Al-Kitab Journal for Pure Sciences (2024); 8(1):81-91.
https://doi.org/10.32441/kjps.08.01.p8

Al-Kitab Journal for Pure Sciences
ISSN: 2617-1260 (print), 2617-8141(online)
https://isnra.net/index.php/kjps

Study of the Effect of Thin Layer Thickness on the Structural Properties of Copper Phthalocyanine (CuPc) Films Prepared by Vacuum Thermal Evaporation Method

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Citation: Alhiti LS, Jawad RA, Abd Alwaahed RA, Alhassan HM. Study of the Effect of Thin Layer Thickness on the Structural Properties of Copper Phthalocyanine (CuPc) Films Prepared by Vacuum Thermal Evaporation Method. Al-Kitab J. Pure Sci. [Internet]. 2024 Apr. 07 [cited 2024 Apr. 07];8(1):81-91. Available from: https://doi.org/10.32441/kjps.08.01.p8.

Keywords: CuPc thin films, vacuum thermal evaporation technique (PVD), atomic force microscope (AFM), thickness, root mean square (R.M.S.), structural characteristics.

Article History

Received 03 Feb. 2024
Accepted 25 Mar. 2024
Available online 07 Apr. 2024

Abstract:

The structural properties of thin films prepared with different thicknesses before and after the annealing process and at different temperatures were studied. X-ray diffraction (XRD), atomic force microscopy (AFM), and emission scanning electron microscopy (FESEM) were used to study the structural properties. X-ray diffraction analysis revealed that the thin films prepared with different thicknesses, as well as those annealed at temperatures of 300 and 373 K, were composed of the β-phase, which is widely known as the most stable phase. The analysis also showed that the material has a polycrystalline structure characterized by a monoclinic crystal system. The density shows a constant increase in all thin films, with the dominant trend being (312) for all films. Atomic force microscopy (AFM) measurement results indicated that there was an increase in roughness with a change in the thickness of the thin films. In addition, there was an increase in the crystalline size of the thin films that underwent annealing at 300 and 373 K. However, there was a decrease in crystallite size at the annealing temperature of 473 K due to the phase change of the thin film material.

Keywords: CuPc thin films, vacuum thermal evaporation technique (PVD), atomic force microscope (AFM), thickness, root mean square (R.M.S.), structural characteristics.

دراسة تأثير سمك الأغشية الرقيقة على الخواص الهيكلية لأغشية فثالوسيانين النحاس (*CUPC*) المحضرة بطريقة التبخير الحراري الفراغ

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الخلاصة:

تم دراسة الخصائص الهيكلية للأغشية الرقيقة المحضرة بسماكات مختلفة قبل وبعد عملية التلدين وبدرجات حرارة مختلفة. استخدمت الدراسة حيود الأشعة السينية (*XRD*) ومجهر القوة الذرية (*AFM*) والمجهر الالكتروني الماسح للانبعاث (*FESEM*) لدراسة الخصائص الهيكلية. كشف تحليل حيود الأشعة السينية بأن الأغشية الرقيقة المحضرة بسماكات مختلفة وكذلك التي تم تلدينها عند درجات حرارة ٣٠٠ و٣٧٣ كلفن كلفن، كانت تتكون من الطور بيتا (*β-phase*) والذي يعرف على نطاق واسع بأنه الطور الأكثر استقرار. كذلك بينت التحاليل ان المادة لها بنية متعددة البلورات والتي تتميز بنظام بلوري احادي الميل. تظهر الكثافة زيادة ثابتة في جميع الاغشية الرقيقة، مع كون الاتجاه السائد (٣١٢) ولجميع الاغشية. أشارت نتائج القياس لمجهر القوة الذرية (*AFM*) ان هناك زيادة في الخشونة مع تغير سمك الاغشية الرقيقة. بالإضافة إلى ذلك، كان هناك زيادة في الحجم البلوري للأغشية الرقيقة التي خضعت للتلدين عند ٣٠٠ و٣٧٣ كلفن. ومع ذلك، كان هناك انخفاض في الحجم البلوري عند درجة حرارة التلدين ٤٧٣ كلفن نتيجة لتغير الطور لمادة الاغشية الرقيقة.

