Characteristics of TiO_2-Cu thin films deposited using electrospray technique

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Abstract: In this current research, TiO_2 thin films were deposited on the cleaning p-type silicon substrates via using electrospray technique. Various deposition electric potentials were utilised within the scope of 0–5 kV. To understand potential factors affecting TiO_2-Cu thin films, the structural, morphological, optical characteristics and the surface chemical composition were explored. The X-ray diffraction peaks showed that all TiO_2-Cu samples were composed of multiphase according to the preparation conditions. The prepared films were characterised by the emergence of multiple phases of Ti-O, Cu-O, and Cu-Ti-O systems. Both particle size and porosity of films were affected by the applied electrical potential, where the size was directly proportional to the potential (12.6, 7.6, and 16.3 nm) with free, 3.6 and 4.5 kV

respectively, while dropped with 5 kV to 7.2 nm. The porosity behaved similarly to the size distribution as a function of electric potential, the maximum value of it was 53.55% with 4.5 kV. Also, the thickness of the prepared films was directly proportional to the increased which increased from 0.147 μm with free potential to 3.5 μm with 5 kV. PL spectroscopy was used to analyse the optical properties in order to confirm optical absorption in the visible light field. All prepared films showed highest peaks between 342–344 nm with change in both width and intensity. The results provide insights into the enhanced properties of TiO_2-Cu thin films under different electric potential. According to these properties, the samples at (4.5 kV and 5 kV) are expected to be appropriate to use in gas sensor and bio-sensing applications.

Keywords: TiO_2-Cu; AEP; electrospray; thin film; characteristics; PL spectra.

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1 Introduction

Titanium dioxide (TiO_2) thin films are development semiconductor materials in various applications such as sensors, photo-catalysis, photo-semiconductors in agriculture and solar cells [1–3]. TiO_2 has a wide optical band-gap (3–3.92) eV according to the synthesis conditions [4,5]; it has electrical, optical properties, and fascinating chemistry with three distinct crystalline structures: rutile, anatase, and brookite [6]. TiO_2 can be supported by some metallic nanoparticles (MNPs) such as gold [5], silver [7], platinum (Pt), palladium (Pd) [8], and copper to increase the surface activities [9]. Cu is a possible metal dopant for the photocatalytic mechanism since the addition of Cu will improve the visible light absorption of TiO_2 [10]. Its thin films can be synthesised via several methods such as flame spray, electrochemical (anodisation) oxidation, chemical and physical vapour, sol-gel, hydrothermal, spray pyrolysis [11], electrospinning [12], and atomic layer deposition (ALD), sputtering methods [13]. Although the electrospray has been a long time since it was investigated since the 1960s [14], however, it did not receive attention until the 1990s [15,16]. This technique is appropriate to utilise in several applications such as paint, pesticides, and inks [14]. Recently researchers have turned to use it in the manufacture of organic light-emitting diodes (OLEDs) and small-scale devices [14]. TiO_2 is one of the materials that can be successfully synthesised using this method [14,17,18].

In the recent years some studies on the preparation of TiO_2 nanoparticles (TNPs) and films were performed using electrospray technique. Halimi et al. [19] deposited TiO_2 nanoparticles (TNPs) using electrospray method with 2.1 kV of applied potential. Influence of the counter electrode distance with the deposited droplet size on the substrate was investigated. Li et al. [20] used several compounds include TNPs to detect the distribution of molecules within tissue, they found that TNPs obtained were the thinner than other compounds (less than ~1 μm), and clear matrix crystallinity. Tang and Gomez [21] tested three parameters particle (size and velocity), and solution evaporation to control on the porosity and size distribution of the prepared TiO_2 films via electrospray. In this study, the increasing of the applied potential leads to increase of the film thickness while both size of particles and the deposition area were decreased. Koivisto et al. [22] studied anatase TiO_2-based photoactive coating using the available electrostatic apparatus on surface. Aerosol mass balance modelling has been used to measure the emission and deposited rate of particles. Ag, Cl, and TiO_2 coated with carbon were utilised without observation of spray parameters. In the same year a sol-gel to prepared anatase (TNPs) by Jalvo et al. [23] used as photo-catalytic nanoparticles after were prepared it as surfaces by electrospray technique with 22.3±3.7 mV of positively charged particles on porous and polished substrates. The surfaces bioactivity of the prepared samples depends on the loaded TNPs, and grain size value which ranged between the micro and nano scales [23]. Kashale et al. [24] synthesised Cu-TNPs nanoparticles using green bio-mediate technique with the Bengal gram bean extract.

