Research Article

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Tunable Optical and Sensing Properties of CdO and CdO-In_2O_3 thin Films for NH_3 Detection

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ABSTRACT

The composition, surface properties, optical characteristics, and sensing capabilities of the films were analyzed using XRD, AFM, and UV-Vis spectroscopy techniques. An average crystallite size of 76-93 nanometers was confirmed by x-ray diffraction studies of CdO and In_2O_3 composite nano films phases. The addition of In_2O_3 increased the energy band gap from 3.2 to 3.6 eV according to UV-Vis absorption spectrum, which is expected due to changes in crystallite size. AFM analysis of the thin films indicated homogeneous surfaces, and average particle size in the nanoscale range of 51.5 nm, depending on the mixing ratio. At an NH_3 gas concentration of 46 ppm, the composite films of CdO and In_2O_3 showed the highest sensitivity to NH_3 gas (91.4%) at room temperature.

Keywords: CdO; In_2O_3; Nano composite; Thin film; NH_3 sensor.

1. INTRODUCTION

Diversity of applications of nanomaterials is of great importance. Enabling technologies for manufacturing of nanomaterials have made rapid advancements that allow more efficient devices to be fabricated, relying on the enhanced properties of materials. Several studies have shown that the mixtures of nano oxides are advantageous in preparing nanocomposite improving the performance of sensors (Sukhavattanakul and Manuspiya, 2021). For possible applications in defense, solar cells, optics, and sensors it is necessary to produce thin films of nanocomposites. Solar cells, sensors and electronic devices have been widely used nanomaterials, with nanomaterials outstand in the solar cells and sensors (Chen *et al*. 2021). Chemical spray pyrolysis method is an inexpensive, simple and largely used technique to make the sensors, solar cells and electronic devices. We find that this method is adaptable to a variety of substrates on which the sensor of solar cell is to be deposited. (Ahirrao, 2019; Suhail, 2019). Phototransistors, photodiodes, transparent electrodes, and gas sensors are only a few of the numerous applications that are possible (Vinoth and Gopalakrishnan, 2018; Liu *et al.* 2003).

Since CdO operates with great efficiency in a narrow energy gap of 2.5 eV, it possesses significant radiation absorption and emission properties (Mohammed *et al.* 2020). This material is characterized by its exceptional light transmission in the visible spectrum simultaneously (Korotcenkov and Cho, 2017). Another example of wide bandgap n-type semiconductors is indium oxide (In_2O_3). The latter is frequently used in electrical devices and is considered a key component of transparent conductive oxides. Due to its exceptional chemical stability, electrical conductivity, light transmission, and excellent adhesion to substrates, indium oxide is used in sensing applications (Fahad et al., 2016). Additionally, In_2O_3 is involved in solar cells and sensors related to a wide range of applications (Gründler, 2007; Jasim and Al-Jumaili, 2019; and Al-Jumaili and Jasim, 2019). improvement in sensitivity and selectivity of gas sensors have remained a major focus (Elangovan *et al.* 2004; Yang et al. 2014; Zhang *et al*. 2017). The functional materials used in the gas sensor layer changes the properties if a particular gas is present. As metal oxide semiconductors provide outstanding thermal and physical stabilities, this sensor can monitor harmful toxins. They are high sensitivity, good selectivity, and have good stability (Bai *et al*. 2010; Li *et al*. 2018) metal oxide semiconductor-based sensors. In fact, a large number of investigations have been performed to enhance sensor performance by surface modification, metal doping and mixing various metal oxides (Jassim and Samar, 2022; Ismail *et al*. 2005; Badawi *et al*. 2016). The oxidized metal compounds can have excellent sensitivity and selectivity for gas detection. Consequently, the optical properties of the sensitive materials are thus to be studied as a function of composition ratio and processing conditions. In this work, CdO-In_2O_3 thin films with various In_2O_3 concentrations were made via thermal spray technique. The effect of these components on structural, optical, and electrical properties was investigated and the optimal condition to maximize NH_3 gas detection was also determined.

