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VARIATION IN ABSORPTION COEFFICIENT OF ZnO THIN FILMS WITH ITS THICKNESS PREPARED BY SILAR METHOD

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Abstract
With an emphasis on changes in dipping cycles this work explores the synthesis and characterisation of zinc oxide (ZnO) thin films by the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. ZnO films were made by dipping cycles of 25, 35, and 45 in hot water and ammonium zincate, respectively. With more cycles, XRD demonstrated decreased dislocation density and increasing crystallite size, confirming a hexagonal wurtzite structure. More light was absorbed by thicker sheets, and their shape showed different nanostructures.

Keywords: Zinc Oxide (ZnO) Thin Films, Successive Ionic Layer Adsorption and Reaction (SILAR), Structural Analysis, Optical Properties.

1. INTRODUCTION

Due to its strong pyroelectric and piezoelectric characteristics, as well as the lack of a wurtzite center of symmetry, ZnO is utilized in mechanical actuators and piezoelectric sensors. This is among the explanations for the usage of ZnO in various applications. These ZnO nanostructures have a bright future in nanotechnology because they are easy to make, even on cheap substrates like glass. ZnO nanostructures have a large surface area and are biosafe, which makes them attractive for biological and sensing applications, S. J. Pearton *et al.* (2004). To the best of our knowledge, each of these applications stems directly from its basic qualities. Zinc oxide is an inorganic substance, as indicated by the symbol ZnO in its chemical formula. Zinc oxide is also utilized in the production of ferrites, batteries, and fire suppressants, among other things. Although zinc oxide is mostly created synthetically, it can be found in nature as the mineral zincite. Zinc oxide occurs naturally as zinccite. ZnO is a type of semiconductor that falls under the II-VI family; its massive band gap can be used to identify it. In semiconductors, n-type doping happens spontaneously and can be caused by zinc interstitials or oxygen vacancies. This is the semiconductor in its natural condition. Not to mention the excellent transparency, strong electron mobility, broad band gap, and wide band gap, another desirable feature is a dazzling luminescence that happens at room temperature. Wide band gap and broad band gap are two more beneficial qualities. Due to these properties, ZnO is starting to offer additional benefits for a variety of emerging applications.

S. Mahmud et al. (2006) One can find ZnO nanostructures in one-, two-, and three-dimensional forms, including nanorods, nanowires, nanobelts, nanosheets, nanoflowers, nanocages, and nanoparticles. The ZnO family of nanostructures probably has the most variety of shapes and properties when compared to other materials. It is an inexpensive, chemically stable, and non-hazardous substance. ZnO nanostructures have been widely used in a wide range of technical applications during the past few years due to their unique luminescent, electrical, mechanical, chemical, magnetic, biological, and optical capabilities. Transducers, nanosensors, nanocantilevers, field effect transistors, transparent solar cell electrodes, flat panel displays, and many more are examples of these uses. ZnO nanostructure-containing nanosized sensors have been created to detect a broad range of gases, biological and chemical substances, and surface-mediated processes.