The resulted Cu-TiO_2 nanoparticles were used as an anode in the Li-ion batteries. That Cu-TiO_2 enhanced structural quality also [24]. This study presents the influence of electric potential on the morphological, structural, and optical characteristics of Cu-TiO_2 thin films prepared using the electrospray method. The characteristics are performed using XRD, FESEM, UV-Vis spectrometer, and photo-luminance (PL) systems.

2 Experimental

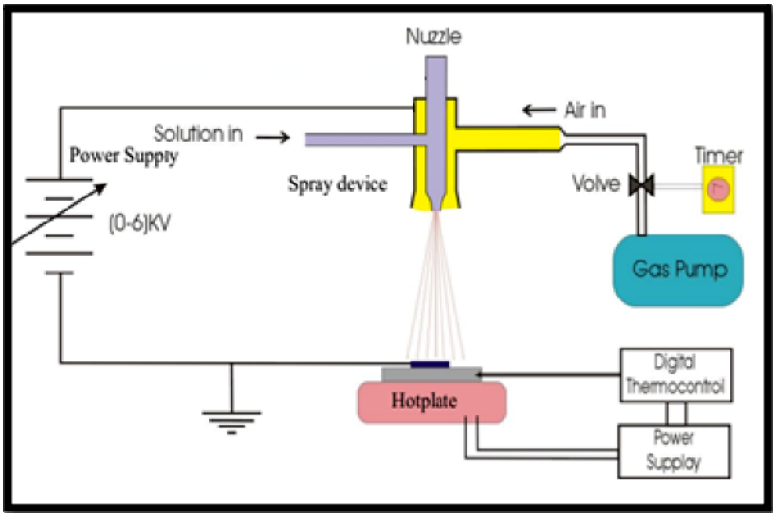
2.1 Solution preparation

Titanium chloride ($TiCl_3$) solution was prepared with a concentration (0.1 M) by diluting the dissolved solution ($TiCl_3$) with an acid (HCl) in ratio (18%) was supplied by (Riedel de Haen), and copper dichloride ($CuCl_2$) solution was prepared at the concentration of (0.1 M) in deionised water. The mixed ratio (3 : 1) of $TiCl_3$ and $CuCl_2$ solutions was used.The study was carried out using four samples for the ratio. The first sample was used without an electric field, while the remaining samples applied an electric field (AEP).

2.2 Thin films preparation

The mixed solution was electro-sprayed at 350°C of substrates temperature on p-type silicon substrates, with 30 cm distance between the spray nozzle and targeted substrates which have the dimensions of 1.5 × 1.5 cm^2, and flow rate of 0.116 ml/s without AEP. The prepared films were left for 15 min at the same preparation temperature, then left cool down at room temperature. Figure 1 illustrates the electrospray system. AEP was changed for each of the remaining samples in order (3.6, 4.5, 5) kV.

Figure 1 Diagram of the utilised electrospray system (see online version for colours)



2.3 Films characterisation

The structural properties of the prepared films were performed on X-ray diffractometer (XRD-6000) using Cu*K*α (λ = 1.54060 Å) radiation and accelerated voltage of 40 kV with 20 A from 2θ = (20 to 80) degree with 0.1° of scanning speed, and energy dispersive spectroscopy (EDX) technique, the phases ration was calculated using. Field emission scanning electron microscope (FESEM) utilised to investigate the morphological properties and the prepared films thickness. Additional, the optical properties were studied by photoluminescence (PL) technique.