2. EXPERIMENTAL DETAILS

CdO-In_2O_3 thin films were deposited on silicon substrates using the chemical vapor deposition method and for a temperature of 300°C. Single crystal oriented (111) p type, resistivity 1--10 Ω m, silicon substrates 1.5 x 1.5 cm (1.1 × 1.5 cm for 200 nm) were used. For the substrate cleaning, the substrates were ultrasonically cleaned for 5 minutes in distilled water and a diluted hydrofluoric acid solution then dried in a hot air (Aljamel and Jassim 2019). Mixing in different volumetric ratios, (30%) CdO, (70%) CdO, and (90%) CdO led to precursor solutions of CdCl2•2H2O and $InCl_2$•$2H_2O$ at a concentration of 0.1 M added to CdO In2O3 solutions. It is these mixtures, called CdIn0, CdIn1, and CdIn2 respectively. Spraying duration was set to 5 seconds and soaking time to 15 seconds at pressure of 3 bar. Spraying rate was 2 ml/min, the distance between the sprayer and the substrates was 25 cm. The film thickness (d = 250 ± 10 nm) was determined using the optical interferometry technique with a He-Ne laser (λ = 632 nm). The structural properties were examined using X-ray diffraction (XRD-6000) with Cu Kα radiation (λ = 0.154 nm) in the 2θ range 20° to 80°. Surface topography was analysed using an atomic force microscope (AFM Atomic Force Microscope, Dual Scope TMDS, Germany, AA3000). Optical properties were measured using UV-Vis spectrophotometer, Shimadzu, UV-2550 Japan. The sensitivity to ammonia gas was measured using a gas sensor system. The system consists of a cylindrical test chamber with a diameter of 30 cm and a height of 35 cm, featuring an inlet for test gas flow and an air entry valve for purging. At the base, there is an electric heater connected to a thermocouple to control the operating temperature. A UNI-T UT8IB digital multimeter measures the resistance, and the resistance changes over time were recorded as the sensor is exposed to the gas flow. The gas is fed through a tube above the sensor within the test chamber to ensure accurate sensitivity measurements.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

Fig. 1 presents the XRD patterns of the prepared thin films of CdIn0, CdIn1, and CdIn2. The XRD pattern for pure CdO, shown in Fig. 1(a), reveals diffraction peaks at the (111), (102), (220), (222), and (211) planes. These peaks confirm the cubic structure of CdO, as indicated by the ICDD card no. 00-044-1159 (Abdullah, 2016). Fig.1(b) displays the XRD pattern for a CdO film with 90% CdO and 10% In2O3. The addition of In2O3 to CdO causes a decrease in the intensity of the CdO peaks. The decrease in peak intensity indicates that the incorporation of In2O3 into the CdO matrix affects the crystallinity of the CdO phase. Fig. 1(c) shows the XRD pattern of a mixed film composed of 70% CdO and 30% In2O3. The intensity of the CdO peak decreases with increasing In2O3 content in this case, indicating that the substitution of In2O3 for CdO decreases the size of CdO crystallites. This confirms the presence of a disrupting effect of In2O3 in CdO lattice and yielding a decrease in peak intensity (Kassim *et al.* 2010). It was done using Debye-Scherrer equation to calculate crystallite size: D=Kλ /βcos θ