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Applications utilizing this material in photonics and optoelectronics could be highly advantageous. Different ZnO morphologies have the ability to be utilized for the purification of water from organic dyes and microorganisms, respectively, due to their photo-catalytic and antibacterial properties Gatou, M. A. et. al, (2023) used zinc acetate, zinc nitrate, zinc sulfate, and zinc chloride the four distinct precursors in the precipitation process to create semiconductor photocatalysts, namely ZnO nanoparticles. The optical, structural, photocatalytic, and anticancer properties of these photocatalysts were then compared with one other. which revealed that the nanoparticles that were synthesized from zinc acetate were more bioactive and have the maximum photocatalysis efficiency than the nanoparticles that were synthesized from the other four tested precursors. Üstün T, Haspulat Taymaz B et. al. (2023) found Photocatalytic degradation of textile effluent to be a promising application for nanostructured semiconductor materials. In just 60 minutes, the degradation yield under UV exposure increased to 98%. When compared to individual ZnO nanoparticles and individual GaN nanoparticles, the GaN/ZnO photocatalyst exhibits a photocatalytic reaction rate that is 2.2 times quicker and 3.6 times faster, respectively. Furthermore, the hybrid nanostructures of GaN and ZnO demonstrate exceptional stability in terms of their photocatalytic capabilities. According to the findings, when exposed to UV radiation, GaN/ZnO hybrid nanostructures show increased photocatalytic activity, which makes them a promising option for degrading textile effluent. Avinash R. Kachere, Prashant M. Kakade et. al. (2022) In their study, a high-quality nanocomposite of zinc oxide (ZnO) and graphene oxide (GO), called as ZnO/GO nanocomposite, was synthesized using the straightforward and effective hydrothermal approach. ZnO and GO were synthesized independently by the modified Hummer's process and the precipitation method, respectively. Furthermore, we studied how different GO concentrations affected the optical and structural characteristics of ZnO nanoparticles. The ZnO/GO nanocomposite exhibits distinctive peaks of ZnO, GO, and other associated components, as revealed by structural characterisation techniques. Rezaei, Alireza et. al, (2022) created Zinc oxide (ZnO) nanoparticles using aqueous solutions of zinc sulphate ($ZnSO_4$) and sodium hydroxide (NaOH) at ambient temperature and at 70 degrees Celsius. The nanoparticles that were produced at these two temperatures were identified and investigated using zeta potential, dynamic light scattering (DLS), infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), dynamic light scattering (DLS), and zeta potential (ZP). The formation of particles of different sizes and morphologies can be significantly influenced by variables including temperature, mixing technique, and stoichiometric ratio, as shown by SEM micrographs. Phase analysis was performed on the synthetic particles using X-ray diffraction. The results showed that temperature significantly affected the rate at which precursors became products, which in turn aided in the creation of the whole single-phase complex. The fact that the FTIR study showed unique peaking supported these conclusions. Scherer's equation and Rietveld analysis were used to determine the crystallite size in order to investigate how the calcination process impacts the crystal size of the generated particles. The results indicate that the calcination process may have a significant effect on the generated particles' crystal sizes. Following the calcination process, it was discovered that both of these methods had increased the average crystal size of zinc oxide particles. Balamurali, S. et. al, (2021) used the inexpensive SILAR process to deposit thin films of Mn-doped ZnO at three distinct concentrations on a glass substrate. The dopant compounds were seen to modify the thin film surface shape in SEM images. The morphology of the nanofilms was comparable to that of the spherical and nanoflake grains. The ZnO-Mn film's surface quality increases with increased Mn doping, although SEM images don't reveal any discernible changes in grain size. Using photoluminescence (PL) spectroscopy, several defects were found throughout the visible spectrum as the Mn% rose. At ambient temperature, measurements of soft ferromagnetism revealed that ZnO thin films doped with a greater concentration of Mn displayed ferromagnetism. Applications in optoelectronics and spintronics profit from this dilute magnetic semiconductor's (DMS) transparency.

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Zongyou Yin et al. (2010) showed that power conversion efficiency (PCE, η), ≈ 0.31%, is higher than that reported in previous solar cells by using graphene films as electrodes when monocrystalline ZnO nanorods (NRs) with high donor concentration are electrochemically deposited on highly conductive reduced graphene oxide (rGO) films on quartz. Yu J., Shafiei M. et al.(2009) investigated gas sensing properties of a Pt/nanostructured ZnO based Schottky diode hydrogen sensor and reported that the lowering of the reverse barrier allows faster response in reverse bias operation than in forward bias operation. Sezen Tekin et al. (2024) successfully coated pristine and Rb-doped ZnO layers onto FTO substrates using the SILAR method. They reported that phonon lifetimes of the ZnO-based thin films slightly increased due to the improved crystal quality with the increasing Rb amount in the SILAR solution and investigated that Rb6:ZnO sensor exhibited the highest photocurrent values (~10^{-4} and 10^{-3}) for all light powers, indicating promising sensitivity to light. GaniYergaliuly et al. (2022) studied the influence of thickness and solvent on various features of ZnO thin films deposited by SILAR. They found that ZnO thin films prepared using aqueous solutions possess high optical band gaps. However, films prepared with ethanol solvent have low resistivity (10^{-2} Ω cm) and high electron mobility (750 cm2/Vs).