الكلمات المفتاحية: الأغشية الرقيقة CuPc، تقنية التبخر الحراري الفراغي (PVD)، مجهر القوة الذرية (AFM)، السمك، متوسط الجذر التربيع (R.M.S.)، الخصائص الهيكلية.

1. Introduction:

Phthalocyanine polymers, a type of organic material with highly functional properties, have made them the subject of intense study in the fields of chemistry and physics. The prominent feature of these materials is their great stability in the face of thermal changes and chemical reactions, which makes them excellent candidates for diverse applications, especially in fields requiring highly stable materials **[1]**. Phthalocyanine can take several crystalline forms, and these different forms are known as polymorphic forms. The most common forms are α-, β-, and γ-. Each of these forms has unique properties that affect how the material is used in practical applications **[2]**. The differences between these shapes are due to the arrangement of atoms within the crystal, which in turn affects the physical and chemical properties of the material **[3]**. The research highlights the structure properties of metal-modified or metal-free phthalocyanine polymers. Examples cited, such as MnPc (manganese phthalocyanine) [4], CuPc (copper phthalocyanine) [5], NiPc (nickel phthalocyanine) [6], FePc (iron phthalocyanine) [7], and CoPc (cobalt phthalocyanine) [8], reflect the diversity in the compositions of these polymers and the resulting applications. One important use of these materials is in gas sensors, where they take advantage of their high sensitivity to chemical changes. They are also used in optical logic displays and in solar energy conversion applications, such as solar cells, due to their ability to absorb and convert light efficiently. In addition, they are used in the manufacture of color filters and as materials for organic lasers, where they provide unique optical properties [9].

The chemical nature of these materials makes them p-type semiconductors, which means they contain electrical holes that facilitate the flow of electricity. The ability to easily evaporate these materials allows the production of high-purity thin films without degradation, enhancing the quality and efficiency of downstream applications [10].

Thermal evaporation was used to create thin film coatings of copper phthalocyanine on quartz substrates in the work that is being presented here [11]. In this work, structural elements were found and addressed. These characteristics include statements about considerations made during research or analysis that are relevant to the study of thin films. X-ray diffraction is an important method for analyzing the crystalline structure of thin films, as X-ray radiation can be used to study the atomic and crystalline structure of materials [12]. Also, advanced techniques like atomic force electron microscopy (AFM), which can show very clear, very small pictures of thin film surfaces, and field scanning electron microscopy (FESEM), which can show very fine details about the structure of surfaces at very high resolution, have been looked at and reviewed [13].In this way, it is demonstrated that analytical aspects have been taken care of using multiple techniques to understand and evaluate the structural and surface properties of the studied thin films.

2. Experimental work:

2.1 Thin film deposition system:

The deposition method used a vacuum thermal evaporation technique, where copper phthalocyanine is heated until it evaporates and then condenses on a colder surface, forming a thin film [14]. Equipment used: An Edwards (E 306 A coating unit) was used, which is known for its ability to achieve high-level vacuums of up to (2×10-5) Torr. The dimensions of the basin used in the deposition process are arranged in a symmetrical and geometric manner with respect to the target or foundation. This arrangement helps in achieving uniformity in the distribution of the evaporated particles of copper phthalocyanine on the substrate. The main goal is to produce a homogeneous and even film of copper phthalocyanine. Achieving homogeneity in the deposited film is essential to obtaining the desired properties and specifications in the final film. Careful regulation of the bed and substrate contributes to ensuring the quality and consistency of the deposited film **[15]**.

2.2 Preparation of copper phthalocyanine films:

Copper phthalocyanine films with a thickness of 200, 215, 235, and 255 nanometers were formed in a molybdenum metal boat when the evaporation chamber pressure reached 2.2 × 10-5 Torr using a unit. The E306 Coating Unit deposits material on glass 18 cm from the evaporation tank at a rate of 2.078813 nm sec-1 at normal temperature. A current transformer sends a high current for deposition. After cooling in the evaporation chamber, the samples are ready for thickness measurement. Subsequently, the lab tests these membranes for their structural, optical, and electrical characteristics.