3 Results and discussion

3.1 XRD patterns analysis

Figure 2 illustrates the XRD pattern of the prepared films. According to ICSD cards 98-000-9852 and 98-016-1908, four peaks relate to anatase phases were observed in the pattern of which did not use AEP, at (112), (020), (022), and (220). The dominant peak was unique monoclinic trititanium pentoxide (Ti_3O_5) at 26.64° (202) with 4.7 nm of crystalline size was seen which is formed as a result of laser, electric field, and temperature effects [25]. In addition to anorthic Ti_8O_{15} (114^{-}) and tetragonal Ti_2O_3 (110) as types of the potentially configurable unstable Ti-O systems due to the heating and increasing of the surface area of TiO_2 particles [26], hexagonal Cu_3TiO_4 (012), and orthorhombic CuO_2 (173) according to ICSD 98-002-6492 and 98-001-5894 for Ti_8O_{15}, 98-002-8354 for Ti_2O_3, 98-010-0133 for Cu_3TiO_4, and 98-015-0886 for CuO_2. The use of AEP (3.6 kV) leads changed the diffraction behaviour of the prepared films. Ti-O systems have been changed in the distribution, where anatase peaks encountered a density decrease and a position shifting. TiO_2 (β) (104^{-}) and rutile (011) be found at 29.75° and 35.6° respectively, while Ti_3O_5 peaks increased with a dominance of peak at 45.92° (403^{-}) with 61 nm of crystalline size. In these conditions, the most important observation is a peak disappearance of Cu-Ti and Cu-Ti-O systems. The prepared films also showed a different pattern with an AEP of (4.5) kV. A dominant phase was Cu_3Ti_3O, which be found at 14.18° (111) with a crystalline size of about 15.15 nm. Other important peaks related to anatase (011) and rutile (110), small Ti-O systems illustrated by peaks of anatase, rutile, β-TiO_2, and brookite with (112), (120), (420), and (321), respectively, while CuO_2 reappeared at 77.49° (027). Again with increasing of AEP to 5 kV, the appearance of the Ti-O system was limited to anatase, rutile, β-TiO_2, and brookite, whilst Cu-Ti-O limited by increased Cu_3Ti_3O peak compare with its dominant peak with 4.5 kV of AEP. The prepared films with 5 kV of AEP have a dominant point to anatase (011). The literature confirms that copper ions do not influence the crystallisation pattern of the systems [27–29], but under the effect of high electric fields has been found, that may be related to decrease of the particle size associated with the increased separation of the solution drops with increasing of AEP.

EDX analysis is demonstrated for a 1 mm area of the areas selected from the surfaces of the prepared films that contained titanium and copper of varying proportions as shown in Figure 3.

Figure 2 XRD patterns of the prepared Cu-doped TiO_2 films with (free, 3.6, 4.5, and 5) kV of AEP (see online version for colours)

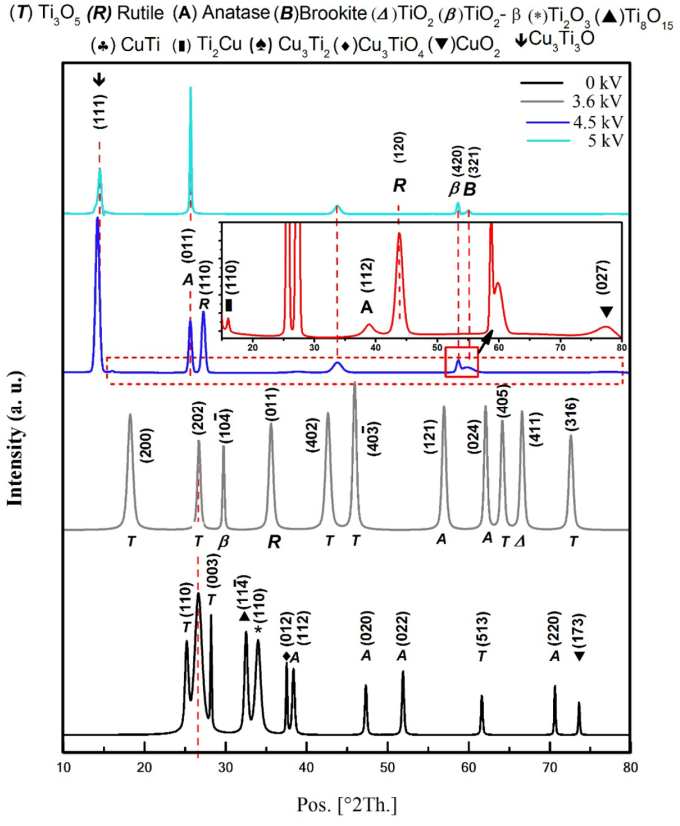
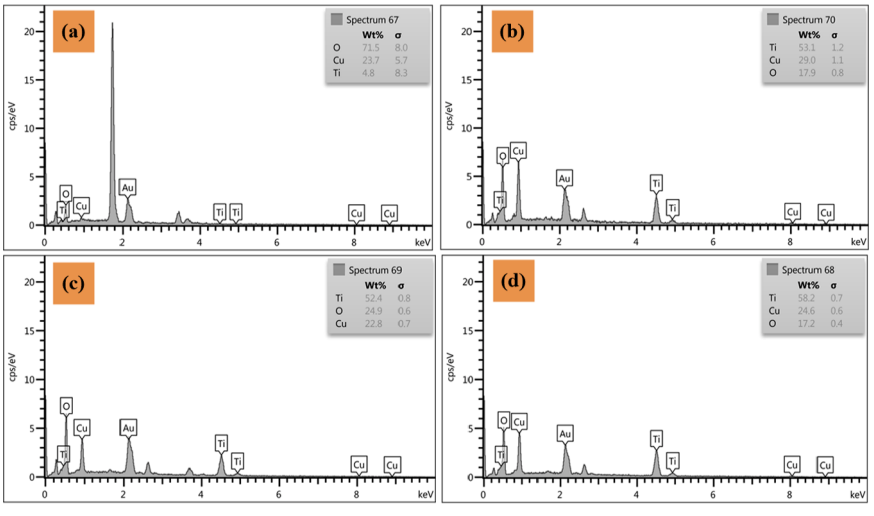