2. Experimental

Utilizing the Successive Ionic Layer Adsorption and Reaction (SILAR) technique, zinc oxide (ZnO) thin films were created. To deposit the ZnO films, this method alternately immerses the substrates in cationic and anionic baths. Ammonium zincate solution, which was made by mixing ammonium hydroxide with an aqueous zinc sulfate solution, was present in the cationic bath. For the best deposition conditions, the pH of the solution was kept between 9.5 and 10. Hot distilled water was used for the anionic bath. Glass substrates were cleaned by a sequence of pre-treatment procedures, including as boiling, acetone washing, and immersion in ionized double-distilled water, before deposition. To achieve crystallization, the ZnO films were coated using dipping cycles of 25, 35, and 45. A complete rinse, air drying, and an hour-long annealing at 400°C were then performed. The gravimetric approach was used to measure the ZnO thin-film thickness. This entails computing the thickness (t) using the substrates' pre- and post-deposition weight differences. The weight difference was converted to film thickness using ZnO's theoretical density. The thickness measurements obtained from several dipping cycles were noted and examined.
ZnO thin-film structural investigation was carried out with CuKα radiation utilizing X-ray diffraction (XRD). The films' orientation and crystal structure were ascertained by analyzing XRD signals. The hexagonal wurtzite structure of the films was identified, and the XRD data was used to estimate the crystallite size. In order to evaluate the quality of the crystal, dislocation density was also computed. ZnO thin-film optical characteristics were assessed with a UV-Vis spectrophotometer. Measurements of absorption spectra were made between 400 and 700 nm in wavelength. The spectra were used to calculate important optical parameters, including as absorption properties and extinction coefficients, which were then used to evaluate the films' appropriateness for different optical applications.

3. Result and discussion.

Numerous studies have been conducted on the structural and optical characteristics of ZnO thin films made using the SILAR process with varying dipping cycles (25, 35, and 45). The films show a hexagonal wurtzite structure with a clear orientation along the (101) plane, according to X-ray diffraction (XRD) examination. By using Scherrer's formula, one is able to ascertain the crystallite size, also known as the particle size (D):

$$D = \frac{K.\lambda}{\beta.cos\theta} \qquad (1)$$

The average crystallite size, denoted as D, is defined by the constant k, which is influenced by the geometry of the crystallites. For spherical particles, k is around 0.95. The full width at half

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maximum (FWHM) intensity of the observed diffraction peak is represented by β. Lastly, λ refers to the wavelength of monochromatic X-ray, which is 1.5406 A°. The dislocation density was determined by use the equation,

$$\delta = \frac{1}{D^2} \qquad (2)$$

Using the Williamson-Hall equation, one is able to determine the average strain that is present in the film,

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \qquad (3)$$

The symbol β represents the full-width half maximum, θ represents the angle at which a certain peak is formed in the XRD data, k represents a constant, D represents the average particle size, and λ represents the wavelength during the XRD analysis. It is possible to determine the lattice constants a and c through applying the formula,

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \quad \& \quad c = \frac{\lambda}{\sin\theta} \qquad (4)$$

The quantity of crystalline per unit, denoted as N_c, was determined using the given relationship,

$$N_c = \frac{t}{D^3} \qquad (5)$$

Additionally, the lattice distortion (LD) that is formed in thin films may be analyzed based on the relation,

$$LD = \frac{\beta}{4\tan\theta} \qquad (6)$$

The X-ray Diffraction method was used to conduct the structural investigation of the annealed zinc oxide thin film. The diffractometer Seimens (D5000, CuKα radiation λ = 1.5406 A^0) was then utilized to carry out the analysis. More dipping cycles resulted in a minor increase in crystallite size (from 29.30 nm at 25 cycles to 31.71 nm at 45 cycles), but a decrease in dislocation density, which suggests better crystal quality, was also seen. Along with this, the films' thickness increased in direct proportion to the number of cycles, rising from 575 nm for 25 cycles to 884.9 nm for 45. Higher extinction coefficients—0.395, 0.869, and 0.995 for 25, 35, and 45 cycles, respectively—with this thickness increase showed improved light absorption. These films are more suited for uses that call for strong light absorption, such solar cells and sensors, because of their enhanced absorption. Larger crystallites and a lower dislocation density in thicker films with more dipping cycles result in higher optical characteristics and enhanced film quality overall, which can increase performance in optical and electrical applications.