2.3 Measuring the thickness of thin films:

The researchers use the indirect gravimetric approach to measure the thickness of thin films through mass measurement. Several steps were involved in this process. In this research, a sensitive scale is used to weigh the substrate before applying the film, and a vacuum thermal evaporation is also used to deposit the thin layer onto the substrate. The substrate is weighed again on the sensitive balance after film deposition. This time, the substrate and thin films will be weighed. To determine the mass of thin films, the researchers subtract the weight of the substrate before deposition from its weight after deposition, and also use film density and mass to calculate the volume of the thin film. The volume divided by the surface area of the film deposit yields the film thickness **[16]**.

This approach is precise and efficient for thin films. Measurement tools like scales must be reliable and calibrated to produce accurate findings. Repeating measurements helps confirm findings and decrease mistakes.

3. Results and discussion:

3.1 X-ray diffraction:

The results of X-ray diffraction (XRD) examinations of CuPc thin films deposited using the thermal evaporation technique in vacuum on glass substrates with different thicknesses (200, 215, 235 and 255) nanometers show that it is a polycrystalline structure of the monoclinic type **[17]**, and compared with the standard values in the card (JCPDS: 00-037-1846), the $(2\bar{1}5)$, and (213), respectively.

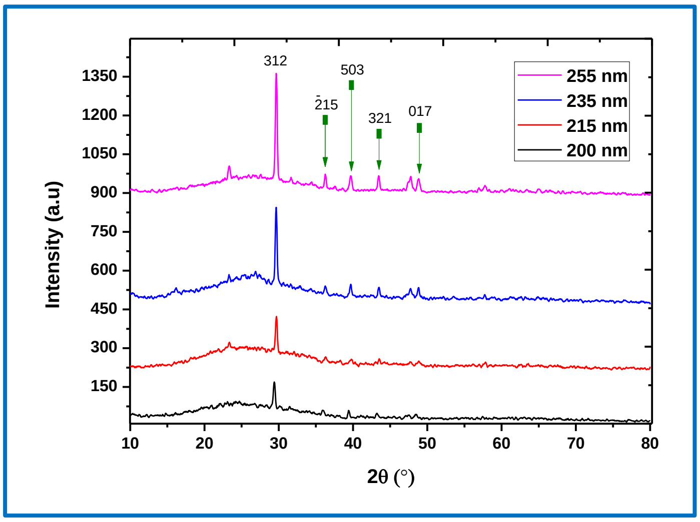

Figure 1: X-ray diffraction pattern (XRD) of copper phthalocyanine CuPc films.

The characteristic and dominant direction was (312), as shown in **Figure 1**. The results also had a good match between the calculated and measured surface area values and the crystal diffraction angles, as shown in **Table 1**.

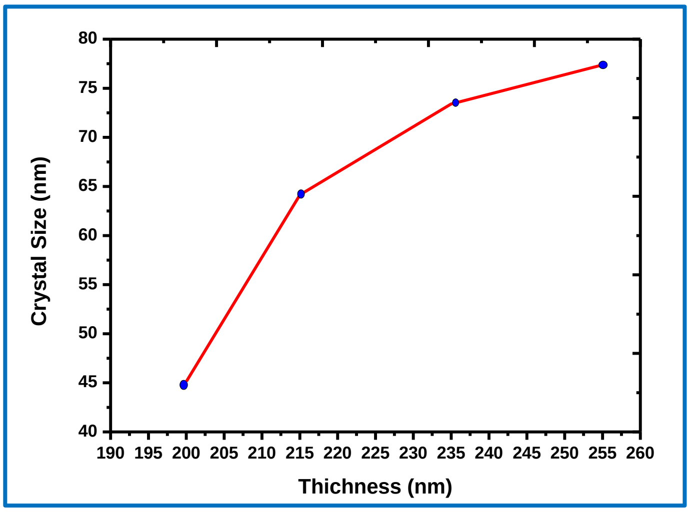

Figure 2: illustrates the relationship between crystal size and the thickness of CuPc thin films.