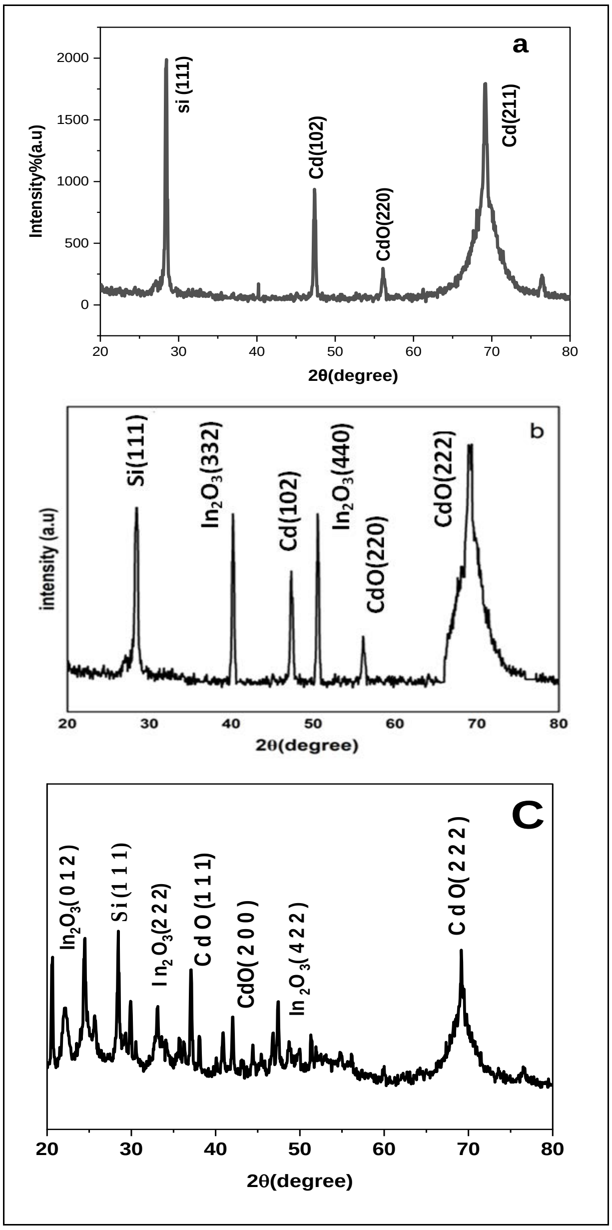

Fig. 1: XRD pattern of (a) CdIn0, (b) CdIn1 and (c) CdIn2

Where:

- D is the average crystallite size (in nanometers).
- KK is the Scherrer constant (usually taken as 0.9).

- λ is the X-ray wavelength (typically Cu Kα = 0.154 nm).
- β is the full width at half maximum (FWHM) of the peak, which is the peak width after correcting for instrumental broadening.
- θ\theta is the Bragg angle measured from the XRD data.

This peak intensity decrease further confirms that the addition of In2O3 decreases the crystal growth of the CdO film since the addition of In2O3 in certain ratios enables the crystallization of the film material. More importantly, increasing the crystalline structure, (if not increasing it in some way) is helpful for the optimal development of a high-quality crystal. Using the Scherrer equation (Adullah, 2016), we calculated the average grain size for the films. It turned out that the particle sizes average to 24 nanometers for CdIn0, 17 nanometers for CdIn1, and 15.3 nanometers for CdIn2. The data reveals clearly that when In2O3 is substituted into CdO, the size of the CdO crystals is reduced. The presence of In^{3+} ions, which are slightly larger than Cd^{2+} ions, creates strain within the CdO lattice, hindering crystal growth. Moreover, In^{3+} ions can act as additional nucleation sites, contributing to the formation of smaller crystals. Films characterized by a high density of defects may exhibit increased strength due to a defect strengthening mechanism, where these defects enhance the material properties by increasing hardness and resistance to stress.

