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Plasma impact on structural, morphological and optical properties of copper acetylacetonate thin films

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ABSTRACT

The influence of plasma exposure on structural, morphological and optical properties of copper (II) acetylacetonate thin films deposited by thermal evaporation technique was investigated. Copper (II) acetylacetonate as-grown thin films were exposed to the atmospheric plasma for different times. The exposure of as-grown cu $(acac)_2$ thin film to atmospheric plasma for 5 min modified its structural, morphological and optical properties. The effect of plasma exposure on structure and roughness of cu$(acac)_2$ thin films was evaluated by XRD and AFM techniques, respectively. The XRD results showed an increment in crystallinity due to exposure for 5 min, but, when the exposure time reaches 10 min, the film was transformed to an amorphous state. The AFM results revealed a strong modification of films roughness when the average roughness decreased from 63.35 nm to ~1 nm as a result of interaction with plasma. The optical properties of as-grown and plasma exposured cu $(acac)_2$ thin films were studied using spectrophotometric method. The exposure of cu$(acac)_2$ thin films to plasma produced the indirect energy gap decrease from 3.20 eV to 2.67 eV for 10 min exposure time. The dispersion parameters were evaluated in terms of single oscillator model for as-grown and plasma exposured thin films. The influence of plasma exposure on third order optical susceptibility was studied.

1. Introduction

Transition metal acetylacetonate complexes is a promising class of β-diketones family because the compounds are considered as important components for wide range of electronic applications such as perovskite solar cells [1–5], polymer solar cells [6–8], ICs and microelectronics technology [9].

Surface properties are extremely significant in performance of many optoelectronic and biomedical applications [10–13]. As to film fabrication, one of the most crucial drawbacks of thermal evaporation technique is the existence of different surface defects and surface roughness. Recently, the surface treatment technology achieved a progress in material processing field by modifying surface properties, controlling surface energy, adhesion promotion and enhancement of device performance [14–23].

Through the last decade, there were many surface modification methods such as chemical etching, electron beam, ion beam, ozone treatment, UV treatment, wet chemical treatments and plasma treatments [24–33]. Atmospheric pressure plasma (APP) is one of the most effective methods of surface modification and it is used for fabricating a wide range of materials which can be considered good nominees for high efficiency next generation solar cells [34]. In this work, we use plasma to modify the surface of copper (II) acetylacetonate thin films and investigate the effect of plasma treatment on the structural and optical properties of the films at different time intervals.

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2. Experimental Procedures

2.1. Thin Film Deposition

Copper (II) acetylacetonate ($C_{10}H_{14}CuO_4$), cu$(acac)_2$, of molecular weight 263.78 g/mol is the material under investigation and their chemical structure is shown in Fig. 1. The material was purchased from Sigma-Aldrich Company with purity ≥99.9%. The cu$(acac)_2$ thin films were prepared through thermal vapor deposition technique on flat glass and quartz substrates using coating unit model (Edwards, E-306A, England) at vacuum pressure 1×10^{-5} mbar. The deposition rate and film thickness were monitored using quartz crystal monitor Edward FTM6 model.

2.2. Characterization Techniques

As-grown cu$(acac)_2$ thin films were exposed to plasma at pressure 4 mbar and power 15 W for different durations using the apparatus shown in Fig. 2. Initially, many trials were performed at different times, until material disruption was noticed. Then, two exposure intervals were chosen for the experiment (5 and 10 min). These time

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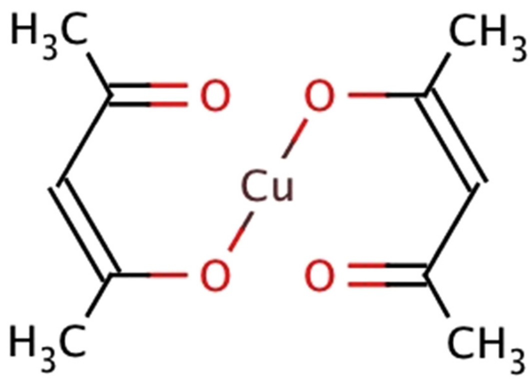

Fig. 1. Molecular structure of copper (II) acetylacetonate.

durations were chosen to represent the point where the maximum crystallinity was achieved (5 min) and the point where film is transformed totally to amorphous (10 min). Below 5 min, there was a monotonic increase in crystallinity and a little decrease in absorption. Hence, these two points were considered as critical points in our study.

The crystal structure characterization of cu(acac)$_2$ thin films was carried out by X-ray diffractometer X'pert pro (Panalytical, Holland) using monochromatized CuK$_{\alpha1}$ ($\lambda = 1.5418$ Å) radiation.

Atomic Force Microscope, AFM, manufactured by Bruker (Model: MLCT-MT-A), was operated in contact mode with nonconductive silicon nitride probe using proscan 1.8 software for controlling the scan parameters. The IP 2.1software was used for image analysis to explore the surface microstructure topology of cu(acac)$_2$ and influence of atmospheric pressure plasma on surface topography. In the study, the scan area was 5×5 μm^2 with 1 Hz scan rate.