Table 1 shows the structural parameters of CuPc films, where the results show that as the thickness of the thin films increases, there will be an increase in crystal size due to columnar growth with increasing film thickness, as shown in **Figure 2**, and an increase in density.

The average crystallite size was calculated, which agrees well with the estimated value obtained from FESEM images.

A copper phthalocyanine (CuPc) film, measuring 255 nm in thickness, underwent annealing at temperatures of 300, 373, and 473 Kelvin. The outcomes of X-ray diffraction (XRD) analyses for these thin CuPc films are presented in **Figure 3**. By examining the XRD results, structural parameters for the CuPc films in the direction of the crystal peak (312) at varying annealing temperatures can be inferred, as detailed in **Table 1**.

As the annealing temperatures rise, the full width at half maximum (FWHM) in the primary orientation decreases significantly. This shows that the lattice quality has improved, as explained in **[18]**.

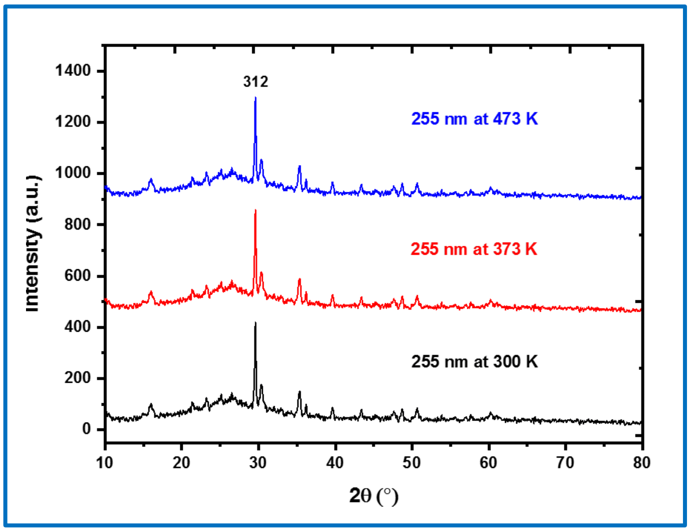

Figure 3: displays the X-ray diffraction (XRD) patterns of copper phthalocyanine (CuPc) films that have been annealed at various temperatures.

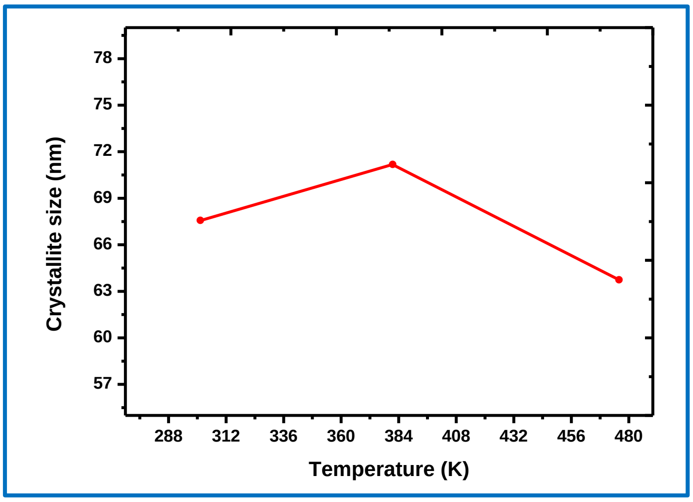

Figure 4: depicts the variation in crystal size as a function of the annealing temperature for copper phthalocyanine (CuPc) thin films.

This improvement allowed for the estimation of crystallite size using the Scherer equation. According to the data in **Table 1**, there is an observable increase in crystal size at annealing temperatures of 300 and 373 Kelvin. This increase can be attributed to regrowth involving phthalocyanine, as the crystallization process of the films is temperature-dependent. However, at a higher temperature of 473 Kelvin, a decrease in crystal size is observed, likely due to a phase change. This pattern aligns with findings from previous research, as noted in **[19]**.

Table 1: Results obtained from XRD for CuPc films and different thicknesses.

