

## RESEARCH ARTICLE

# Structural and Optical Characterization of Chemically Deposited Polycrystalline Cadmium Selenide Thin Films

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**ABSTRACT:** Cadmium selenide (CdSe) thin films were successfully deposited onto glass substrates using the chemical bath deposition (CBD) technique at a controlled temperature of 70 °C. The resulting films were subjected to comprehensive characterization to assess their surface morphology, crystal structure, and optical properties. X-ray diffraction (XRD) analysis confirmed the polycrystalline nature of the films, identifying a predominant cubic structure with a well-defined (111) orientation. The structural parameters, including lattice constants and crystallite size, were systematically calculated, revealing insights into the film's crystalline quality. Energy-dispersive X-ray analysis (EDAX) confirmed a slight deviation from stoichiometry, suggesting the presence of intrinsic defects within the CdSe lattice. Optical characterization revealed that the films exhibit a direct allowed transition, as evidenced by the absorption coefficient and transmittance measurements. The optical band gap energy was determined, aligning with the expected values for CdSe thin films. The interplay between structural and optical properties is discussed in detail, highlighting the influence of crystallite size and defect states on the optical behavior. Furthermore, the films demonstrated semiconductor-like behavior, as evidenced by high-temperature electrical conductivity measurements. The observed electrical properties are attributed to grain boundary scattering effects, reinforcing the potential application of these films in optoelectronic devices.

**Keywords:** Cadmium Selenide, Polycrystalline thin films, Chemical bath deposition, High-temperature conductivity.

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## 1. INTRODUCTION

The Chemical Bath Deposition (CBD) technique has garnered significant attention in recent decades, particularly for the deposition of thin films, due to its numerous advantages [1]. One of the primary reasons for its popularity is its cost-effectiveness, as it does not require expensive or sophisticated vacuum equipment [2]. This makes CBD an accessible and practical method for depositing a wide range of materials, including sulfides and selenides, such as ZnS, CdS, PbS, CdSe, CuS<sub>2</sub>, ZnSe, Sb<sub>2</sub>S<sub>3</sub>, TiS, and HgS [1-9]. The ease of operation and the ability to deposit films from a

variety of materials have made CBD a widely used technique in materials science and electronic applications.

In recent years, the development of nanocrystalline materials has opened new avenues in the field of electronic applications. The ability to tune the crystallite size of a film allows researchers to modify the material properties, leading to enhanced performance in various applications. The technological potential of nanoparticles has further fueled interest in CBD methods, as they enable the precise control of material properties at the nanoscale [10]. Among the various semiconductor materials, cadmium chalcogenides, particularly cadmium selenide (CdSe), have emerged as promising candidates due to their excellent chemical, optical, and electrical properties. CdSe is particularly attractive for use in photoconductive and photovoltaic cells, thin-film transistors, sensors, lasers, and other optoelectronic devices [1-8].

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The deposition of CdSe thin films using the CBD technique has drawn significant attention because of its simplicity and numerous advantages over other deposition methods. Unlike methods that require sophisticated instruments and complex procedures, CBD offers a straightforward approach that minimizes material wastage and eliminates the need for toxic gases or vacuum conditions [11-13]. This makes it an economically viable option for the large-area deposition of thin films, which is essential for scaling up production for commercial applications. The CBD process operates on the principle of ion-by-ion condensation in a solution state, which is analogous to the grain-by-grain deposition observed in vacuum-based processes [12]. This slow and controlled growth mechanism allows for the formation of uniform and high-quality thin films.

CdSe materials have shown great potential in the fabrication of heterojunction solar cells, owing to their favorable electrical and optical properties. The study of CdSe thin films can also be extended to other II-VI compound semiconductors, such as CdTe and ZnTe, which are also known for their optoelectronic properties [7, 13]. Moreover, CdSe films possess higher carrier mobility compared to the widely used silicon films, making them suitable for high-performance electronic devices [4]. Numerous researchers have reported on the structural properties of CdSe thin films, contributing to a growing body of knowledge that supports their application in advanced electronic and optoelectronic technologies [2, 4, 14-17].

In this study, we aim to further investigate the structural and optical properties of CdSe thin films deposited by the CBD method. By systematically characterizing these films, we seek to provide a deeper understanding of the relationship between their structural parameters and optical behavior, which is crucial for optimizing their performance in various applications.