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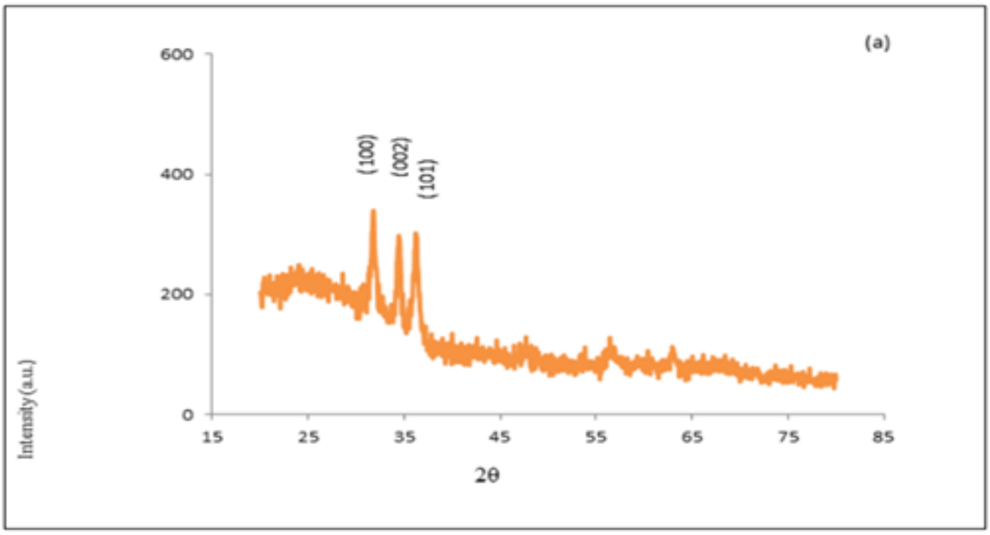
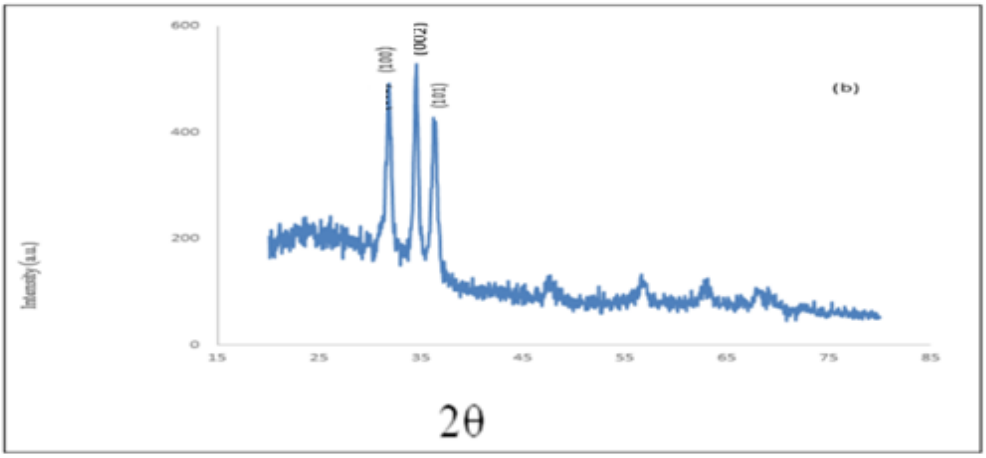
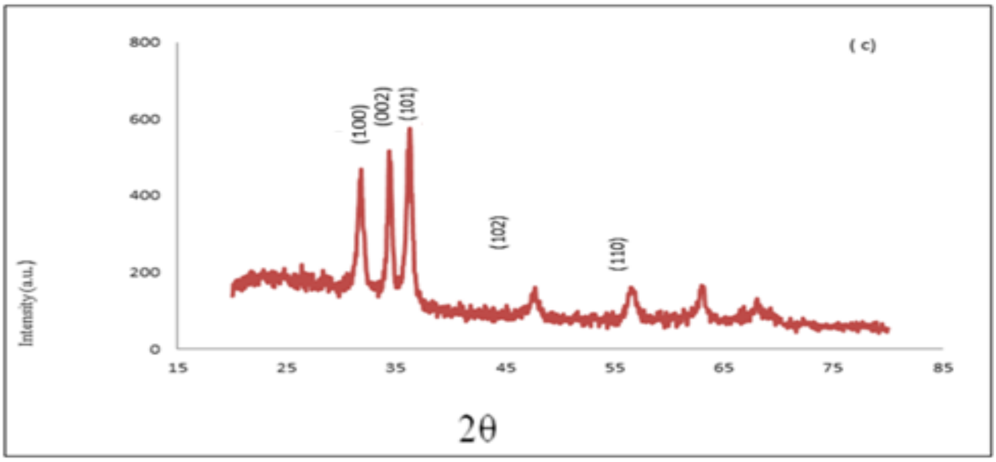