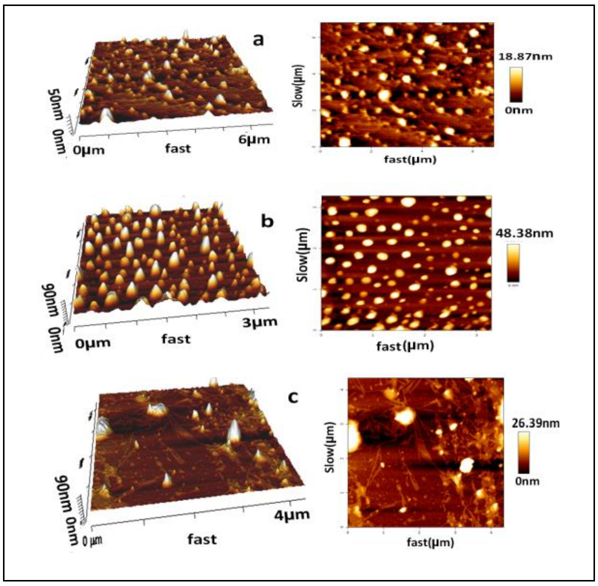

Fig. 2: The AFM image of (a) CdIn0, (b) CdIn1 and (c) CdIn2

3.2 Atomic Force Microscopy

Examination of the film's surface morphology using atomic force microscopy (AFM) provided important insights into its suitability as a gas sensor (Fig. 2). For the CdIn0 film, the AFM images showed an average grain size of 76 nm, a root mean square roughness (RMS) of 2.92 nm, and an average roughness of 2.34 nm, a relatively smooth surface indicating a uniform grain distribution with positive values for consistent sensor performance. In contrast, the CdIn1 film exhibited an increased average grain size (68.8 nm) as well as higher roughness values, specifically an RMS roughness of 5.21 nm and an average roughness of 4.20 nm. These changes suggest that the addition of In_2O_3 introduces more surface irregularities. This could increase the number of active sites for gas interactions but also affect the uniformity of the film. he CdIn2 films bear an average particle size of 51.5 nanometers with marked roughness based on average Root Mean Square roughness of 6.33 nm and the average roughness is 51.5 nm. This resulting high roughness indicates a denser granular structure potentially having more active sites and thus greater sensitivity in gas sensors. With this, though, improved may also affect the mechanical stability of the film. Thus, while increasing particle size and roughness increases gas absorption and sensor sensitivity, this must be done at a thin enough concentration/density to restrain degradation of the sensor performance and stability.

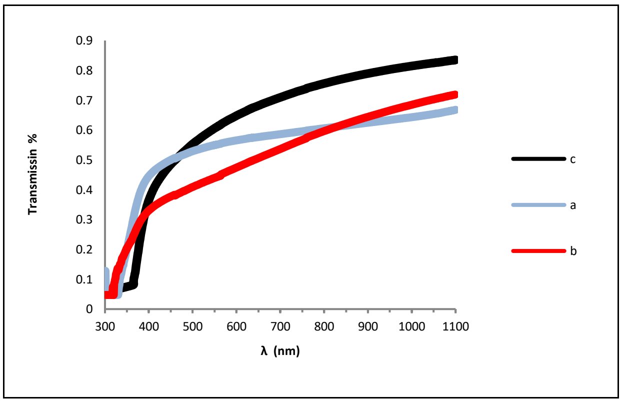

Fig. 3: The transmittance spectra of (a) CdIn0, (b) CdIn1 and (c) CdIn2 thin films

3.3 Optical Analysis

Factors, which include thickness, material composition and surface characteristics, affect the transmittance of a film. Fig. 3 shows the transmittance spectrum for the CdIn0, CdIn1, and CdIn2 films. The CdIn0 films stand out for their high transmittance, which reaches an astounding 57% at 600 nm, a wavelength in the visible light spectrum. This transmittance level suggests that CdIn0 films, let a considerable amount of visible light to flow through them, indicating that their absorption and scattering in this wavelength range are comparatively low. These qualities are seen to be advantageous. The transmittance values of the CdIn composite thin films are greater in comparison. In particular, transmittance levels of 70% and 90% are demonstrated by the CdIn1 and CdIn2 thin films, respectively. The better optical characteristics of the material can be the reason for the notable increase in transmittance that occurs with the addition of In_2O_3. Because of well-known high transparency of In_2O_3 in the visible spectrum, the overall light transmission of the composite films is improved. The significant increases in transmittance seen for CdO- In_2O_3 films suggest that the addition of In_2O_3 efficiently lowers light absorption and scattering, increasing the quantity of light transmitted.

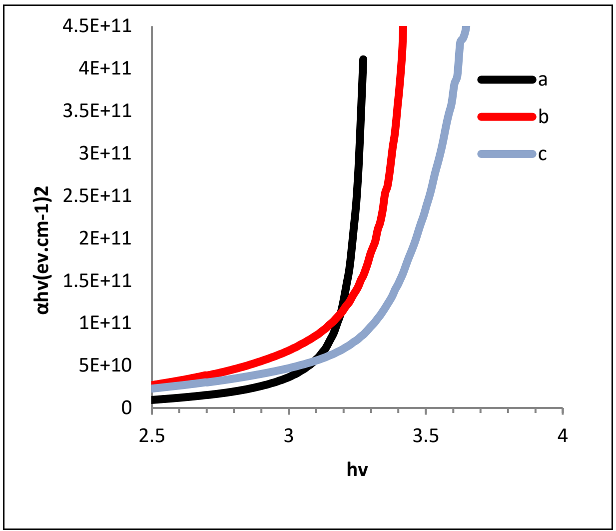

Fig. 4: Optical energy gap of (a) CdIn0, (b) CdIn1, (c) CdIn2 thin films

Table 1. The relative sensitivity values (S%), response time, and recovery time for CdIn1 thin films