## 2. EXPERIMENTAL DETAILS

All chemicals utilized in this study were of analytical grade, ensuring high purity and reliability in the experimental procedures. The deposition of cadmium selenide (CdSe) thin films was performed on ultrasonically cleaned glass substrates using a simple, cost-effective, and scalable chemical bath deposition (CBD) process, as previously reported in the literature [17, 18]. This method was chosen for its efficiency and ability to produce uniform thin films in a dry alkaline medium, making it suitable for large-scale applications.

The precursors for the deposition process were cadmium chloride ( $\text{CdCl}_2$ ) and sodium selenosulfite ( $\text{Na}_2\text{SeSO}_3$ ), both of which were of analytical reagent (AR) grade. Sodium selenosulfite was synthesized by refluxing 4 grams of selenium powder with 90 grams of anhydrous sodium sulfite in 200 milliliters of double-distilled water at a temperature of 70 °C for 4 hours [17, 18]. This reaction produced a clear solution of sodium selenosulfite, which served as the selenium source in the deposition process.

For the deposition of CdSe thin films, a 10-milliliter solution of 1 M  $\text{CdCl}_2$  was prepared and transferred into a beaker. To this solution, 15 milliliters of anhydrous ammonia were added to adjust the pH of the reaction mixture to  $10 \pm 0.2$ . This pH adjustment is crucial as it influences the growth rate and quality of the resulting thin films. After ensuring the pH was within the desired range, an appropriate amount of sodium selenosulfite was added to the reaction bath. The total volume of the reaction solution was then adjusted to 180 milliliters with double-distilled water, ensuring consistent concentration and film growth conditions.

The cleaned glass substrates were mounted on a substrate holder and rotated at a constant speed within the reaction mixture to ensure uniform deposition across the entire surface. The rotation of the substrates during deposition is critical for achieving high-quality films, as it promotes uniform film thickness and homogeneity.

The structural characterization of the deposited CdSe thin films was performed using X-ray diffraction (XRD). The XRD patterns were obtained using a Philips X-ray diffractometer (model PW-1710) equipped with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The diffraction patterns provided detailed information about the crystalline structure, orientation, and phase purity of the films. Surface morphology and compositional analysis were conducted using a JEOL JSM-6360 scanning electron microscope (SEM) coupled with energy-dispersive spectroscopy (EDS) capabilities. The SEM analysis allowed for the examination of the surface features of the films, including grain size, texture, and uniformity. The EDS analysis was employed to quantitatively assess the elemental composition of the films, confirming the presence of cadmium (Cd) and selenium (Se) in the correct stoichiometric ratios.

These experimental procedures ensured the successful deposition and comprehensive characterization of high-quality CdSe thin films, paving the way for their potential application in optoelectronic devices.

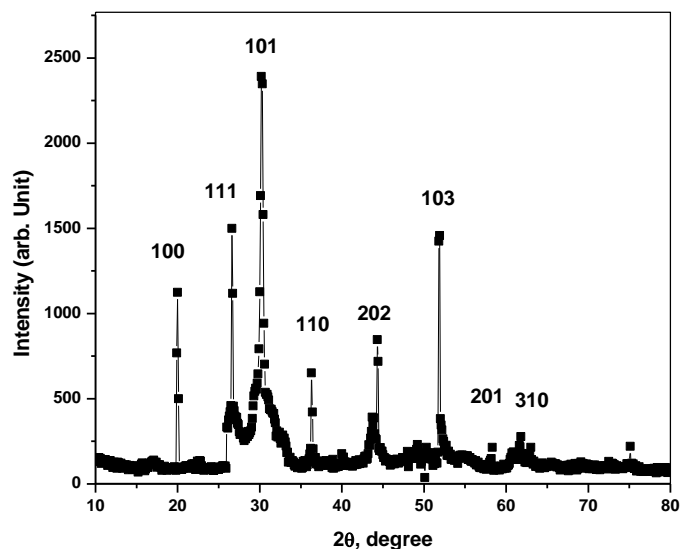
## 3. RESULTS AND DISCUSSION

The as-deposited CdSe thin film exhibited strong adhesion to the glass substrate, displaying a characteristic dark yellowish color, indicative of the film's composition and thickness. The growth kinetics of the CdSe thin film, driven by the chemical bath deposition (CBD) process, suggested a two-step mechanism: initial ion-by-ion condensation followed by cluster-by-cluster deposition. This sequential deposition process facilitated the formation of a uniform thin film with a terminal layer thickness of approximately 0.443 nm, which is consistent with the expected thickness for thin films grown under similar conditions.