Thickn. (nm)	2θ(std.) (°)	2θ(Exp.) (°)	I (a.u)	d_{hkl}(std.) (Å)	d_{hkl}(Exp.) (Å)	FWHM (°)	C.S. (nm)	hkl
200	29.47	29.563	169.34	3.027	3.015	0.23	37.12	**312**
	36.07	36.18	60.26	2.488	2.480	0.20	54.13	$\underline{2}15$
	39.47	39.63	59.50	2.281	2.272	0.18	50.99	**503**
215	29.47	29.575	299.28	3.027	3.014	0.21	43.52	**312**
	36.07	36.19	73.14	2.488	2.479	0.22	61.17	$\underline{2}15$
	39.47	39.65	63.74	2.281	2.271	0.23	71.38	**503**
235	29.47	29.614	397.89	3.027	3.012	0.205	62.24	**312**
	36.07	36.24	92.80	2.488	2.478	0.24	69.16	$\underline{2}15$
	39.47	39.66	98.74	2.281	2.270	0.28	73.94	**503**
255	29.47	29.62	493.96	3.027	3.011	0.184	66.91	**312**
	36.07	36.27	103.96	2.488	2.475	0.141	88.07	$\underline{2}15$
	39.47	39.60	96.60	2.281	2.270	0.29	74.91	**503**

3.2 Results of atomic force microscopy (AFM) examinations:

The surface relief and topography of CuPc thin films with different thicknesses (200, 215, 235, (and) 255) nm were studied using atomic force microscopy (AFM). This microscope is characterized by its high resolving power, which reaches (0.1–1.0) nanometers, and a magnification power estimated at ($5 * 10^2$ - 10^8), which enables the nature of the surface to be examined accurately.

Table 2: displays the average grain size, surface roughness, and root mean square values for CuPc films with different thicknesses, including 200, 215, 235, and 255 nanometers.

Thickness (nm)	D (nm)	Roughness Average (nm)	R.M.S (nm)
200	62.80	3.26	3.9
215	73.01	4.28	4.95
235	80.98	5.25	6.29
255	88.80	7.75	8.99

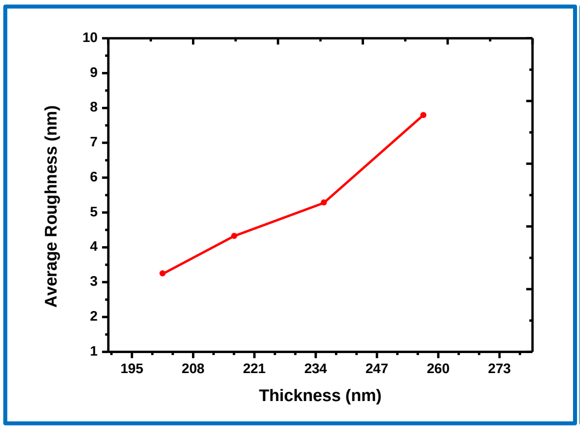

Figure 6: shows the roughness rate as a function of varying thickness for CuPc thin films.

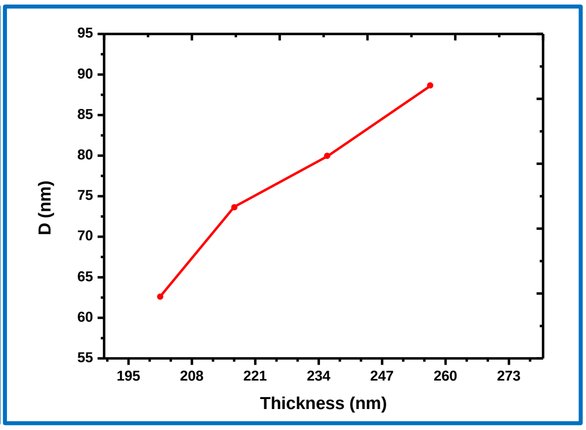

Figure 5: shows grain size as a function of varying thickness for CuPc thin films.