Concentration	Sensitivity (%)	Response Time (s)	Recovery Time (s)
17 ppm- RT	45.6	15.8	8.8
46 ppm-RT	91.4	13.9	7.9
112 ppm-RT	60.8	13.9	12.9
112 ppm-50°C	24.4	14.2	15.3
62 ppm-100°C	19.6	11.6	17.7

3.4 Bandgap Energy

The optical energy gap of the thin films CdIn0, CdIn1, and CdIn2 is shown in Fig. 4. Transmittance is a crucial component for applications like optical coatings, transparent electrodes, and sensors, since it is one of the fundamental optical properties that controls how much light can flow through a material. In this context, we studied the transmittance characteristics of CdIn0, CdIn1, and CdIn2 thin film compositions. At 600 nm, the transmittance of the pure CdIn0 films was found to be 57% in the visible spectrum. This means that incident light passes through 57% of these films, with some absorption and scattering to 43% of it. The moderate level of transparency observed here indicates that CdIn0 thin films can be applied in those applications where some transparency is acceptable, but the film must also be able to absorb or interact with the light. Typically, this level of transmittance occurs for materials used in optical applications in which transparency is desired approximately balanced with light absorption. Adding 10% In_2O_3 into the CdO films increases the transmittance to 70% at 600 nm. The reason for this enhancement can be related to the optical properties of In_2O_3 – as In_2O_3 is a transparent material.

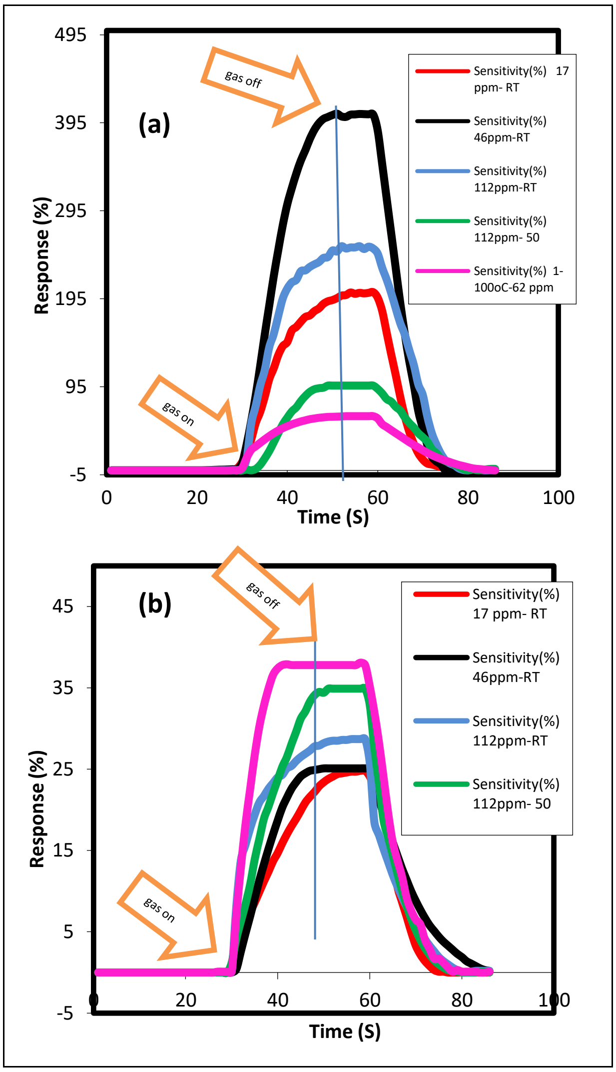

Fig. 5: NH_3 gas sensing response for (a) CdIn1, (b) CdIn2 thin films

The overall transparency of the film is improved by blending In_2O_3 with CdO, since In_2O_3 can block the light transmitted or scattered in the thin film. This increase from 57% to 70% indicates that even a small amount of In2O3 can greatly improve the light transmission potential of the composite film (Kassim *et al.* 2010; Abdullah, 2016). At 30% In_2O_3 content, we achieve 90% transmittance at 600 nm. Most of this substantial improvement in transparency is attributable to the higher amount of In_2O_3, which offers superior optical properties than any CdO alone. Close to 90% transmittance indicates that these films allow most of the visible light to pass through, making them suitable for applications requiring excellent light transmission. Such high transmittance is desirable for advanced sensor applications where maximum visibility is crucial.