The elemental composition of the CdSe thin film was determined using energy-dispersive X-ray spectroscopy (EDS). The analysis revealed that the film consisted of 54.13% cadmium (Cd) and 44.55% selenium (Se), indicating a slight excess of cadmium in the film. This compositional deviation

suggests the presence of intrinsic defects, such as cadmium interstitials or selenium vacancies, which could influence the optical and electrical properties of the films. The observed orange-red color of the grown CdSe thin film further corroborated the EDS findings, as the color is typically associated with cadmium-rich CdSe compositions. These compositional characteristics are consistent with data reported in the literature, where similar deviations from stoichiometry have been observed in CdSe thin films [19].

Cadmium selenide can crystallize in either a cubic (zincblende or sphalerite) or hexagonal (wurtzite) structure, with the hexagonal phase being thermodynamically stable and the cubic phase metastable [19]. The X-ray diffraction (XRD) analysis of the CdSe thin film, shown in Figure 1, revealed a polycrystalline structure with broadening of the diffraction peaks, indicating the presence of fine crystallites or nanocrystalline domains within the film. The most prominent diffraction peaks were observed at 21.62°, 24.02°, 26.64°, 31.84°, and 39.88° in 2θ angular units. The peak at 21.62° was indexed to the (100) plane of the hexagonal wurtzite structure, while the low-intensity reflection at 25.74° was assigned to the (111) plane of the cubic sphalerite structure. These observations are in agreement with the standard diffraction data for CdSe thin films [17, 19].



**Fig. 1.** Typical XRD pattern of CdSe thin film.

The broad hump observed in the XRD pattern is attributed to the amorphous nature of the glass substrate, as well as the possible presence of an amorphous phase within the CdSe film. Such broadening can also result from the nanoscale dimensions of the crystallites, which lead to a decrease in peak intensity and an increase in peak width. The average crystallite size of the films was calculated from the recorded for (101) plane using Scherrer formula as given in eq. (1):

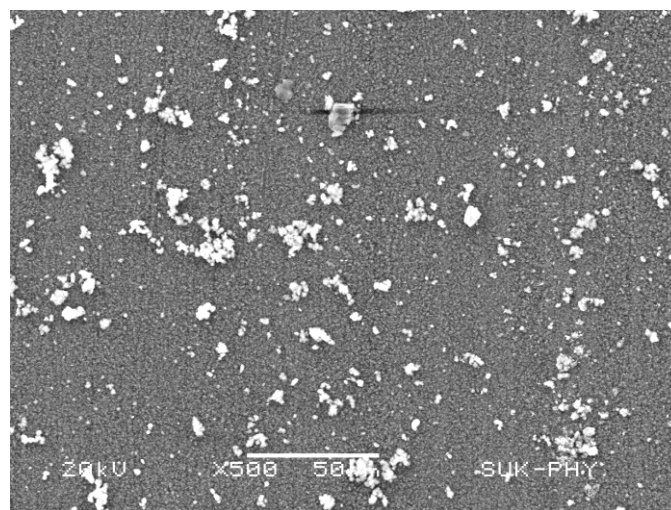
$$D = 0.89 \lambda / \beta \cos \theta \quad (1)$$

where  $D$  is the average crystallite size,  $\lambda$  is the wavelength of the incident X-ray,  $\beta$  is the full range at half outside of X-ray diffraction and  $\theta$  is the Bragg's angle. To quantify the crystallite size, the Scherrer formula was applied to the (101) diffraction peak, yielding an average crystallite size of approximately 21.53 nm. This value is typical for nanocrystalline CdSe films and reflects the controlled growth conditions achieved during the deposition process.