The AFM provides statistical values for the average grain size and distribution on the surface, in addition to the degree of surface roughness using the root mean square of roughness (RMS). This also allows 2D and 3D images to be displayed for comprehensive surface inspection. The grain size and average roughness were determined as a function of thickness, as shown in **Figures 5 and 6**. The results showed an increase in grain size, which is consistent with the results of XRD analysis, as well as an increase in average roughness with increasing thickness.

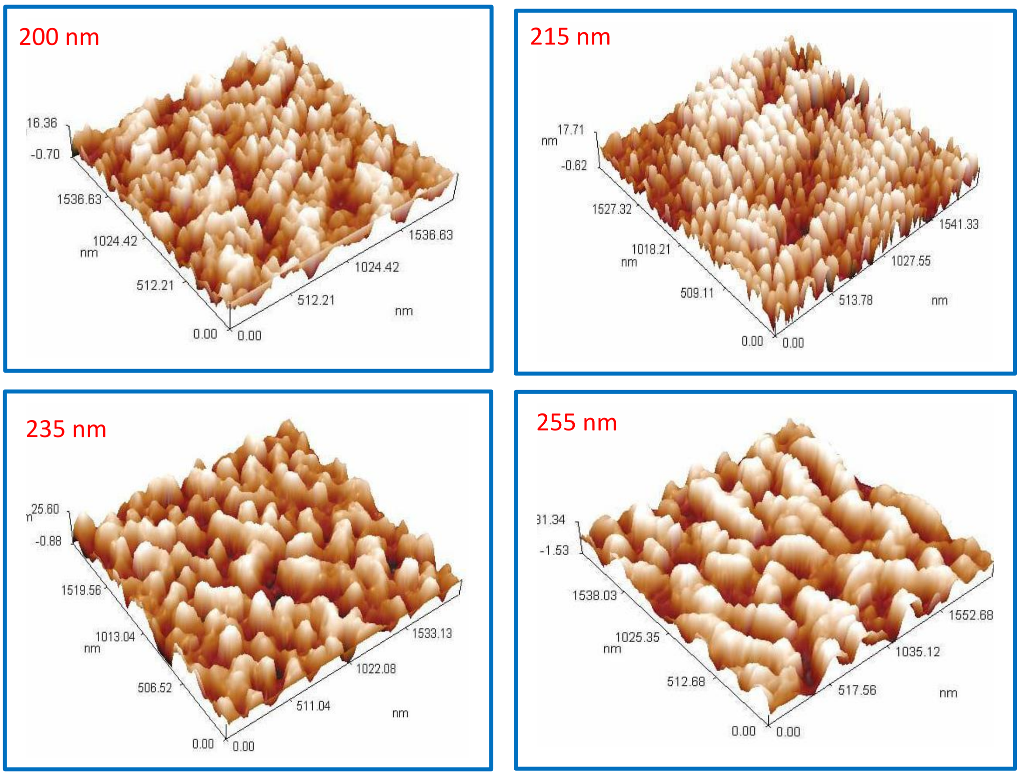

Figure 7: shows three-dimensional atomic force microscopy (AFM) images of thin films of copper phthalocyanine (CuPc) with different thicknesses.

Figures 7 A, B, and D show two-dimensional images from atomic force microscopy (AFM) as well as grain distribution diagrams of the surface of CuPc thin films, which are 200, 215, 235, and 255 nm thick, respectively. The images taken at 25 °C, show the presence of a large number of tubular-shaped CuPc grains. This pattern indicates a crystalline nature resulting from the high active content of the expelled species, as described in ref **[20]**.

3.3 Results of field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscopy (FESEM) provides topographical and elemental information at magnifications between 10X and 300,000X, with an almost unlimited depth of field. Compared to scanning electron microscopy (SEM), FESEM produces sharper images and less electrostatic distortion. All films prepared and deposited on glass substrates were examined using this technique to obtain a clear image of the features, which helps in identifying the surface nature of the films and observing changes in grain size based on the change in thickness.

The FESEM image shown in **Figure 8** of the prepared film reveals particles of larger size, ranging from 15 to 30 nm. There is a noticeable increase in particle size in parallel with the increase in the thickness of the thin film, and this is consistent with the measurements extracted from XRD and AFM analyses. It is noted that the granular size is larger than the existing crystalline size.