Figure 3 The EDS of the prepared films (a) the prepared film under free AEP, (b) under 3.6 kV of AEP, (c) under 4.5 kV of AEP, and under 5 kV of AEP (see online version for colours)



3.2 Morphological characteristics

The size and formation of nanoparticles have been determined using FESEM system. The size, porosity, and shape of the prepared films were affected by AEP. The prepared films with free AEP exhibited uniform size distribution of spherical particles about 12.6 nm of average size, with 33.38% of porosity, and 0.247 µm of the thickness as shown in Figures 4(a) and 5(a), where the spherical shape prevails in the nanoparticles. The deposited films under 3.6 kV showed various aggregating and shapes were consisted of particles with 7.6 nm of average size, 34.9% of porosity, and 2.2 µm of the thickness, as shown in Figures 4(b) and 5(b). As shown in Figure 4(c) and 5(c), a typical scan of the FESEM for 4.5 kV depicts particle structures such as an irregular polyhedron size of about 20–100 nm consist of aggregated particles with 16.30 nm of average size, with 2.628 µm, and 53.55% of thickness and porosity. The particle size is a heterogeneous approach for the deposited nanoparticles under the influence of the electric potential, and there is a tendency for the property of particle accumulation to form larger particles [30]. Some collections showed as microflowers, that is maybe due to the difference in phases where existed due to influence of the electric field and heating. Also, as shown under 5 kV electric potential in Figures 4(d) and 5(d), the particle size increased by about 100–400 nm in heterogeneous approach, with 7.2 nm of average size, 3.524 µm of thickness, and 43.41% of porosity, and neck phenomenon can be clearly seen in one of the steps, which has been stabilised by heating as shown in the secondary image at the top right of Figure 4(d). The differentiation in the assembly methods of nanoparticles of the deposited films under the influence of the electric field is due in addition to the effect of the electric field on the phenomenon of composition segregation impurity to reduce the surface energy [31]. Figure 6 illustrates the influence of APE on both the thickness and porosity of the prepared films.

Figure 4 The surface and cross section FESEM images of the prepared films (a) the prepared film under free AEP, (b) under 3.6 kV of AEP, (c) under 4.5 kV of AEP, and under 5 kV of AEP (see online version for colours)

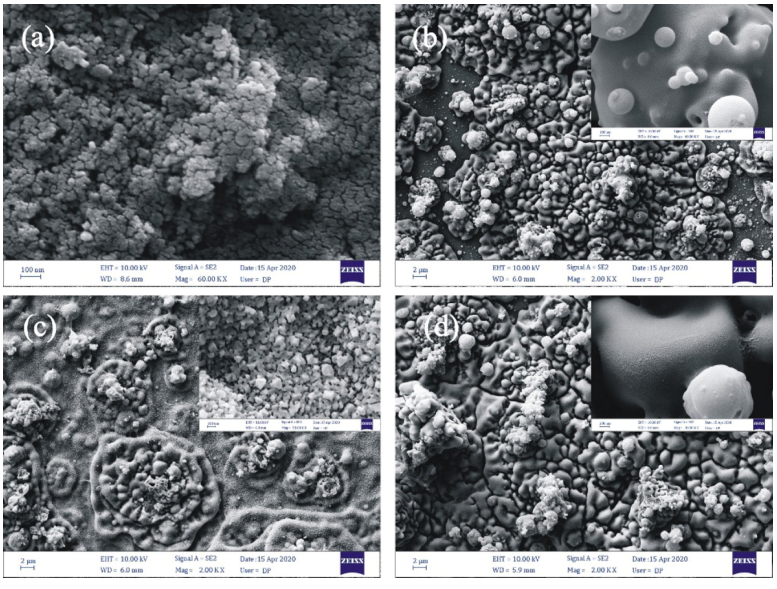


Figure 5 Cross section FESEM images of the prepared films (a) the prepared film under free AEP, (b) under 3.6 kV of AEP, (c) under 4.5 kV of AEP, and under 5 kV of AEP (see online version for colours)

