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Synthesis and characterization of ceramic nanocomposite thin films SiO_2-NiO for gas sensing

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ABSTRACT

This paper focuses on the preparation and characterization of thin films of SiO_2-NiO ceramic nanocomposite. These films were synthesized using the sol-gel method and deposited onto a quartz substrate through spin coating after hydrofluoric acid (HF) treatment for the glass substrate. The films synthesized using 70% SiO_2-30% NiO mole ratio. Subsequently calcined at three different temperatures: 500 °C, 700 °C, and 900 °C. The diagram of X-ray diffraction (XRD) revealed the presence of large quantities of semiconductor NiO at 2θ = 37.4°, 62.8°, 75.5°, and 79.4° in addition to the presence of SiO_2 in the structure, at 2θ = 43.3°. The surface properties were studied using scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR). The test results demonstrated structural and surface properties compatible with the requirements of sensing applications. FT-IR spectra shows absorption bands of Si-O-Si, Ni-O and O-H. This coating has shown good sensitivity and effective response toward ammonia gas under various measurement conditions, including temperatures ranging from 50 to 200 °C. The film calcinated at 500 °C exhibited high sensitivity to NH_3 gas at room temperature due to the presence of hydroxyl groups (OH^-), which increased its ability to adsorb the gas. Additionally, the film calcinated at 900 °C showed even higher sensitivity compared to the film calcinated at 700 °C.

Keywords: thin film, SiO_2, nickel oxide, nanocomposites, electrical gas sensor, sol-gel method.

INTRODUCTION

Semiconducting nanostructured metal oxides are desirable for creating inexpensive chemical gas sensors that are sensitive to dangerous gases. Metal oxide materials have a vast surface area for contact with gaseous mediums due to their small grain size and porous nature. This allows for high sensitivity to diverse gases [1, 2]. Various techniques are currently employed to produce nano-materials, including wet chemistry, chemical vapor deposition (CVD) [3], and physical vapor deposition (PVD) [4]. An essential aspect of semiconductor gas sensors is the ability to effectively utilize nanoscale metal oxides that possess very consistent structural characteristics, and physical characteristics (porosity, thickness, and grain size). The fabrication technology can be used for precise regulation of the process parameters. So far, different methods have been used to make NiO thin films. These include pulsed laser deposition [5], sputtering [6], heat evaporation [7], sol-gel [8], and electrochemical deposition [9]. The sol-gel method is one of the best because it is easy to use, economical, and reusable process [10, 11]. Also, it's easy to make high-quality thin films on top of a variety of substrates that come in different forms. In particular, films made using the sol-gel method have some important features, such as high porosity and uniformity, as well as good nano crystallinity [10]. These are all properties that are needed to make metal oxide semiconductor (MOS) gas sensors better at sensing gases. Nickel oxide, the metal oxide that was taken into consideration for this work, possesses a number of extremely intriguing qualities, including outstanding electrical properties and strong chemical stability. As a result, it is commonly used as a model for positive metal oxide materials (p-type) [12, 13]. Thin films are created using different process such as sputtering pulsed laser deposition or sol-gel techniques [14] that are on nanocrystalline scale. Nickel oxide is a material that provides sensing properties when they are exposed to a variety of gases, including NO_2 [15], CO [16], H_2S [17, 18], and HCHO (formaldehyde) [19, 20]. Usually, a change in the sensor's electrical properties (resistance) is used to detect gas. However, optical changes are also a choice [21].

This research aims to create a ceramic nanocomposite porous coating layer composed of SiO_2-NiO. The goal is to use this coating in gas sensing applications. The focus will be on studying the coating's structural, physical, and chemical properties, with an emphasis on the impact of nanotechnology in enhancing sensitivity and accuracy in detecting specific gases like ammonia. The study will also test the coating's response in different environmental conditions including variations of operating temperature, and analyze its efficiency in detecting low gas concentrations.