The observed crystallite size and the polycrystalline nature of the CdSe thin film have significant implications for the film's properties. The small crystallite size is likely to enhance the optical band gap of the film due to quantum confinement effects, while the presence of both hexagonal and cubic phases may lead to unique electronic properties that could be exploited in various optoelectronic applications. The results obtained from the XRD and EDS analyses provide a comprehensive understanding of the structural characteristics of the CdSe thin films, laying the groundwork for further investigations into their optical and electrical behavior.

The results demonstrate that the CBD method is effective in producing high-quality CdSe thin films with controlled composition and crystalline structure, making them suitable for a wide range of technological applications. Further studies, such as optical absorption and photoconductivity measurements, will be essential to fully elucidate the potential of these films in optoelectronic devices.

The surface morphology of the CdSe thin film was examined using scanning electron microscopy (SEM), as depicted in Figure 2.



**Fig. 2.** Typical SEM image of CdSe thin film.

The SEM analysis provided valuable insights into the microstructural features of the film, revealing that the crystalline grains appear to be fused together. This fusion likely results in overgrowth, where adjacent grains coalesce, leading to a densely packed structure. This overgrowth phenomenon can complicate the precise determination of

individual grain size because the boundaries between grains become less distinct. The resulting surface texture shows a uniform and continuous layer, which could influence the film's optical and electrical properties by reducing the scattering of charge carriers and light at grain boundaries. However, while the overgrowth enhances film uniformity, it also obscures the granular structure, making it challenging to distinguish and measure the size of individual crystallites. The dense packing of grains, as observed in the SEM micrograph, suggests that the film possesses a low level of porosity, which is advantageous for applications requiring high optical transparency and electrical conductivity. The surface features, including the smoothness and continuity of the film, indicate a high-quality deposition process, which is critical for achieving consistent performance in optoelectronic devices.

Optical properties of CdSe thin films have been extensively studied due to their significant implications in optoelectronic applications. Several researchers have reported that CdSe thin films exhibit an absorption edge around 730 nm, corresponding to a direct band gap energy of approximately 1.72 eV [10, 16, 19]. This characteristic makes CdSe thin films particularly suitable for applications in devices that operate within the visible and near-infrared (NIR) spectral regions. In this study, the optical absorption spectra of CdSe thin films deposited on glass substrates were examined over a wavelength range of 200 to 900 nm. The primary goal was to determine the optical band gap ( $E_g$ ), absorption coefficient ( $\alpha$ ), and the nature of the optical transitions occurring within the films. The absorption spectra, as shown in Figure 3, reveal a strong absorption of solar energy within the visible (VIS) and near-infrared (NIR) regions, with the as-deposited film displaying maximum absorbance within the visible spectrum. This high absorbance in the visible range indicates that the CdSe thin film is highly efficient at capturing solar energy, making it an excellent candidate for use in photovoltaic devices, such as solar cells.

To further elucidate the optical properties, the Tauc plot method was employed, where  $(\alpha h\nu)^2$  was plotted against photon energy ( $h\nu$ ), as depicted in Figure 4. This method is widely used to estimate the optical band gap of semiconductor materials. The plot for the CdSe thin film demonstrates a linear relationship at higher photon energies, which confirms the presence of direct band-to-band transitions. The extrapolation of the linear portion of the Tauc plot to the energy axis provides an estimate of the optical band gap. For the CdSe thin film studied, the band gap was found to be approximately 1.72 eV, consistent with the values reported in previous studies [16, 19].

The slight variations in the band gap energy observed in different studies can be attributed to factors such as film thickness, deposition conditions, and the presence of intrinsic defects or impurities. These factors can influence the electronic structure of the film, thereby affecting the band gap energy. For instance, a decrease in the band gap energy might be observed with increasing film thickness or the presence of cadmium-rich compositions, which introduce

additional electronic states within the band gap.