(a) 25 cycles



(b) 35 cycles



(c) 45 cycles

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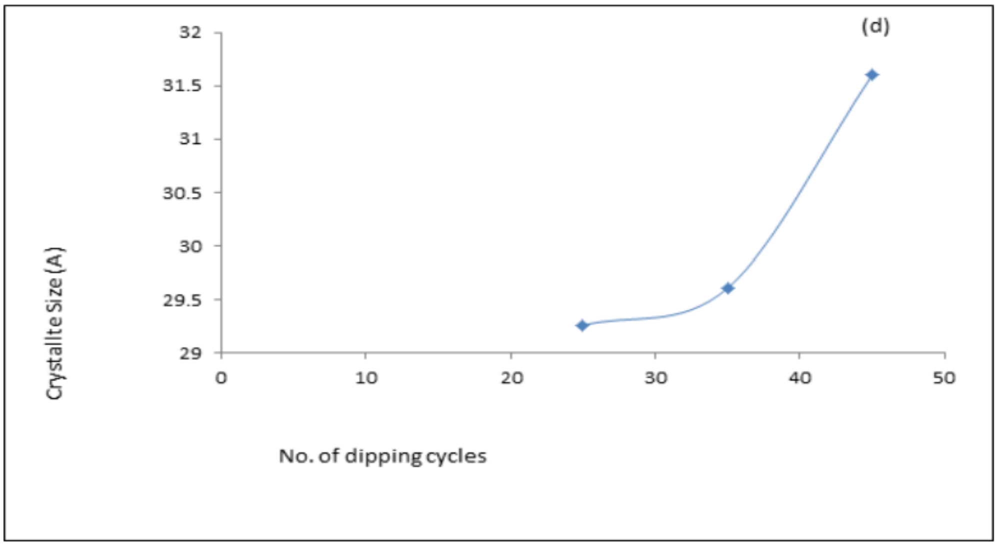

(d) Change of Crystallite Size during Dipping Cycles in the 101 planes
Figure 1: Spectra of ZnO thin films according to XRD

Table 1: X-ray diffraction (XRD) characteristics of ZnO thin films after 25, 35, and 45 cycles of dipping

2θ	Plane (hkl)	No. of cycles	d (Ā)	FWH M (β) (10^{-3} radian)	Crystallite Size (D) (nm)	($\delta \times 10^{14}$) (lines/m^2)	Strain(ε) (lines^{-2} m^{-4})	Lattice constants (Ā)		Nc (10^{16})	Lattice Distortion (LD) ($^{\times}10^{-3}$)
								a	c		
36.4	101	25	2.57	5.25	29.30	11.79	0.0042	2.82	4.8	3.51	1.75
		35	2.57	5.10	29.64	11.76	0.0040	2.86	4.82	3.53	1.78
		45	2.63	4.85	31.71	10.11	0.0039	2.88	4.87	3.54	1.79

The optical absorption spectra of the ZnO thin films were measured using a UV-VIS spectrophotometer (Perkin Elmer) at room temperature. The wavelength range that was used was between 400 and 700 nm. As the thickness of the ZnO thin film rises, the absorbance of the film also increases as the dipping cycle continues. Despite the fact that the absorbance edge is not visible in the graph, it has been claimed that it happened before the wavelength of 400 nm.