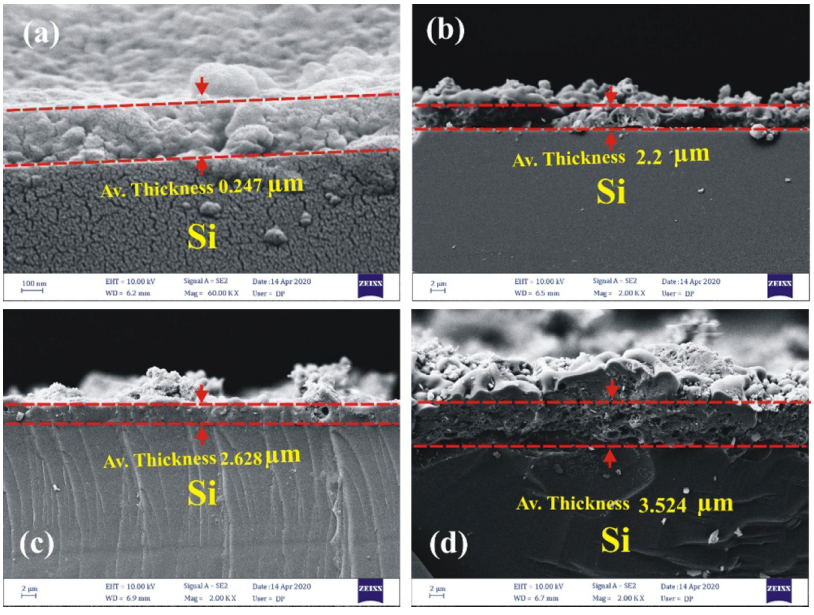
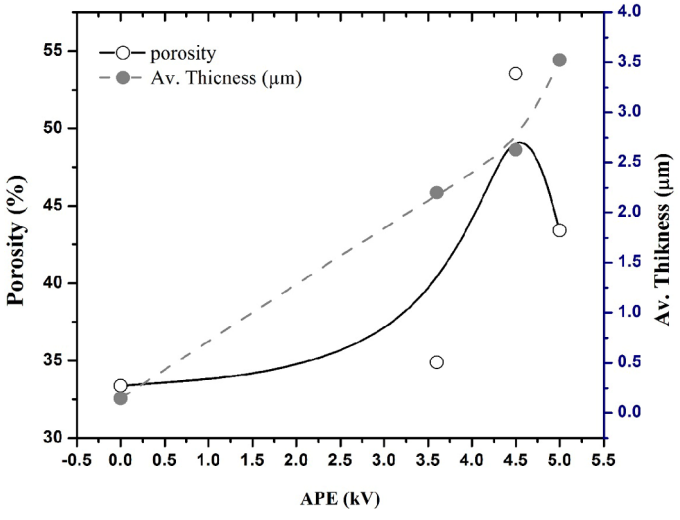


Figure 6 The influence of APE on both thickness and porosity of the prepared films (see online version for colours)



3.3 Photoluminescence characteristics

The study of PL emission spectra is helping in understanding the behaviour of the electron-hole ($e^- - h^+$) pair in materials, the separation, recombination of ($e^- - h^+$) pairs processes, the efficiency of charge-carrier transfer [32,33], the oxygen vacancies, the near-band edge (NBE), and the self-trapped exciton (STE) [2]. Figure 7 illustrates PL

spectra of the prepared films with various AEP of the Cu-TiO_2 films and fitting Gaussian peaks were recorded in the range of 250–550 nm with an excitation wavelength of 350 nm at room temperature. All prepared films showed the highest peaks between 342 nm to 344 nm with a change in both broad, and intensity [34]. These peaks can be attributed to the photon emission which results from the self-absorption effect [33,35]. This points out to change in the oxygen vacancies corresponding to preparation conditions. Fitting Gaussian peaks in the PL spectra are listed in Table 1.