The optical properties of as-grown and plasma exposed cu(acac)$_2$ thin films were investigated using transmittance $T(\lambda)$ and reflectance $R(\lambda)$ measurements at normal incidence via JASCO model V-570 UV–vis-NIR double beam spectrophotometer in the spectral range of 200–2500 nm at room temperature.

3. Results and Discussion

3.1. Crystal Structure Characterization

In Fig. 3, it is obvious that the plasma exposure time variation caused a significant change in cu(acac)$_2$ structure. The XRD pattern showed presence of a diffraction peak at 11.44° related to orientation ($\bar{1}01$) and its intensity increases with the exposure time increasing. Besides, a broad hump is evident which emphasizes the formation of mixed phase between amorphous and crystalline natures within the film. When the exposure time reaches 10 min, the film is transformed totally to amorphous phase.

In general, thin film grown by thermal evaporation technique usually contains different surface defects and possesses rough surface. The defect states may be responsible for amorphous phase presence and, so, the as-grown structure may exhibit poorer crystallinity. Upon plasma treatment, these surface defects may be released due to the bombardment of energetic plasma ions, which also induce the recrystallization of cu(acac)$_2$ [35]. The high entropy in amorphous phase region exists in as-grown film and made it a vulnerable toward plasma ions. Hence, through the elastic collisions between plasma ions and cu (acac)$_2$ particles, these particles would be rearranged providing an enhancement in crystallinity [36]. Moreover; crystallinity enhancement and film densification upon plasma treatment were achieved not only from thermal energy induced by plasma but also by the intense electric field around the film, as interpreted previously by Ohsaki et al. [37]. The crystal quality deterioration of 10 min exposured cu(acac)$_2$ thin film may be attributed to crystalline - amorphous transformation due to decomposition of cu(acac)$_2$ molecules leading to CuO formation [38–39]. Previously, many studies were aimed at the investigation of influence of plasma treatment on crystal structures, where mostly the plasma treatment would induce a modification in crystallinity to a definite limit at which the material decomposes [10,37,40–43].

A significant broadening of ($\bar{1}01$) diffraction peak, as shown in the inset of Fig. 3, depicts the crystallite size decrease, as deduced from Scherrer's equation [44]. The average crystallite size decreased from 18.9 nm to 10.4 nm while the microstrain ε was increased from 1.83 $\times 10^{-3}$ to 3.3 $\times 10^{-3}$ for as-grown film and 5 min bombarded film, respectively. The average crystallite size decrease with increasing the exposure time was obtained previously [45–46].

3.2. Surface Morphology and Roughness Characterization

The AFM images of as-grown and plasma treated cu(acac)$_2$ thin films are shown in Fig. 4. An obvious decrease in grain size appeared when the exposure time increases to 5 min, while increasing exposure time to 10 min transformed film to amorphous. These results are consistent with the XRD results. For detailed study of surface roughness, 3D AFM images shown in Fig. 5 were analyzed. The estimated values of roughness parameters such as root mean square roughness, R_q, average roughness, R_a, maximum roughness peak height, R_p, maximum height valley depth, R_v, and peak-valley roughness, R_{p-v} are tabulated in Table 1.

According to the values of root mean square and average roughness, a magnificent enhancement of film roughness was obtained when the film was exposed to plasma for 5 min due to recrystallization of cu (acac)$_2$ film [47] or due to removal of some molecular layers [48]. As the crystallite size decreases, surface morphology density increases and, hence, the film surface becomes smoother [49–51]. A slight increase in all roughness parameter values was observed when exposure time reached 10 min which means that a long exposure time would damage the film surface. The result indicates that, when the exposure

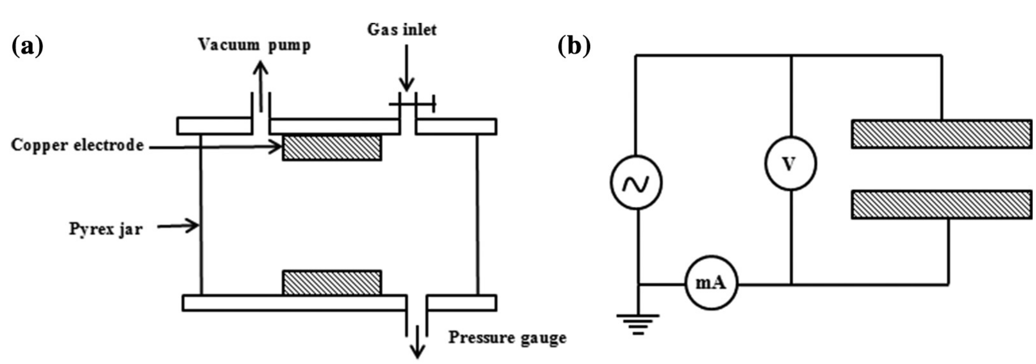

Fig. 2. Schematic diagram of (a) setup of plasma exposure apparatus and (b) electric circuit.