs under the influence of white light emitted from 150 W halogen lamb. The intensity of incident light was measured using Radiometer / Photometer model IL1400 A. The capacitance-voltage characteristics of the fabricated photodiode were investigated under dark conditions at different frequencies in forward and reverse biasing using HIOKI 3531-Hi-tester LCR meter.

3. Results and discussion

3.1. Microstructural properties of $Cu(acac)_2$ thin film

Fig. 2 shows the HRTEM micrograph of as-grown $Cu(acac)_2$ thin film with average crystallite size about 27 nm. The as-grown $Cu(acac)_2$ thin film exhibits a polycrystalline nature due to the clearly resolved lattice fringes shown in Fig. 2. The measured lattice fringes spacing of $Cu(acac)_2$ thin film was about 7.7 Å and 5.7 Å which correspond to ($\bar{1}$ 01) and (200) plane, respectively [39–41]. Further evidence about the polycrystalline nature of $Cu(acac)_2$ film were evaluated from the selected area electron diffraction (SAED) pattern showed in the inset of Fig. 2. The SAED pattern of as-grown $Cu(acac)_2$ thin film confirmed the co-existence of amorphous nature with a crystalline due to the occurrence of distinct and diffused rings [42]. These spotty rings discriminate the polycrystalline nature and the preferential growth in [$\bar{1}$ 01] direction [43]. These two rings mentioned in the SAED pattern of as-grown $Cu(acac)_2$ thin film of 7.78 Å and 5.64 Å were indexed as (101) and (200) planes. The HRTEM results are in agreement with the results of XRD in our previous work on $Cu(acac)_2$ thin films [44].

3.2. Optical properties of $Cu(acac)_2$ thin film

The estimation of optical constants of $Cu(acac)_2$ thin film using spectrometric ellipsometry (SE) depends on the change of polarization state of the reflected beam from the film surface. These changes are represented by the variation of two ellipsometric parameters; the relative amplitude, ψ, and phase angle, Δ, as a function of wavelength. The wavelength and film thickness dependence of $Cu(acac)_2$ optical constants were evaluated in a two-step process. The first step was the fitting of the measured values of $\psi(\lambda)$ and $\Delta(\lambda)$ with a three-layer model (air/organic film/Si), while the second step was the minimization the differences between experimental and calculated values. Starting from the transparent region, the ellipsometric analysis was started using a Cauchy dispersion relation. Extending to the absorption region where Cauchy dispersion relation is not applicable, a combination of Tauc-Lorentzian oscillator model and Gaussian oscillator model was applied [45]. The accurate values of thin film thickness and optical constants resulted from the optimization process within absorbing region were based on the estimated values in the non-absorbing region using Cauchy relation [45–47].

Fig. 3 depicts the wavelength dependence of the measured and optimized values of amplitude ratio, ψ, and phase angle, Δ, for different incidence angles. The calculated values of ψ and Δ were obtained by the