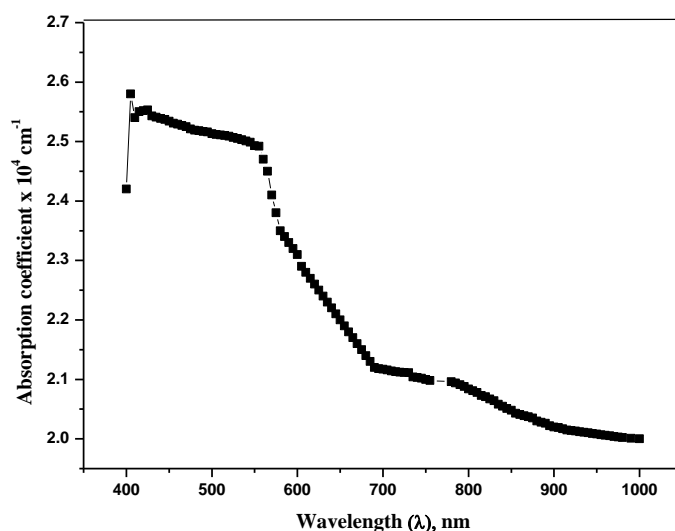


Fig. 3. Plot for Absorption coefficient vs Wavelength for the deposited CdSe thin film.

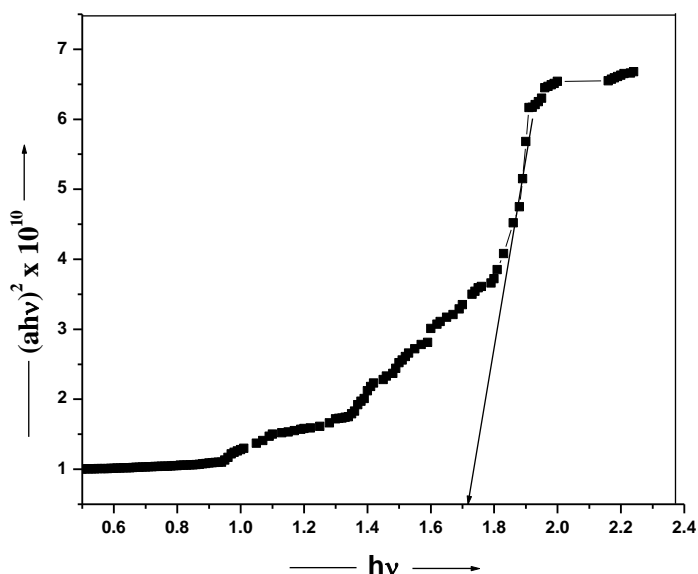


Fig. 4. Plot for  $(\alpha h\nu)^2$  vs  $h\nu$  for the deposited CdSe thin film.

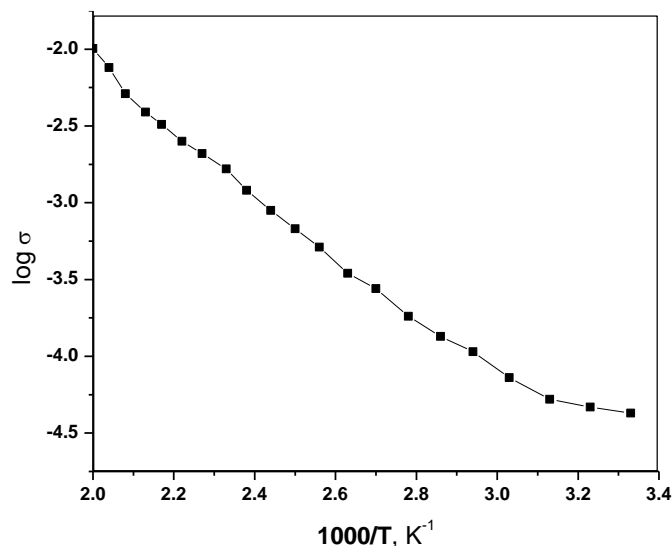
The linear behavior observed in the  $(\alpha h\nu)^2$  vs  $h\nu$  plot reinforces the conclusion that the optical transitions in the CdSe thin films are of a direct nature. This means that electrons can transition from the valence band to the conduction band without the need for a change in momentum, making these materials highly efficient for light absorption and emission processes. Such properties are crucial for the design and optimization of optoelectronic devices, including light-emitting diodes (LEDs) and laser diodes.

The optical studies confirm that CdSe thin films possess desirable optical properties, with a direct band gap energy around 1.72 eV and strong absorbance in the visible region.

These findings highlight the potential of CdSe thin films for applications in solar energy harvesting, photodetectors, and other optoelectronic devices. Further studies could explore the impact of varying deposition parameters on the optical properties, enabling fine-tuning of the material for specific applications.