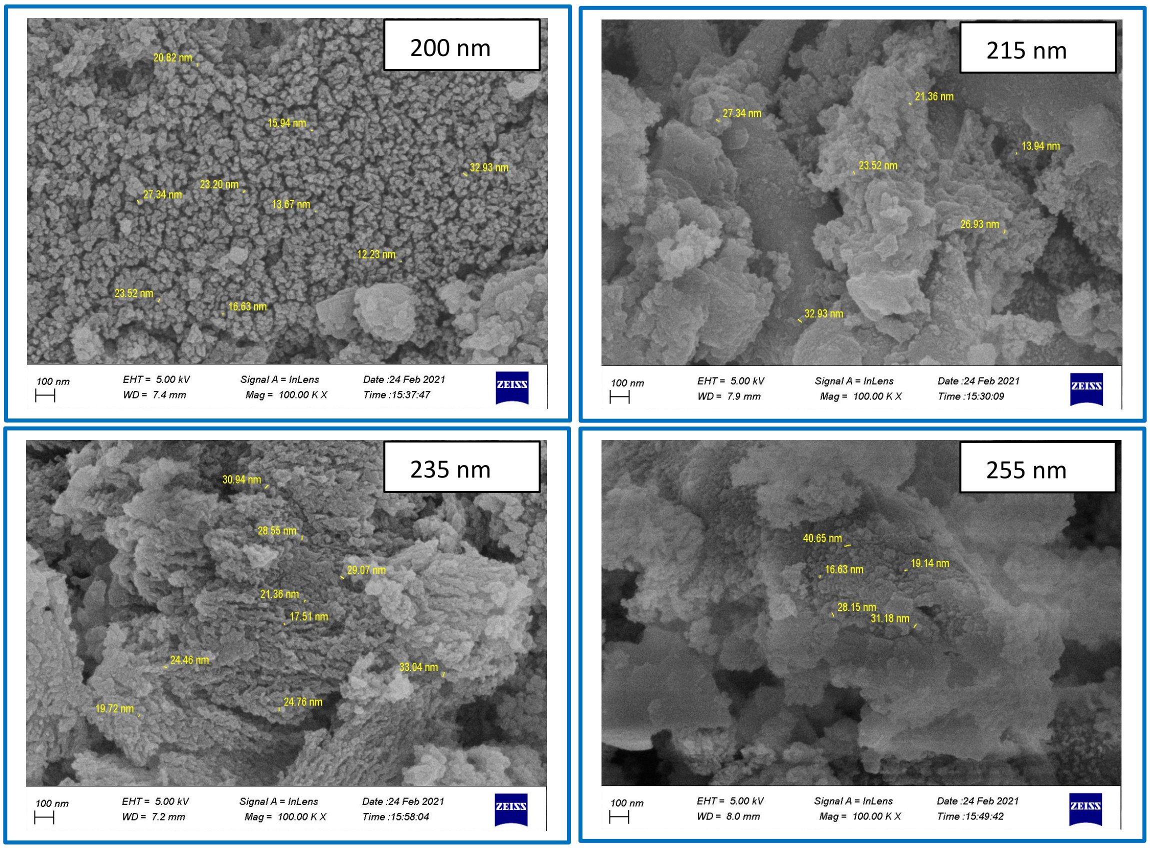

Figure 8: displays field emission scanning electron microscope (FESEM) images of copper phthalocyanine (CuPC) films with varying thicknesses.

4. Conclusion:

The research revealed the effect of thin film thickness on the structural properties of copper phthalocyanine (CuPc) films. It was found that there is a relationship between the structural properties and the thickness of the thin films, as the best properties that were reached, were for the thin films with a thickness of 255 nanometers. X-ray diffraction (XRD) analysis also indicates changes in the size of crystalline grains with a change in the thickness of the prepared thin films, which is a crucial factor that affects the structural integrity of the material. Atomic force microscopy (AFM) has revealed valuable information on the evolution of surface features, providing a comprehensive understanding of structural modifications whereby this tuning can be exploited to customize the material for specific applications in organic electronics and optoelectronic devices.

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