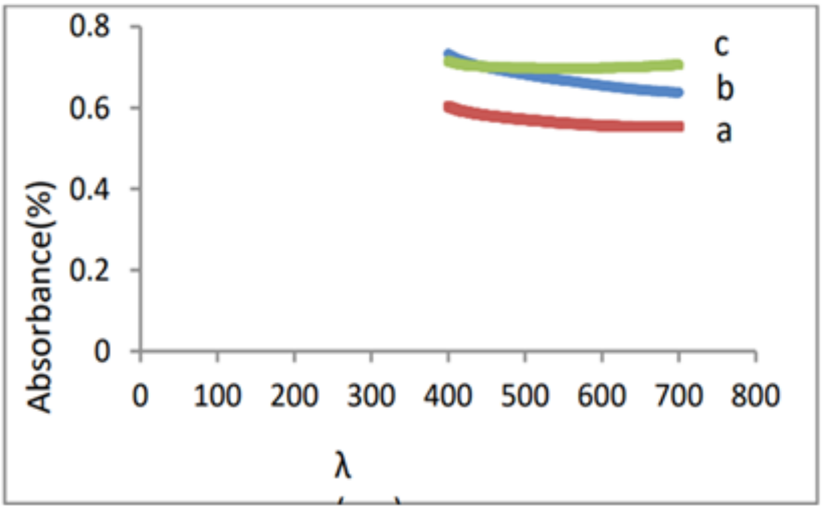

Figure 2: At a=25, b=35, and c=45 cycles, the absorbance against wavelength λ (nm) of ZnO thin films were measured and analyzed

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Applying the calculation method provided by equation, the average extinction coefficient, denoted by the letter K, was computed.

$$K = a\lambda/4\pi \qquad (7)$$

The values of 0.395, 0.869, and 0.995 were measured at 25, 35, and 45 cycles respectively. Increasing the number of dipping cycles resulted in substantial changes to the optical characteristics of ZnO thin films that were produced using the SILAR process. Specifically, the extinction coefficient, which is a measurement of the amount of light that is absorbed by the film, rose as the number of dipping cycles inside the film increased. As a result of this tendency, thicker films are able to absorb more light, which makes them more suitable for applications that need effective light absorption, such as solar cells and sensors.

Table 2: Dipping Cycles and Their Effects on Optical Properties

Dipping Cycles	Average Extinction Coefficient (K)
25	0.395
35	0.869
45	0.995

There is a direct correlation between the increasing thickness of the films and the greater extinction coefficient. This is because the increased thickness allows for more interaction with available light. An improvement in the performance of ZnO thin films in optical applications may be inferred from the boost in optical characteristics, in particular the rise in the extinction coefficient. The films have a higher extinction coefficient, which indicates that they are more effective at absorbing light. This is advantageous for applications such as photodetectors and optical sensors. Because of this enhanced absorption, these devices may undergo improvements in their sensitivity and accuracy, which may ultimately result in improved performance in practical applications.

4. CONCLUSION

The study investigated the properties of ZnO thin films made with dipping cycles using the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The films showed a thickness increase with dipping cycles, retaining a hexagonal wurtzite structure with enhanced crystallite size and decreased dislocation density. The optical characteristics of ZnO thin films have undergone significant changes as a result of the rise in film thickness that occurs as a result of an increased number of dipping cycles. Films that are thicker have a greater capacity to absorb light, which is advantageous for applications that need a high level of light absorption. There is a direct correlation between the increasing thickness of the films and the greater extinction coefficient. This is because the increased thickness allows for more interaction with available light. An improvement in the performance of ZnO thin films in optical applications may be inferred from the boost in optical characteristics, in particular the rise in the extinction coefficient. The films have a higher extinction coefficient, which indicates that they are more effective at absorbing light. This is advantageous for applications such as photodetectors and optical sensors. Because of this enhanced absorption, these devices may undergo improvements in their sensitivity and accuracy, which may ultimately result in improved performance in practical applications.

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