Figure 7 PL spectra of the Cu-TiO_2 thin films (see online version for colours)

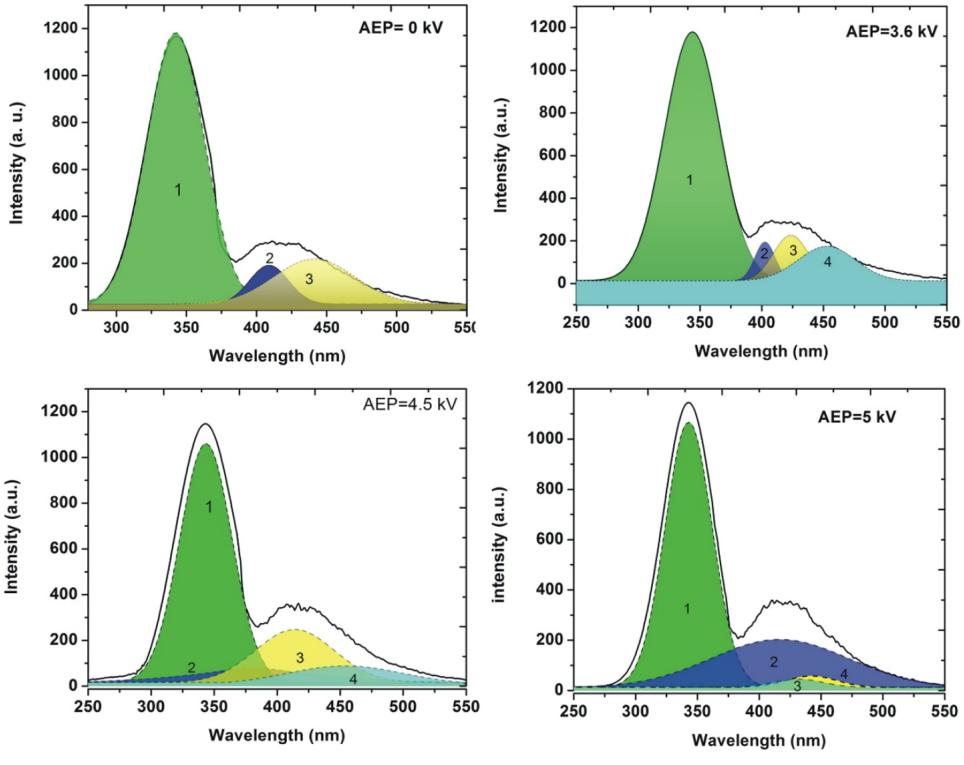


Table 1 The centre of mean PL fitting peaks for the prepared films

AEP (kV)	*Peak1*		*Peak2*		*Peak3*		*Peak4*	
	Centre (nm)	*Height*	*Centre* (nm)	*Height*	*Centre* (nm)	*Height*	*Centre* (nm)	*Height*
0	342	1157	409	165.4	441	191.8	–	–
3.6	344	1167	403	182.6	424	214.1	453	162.2
4.5	343	1060	381	78.77	414	248.3	454	88.05
5	343	1067	417	203.5	432	45.65	442	58.9

4 Conclusion

To obtain thin films of different phases from the Cu-Ti-O and Ti-O systems the electrospray technique can be used in place of traditional techniques, which are expensive and rarely succeed to introduce copper into the crystal structure of the resulting composites. Moreover, the results showed that the number and distribution of phases depend on the applied electric potential if the temperature is left in a prospective study. The properties of the prepared films by this technique may qualify them to work as (bio or gaseous) sensors or photodetectors. Thin films of TiO_2-Cu were developed by a local electrospray method, using $TiCl_3$ and $CuCl_2$ as a precursor solution, on cleaning glass substrates. Thin films were prepared without electric potential and with an electric potential during preparation. In order to understand the factors influencing the deposited TiO_2 films, the impact of the electric potential on the morphological, structural, optical and surface chemical composition has been investigated. The XRD measurements revealed that the films had an anatase structure, with the (111) desired orientation. The average crystalline size increased to 20 nm with the applied electric potential from 12.6 nm with no electric potential. The FESEM images of the TiO_2-Cu thin film indicated that the film deposited under 4.5 kV had well-formed grains and smoother surfaces due to the homogeneous reaction and improvement in the crystallinity. The optical properties revealed that all samples have highest peaks between 342–344 nm with change in both broad, and intensity because of the photon emission which result from the self-absorption effect. The thin film offers a good performance for use as a biosensor.

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