The electrical conductivity of the polycrystalline CdSe thin film was measured over a temperature range of 300 to 550 K during both heating and cooling cycles. The measurements revealed a clear increase in electrical conductivity as the temperature increased, which is indicative of the semiconducting nature of the material. This temperature-dependent behavior of conductivity is a common characteristic of semiconductors, where thermal energy provides sufficient energy to excite more charge carriers from the valence band to the conduction band, thereby enhancing conductivity.

Figure 5 illustrates the relationship between electrical conductivity and temperature for the CdSe sample. The graph shows that as the temperature rises, the electrical conductivity initially follows a straight-line region with a low gradient. This region corresponds to a lower temperature range where the conduction mechanism is likely dominated by intrinsic carrier generation. As the temperature increases further, the conductivity curve transitions to a region with a steeper gradient. This change suggests that different conduction mechanisms are at play in the lower and higher temperature regions.



**Fig. 5.** Variation of electrical conductivity with working temperature for the deposited CdSe thin film.

In the higher temperature region, the conductivity data fits well with an exponential temperature variation model, which is described by the equation:

$$\sigma T^{1/2} = \sigma_0 \exp\left(\frac{-E_{a\sigma}}{KT}\right) \quad (2)$$

where  $\sigma_0$  is the pre-exponential factor,  $E_{a\sigma}$  is the conductivity activation energy, and  $K$  is the Boltzmann constant. The exponential dependence of conductivity on temperature in this region indicates that the conduction mechanism is likely influenced by thermally activated processes, such as grain boundary scattering.

Grain boundary scattering is a mechanism where charge carriers encounter resistance as they move across grain boundaries in polycrystalline materials. In the case of CdSe thin films, the grain boundaries can act as potential barriers, hindering the free flow of charge carriers. At lower temperatures, the charge carriers may have insufficient energy to overcome these barriers, resulting in lower conductivity. However, as the temperature increases, the carriers gain more thermal energy, which allows them to overcome the grain boundary barriers more easily, leading to an increase in conductivity.

The activation energy  $E_{a\sigma}$  provides insight into the energy required for charge carriers to participate in conduction. A higher activation energy typically suggests that more energy is needed to excite carriers across the grain boundaries or through localized states within the material. The observed temperature-dependent behavior and the calculated activation energy are consistent with the semiconducting nature of CdSe, where conductivity is enhanced with increasing temperature due to the increased availability of thermally excited charge carriers.

The findings from this study contribute to a better understanding of the electrical transport properties of CdSe thin films, particularly in terms of the conduction mechanisms that dominate in different temperature regions. This understanding is crucial for optimizing the material's performance in various applications, such as in sensors, photovoltaic devices, and other semiconductor-based technologies. Further investigation into the effects of grain size, film thickness, and doping on the electrical properties of CdSe thin films could provide additional insights into tailoring these materials for specific applications.

## 4. CONCLUSION

Non-stoichiometric CdSe thin films were successfully prepared using the Chemical Bath Deposition (CBD) technique by carefully optimizing various deposition parameters, including deposition temperature, time, pH of the reaction mixture, and the concentration and volume of the chemical bath solution. These optimizations were crucial in achieving the desired film quality and properties. The X-ray diffraction (XRD) analysis of the deposited films revealed their polycrystalline nature, with a cubic structure and the (101) plane as the preferred orientation. The presence of this specific crystalline orientation suggests that the deposition conditions were favorable for the growth of CdSe crystals in this particular configuration. The average crystallite size, calculated using the Scherrer formula, was found to be approximately 21.53 nm, indicating the nanocrystalline

nature of the films. Furthermore, optical studies of the films revealed a direct band gap of 1.72 eV, which is consistent with the properties required for various optoelectronic applications. The direct band gap suggests that the films can effectively absorb and emit light, making them suitable for use in devices such as photodetectors, solar cells, and other semiconductor applications. Finally, the study demonstrates the effectiveness of the CBD technique in producing high-quality CdSe thin films with desirable structural and optical properties. The insights gained from this work contribute to the ongoing development of CdSe-based materials for advanced technological applications. Further research could explore the effects of varying the deposition parameters even further or doping the films with other elements to enhance their properties for specific applications.

### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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