Table 2. The relative sensitivity values (S%), response time, and recovery time for CdIn2 thin films

Concentration	Sensitivity (%)	Response Time (s)	Recovery Time (s)
17 ppm- RT	24.8	18	13.3
46 ppm-RT	25.1	13	18.4
112 ppm-RT	28.7	13.9	13.6
112 ppm- 50°C	34.9	15.1	11.4
112 ppm- 100°C	38.1	7.4	12.6

3.5 Measurement of NH_3 Sensing

The sensitivity of metal oxide films to gases is influenced by a complex interplay of factors, including temperature, material composition, crystal structure, particle size, surface topography, and porosity. Temperature, for example, because it determines how a gas interacts with the sensor surface. In addition to the increase in sensitivity, this improvement is likely due at least partially to higher temperatures being generally better from the standpoint of gas-phase molecular mobility (as well as surface reaction rates) needed for a sensor response. For example, oxygen molecules draw electrons out of the metal oxide surface and they become negative ions when they bind with it. This technique slightly raises the metal oxide's surface resistance property which is very significant in gas detection. For example, when ammonia gas is introduced, it reacts with the adsorbed oxygen as well as the surface granules of the metal oxide. The NH_3 molecules lose electrons to the surface, which makes the surface resistance larger. The sensor responds by sensing even minute changes in its resistance, before and after the gas is introduced and removed respectively. This ability makes the sensor an attractive development for use in industrial safety and environmental monitoring, as low detection limits on harmful gases are important to prevent the most dangerous of situations from occurring. These sensors have rapid response and recovery times so that they can offer real-time data, which is important in specific sectors such as petrochemical industries or enclosed environments. Moreover, perovskites can tune the characteristics of their sensing properties based on material composition being tailored towards the application, such as detecting pollutants, monitoring health or maintaining operational safety. Therefore, metal oxide gas sensor can be undoubtedly considered as an element in technology development. The sensitivity calculated according the following relation

$$S = \frac{R_g - R_a}{R_g}$$

R_g − gas resistance
Ra − air resistance

4. CONCLUSIONS

In this work, the successful fabrication of CdIn0, CdIn1 and CdIn2 thin films on silicon substrates using thermal chemical spraying is reported. The structural appeared to be in a crystalline state for the fabricated films. This means that the overall transformation of these thin films using this deposition technique has been successful in creating good quality and similarly crystalline-structured thin films. The optical properties of the films were extensively probed by UV-visible absorption spectroscopy. Incorporation of In2O3 in CdO matrix led to optical bandgap enhancement as also noticed. For example, for the films with 30% content In2O3 in the CdO film have a bandgap energy of 3.6 eV. The change in the energy band gap can be attributed to the fact that doping may cause distortions in the crystal lattice of the semiconductor due to differences in the size and charge of the dopant atoms compared to the host material's atoms. This distortion may lead to changes in electron distribution, thereby increasing the energy band gap. Alternatively, the quantum confinement effect can also be responsible for the increase in the band gap, a phenomenon particularly noticeable in nanostructured semiconductors.

The surface morphology of the films was revealed by AFM. Their average size was 87.5 nm. Additionally, it was found that the surface roughness of the films increased with the In_2O_3 mixing ratio, from 2.34 nm for CdIn0 to 6.23 nm for the highest In_2O_3 concentration studied. The surface roughness, however, increases as the film surface provides more opportunities for interaction of gas molecules with the surface, an aspect important for gas sensing technologies. The sensitivity of the sensor is enhanced by increasing the gas adsorption due to a rougher surface providing additional active sites. Finally, the CdIn2 thin films are promising with tunable optical band gaps that can be tuned by In2O3 concentration. For applications in gas sensors, specifically, these properties are highly desirable, as both specific optical properties and high surface reactivity are necessary. These findings provide insight into the understanding and use of advanced thin film materials with tunable properties as appropriate for many technology applications.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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