EXPERIMENTAL

Sol-gel method was adopted to synthesize nanocomposite thin film of NiO nanoparticles at SiO_2 porous matrix by mixing two prepared solutions: the silica precursors "matrix solution", and another containing the NiO precursor "doping solution" in volume ratio $70SiO_2$-30NiO. At the outset, matrix solution of silica oxide (SiO_2) is prepared by combining tetraethylorthosilicate (TEOS), methyltriethoxysilane (MTES), HCl acid, ethanol (ETOH), and water. The molar ratios for each component are as follows: H_2O: ETOH: HCL: TEOS: MTES (4:4:0.02:1:1). These ingredients are then thoroughly mixed using a magnetic stirrer at room temperature for a duration of 3 minutes. Secondly, the doping solution was prepared by dissolving nickel chloride ($NiCl_2.4H_2O$) in ethanol by stirring for 20 min at room temperature. 3-(2-aminoethylamino) propyltrimethoxysilane (AEAPTMS) was then added in drops to the doping solution during the mixing process. The molar ratios for $NiCl_2.4H_2O$: AEAPTMS were 1:0.25, while the ethanol amount in the second solution was added to reach a specific concentration in both solution (Solution 1+Solution 2) of 50 g/L. After that, the two solutions were cooled using ice bath before mixing them together to control the coating conditions. The coating process is carried out by depositing nano-ceramic films on a quartz substrate using a spin-coating method. Then the substrate was placed in a hot air oven for drying at 65 °C for 24 h. The calcination process was done at different temperatures (500, 700, and 900 °C) at a heating rate of 5 °C/min., for 30 minutes.

CHARACTERIZATION

The structure of SiO_2- NiO nanocomposite coating layer synthesized via sol-gel process and applied on quartz substrate through spin coating has been determined by the X-ray diffraction, type ("Shimadzo, XRD6000, diffractometer, Japan") using (Cu-Kα) with (30 kV, 40 mA) and wavelength of (λ = 1.5406 Å) in the range 2θ = 20–80°. The XRD diffraction pattern was registered at room temperature. The microstructure was investigated via (TESCAN VEGA3) scanning electron microscope (SEM), while vibrational spectra investigated by FTIR, type (Iraffinity- 1Shimadzu) model for condensed powder sample. All the examination was carried out at room temperature for samples annealed at three temperatures: 500 °C, 700 °C, and 900 °C. Thin film composed of NiO nanoparticle in SiO_2 matrix is examined for gas sensor by using NH_3 gas and carried out at four operating temperatures 50, 100, 150, and 200 °C.

RESULTS AND DISCUSSION

Characterization of microstructure

The XRD pattern of the nanocomposite SiO_2-NiO films processed by the sol-gel method-spin coated on quartz substrate and calcinated at (500, 700, and 900) °C are shown in Figure 1. This figure shows the broad signal for SiO_2 at 2θ = 29.9°, 45.4° and 53.2°. The broadening of this peak decreases with increased temperature due to the transformation of SiO_2 into crystalline phase, this corresponds to (JCPDS cards # 01-080-2148), on the other hand, we can observe peak position for SiO_2-NiO at 2θ = 43.3° [22, 23]. The intensity of this peak progressively increases as the annealing temperature increases, indicating an increase in the crystalline phase. The relative intensity of the NiO peak at 2θ = 37.4°, 62.8°, 75.5°, and 79.4° also increases with temperature, corresponding to the cubic phase of NiO (JCPDS cards # 00-047-1049) [24]. This suggests that the NiO diffraction peak is dominant in these films. Additionally, other peaks are observed in the XRD pattern at 2θ = 34.8° and 72.3° for samples annealed at 500 °C and 700 °C, indicating the presence of other metastable nickel oxide phases or nickel hydroxide, which disappear at higher treatment temperatures.

Determination crystallite size (D_{XRD}) of samples from XRD analysis using Scherrer's equation as in Equation 1:

$$D_{XRD} = 0.89\, \lambda / \beta \cos\theta \quad (1)$$

where: λ is X-ray radiation wavelength in A°, θ is the angle of diffraction, and β is the full width at half maximum (FWHM) in radians in the 2θ scale [25]. The crystallite size of SiO_2 and NiO at 500, 700, and 900 °C shown in Table 1.

Figure 2 shows the surface topography of thin films of SiO_2-NiO calcined at 500, 700, and 900 °C using a scanning electron microscope. At a temperature of 500 °C Figure 2A, we notice the presence of aggregates with an irregular surface structure, and this indicates incomplete crystallization. The film annealed at a temperature of 700 °C (Figure 2B) showed an improvement in surface regularity, as some cracks and large voids appeared, which indicates an increase in crystallization of the material. As the temperature increased, the surface regularity also increased when the film was annealed at a temperature of 900 °C. As shown in Figure 2C, there was a noticeable improvement in surface regularity with the presence of clear and well-defined nanoparticles.

The changes that occur in the structure of the SiO_2-NiO nanocomposite at different annealing temperatures (500, 700, and 900 °C) are shown in

Table 1. Crystallite size with different calcination temperature

2Θ	T °C	D (A°)
43.1448	500	2.09504
42.6119	700	2.12000
43.0100	900	2.10130

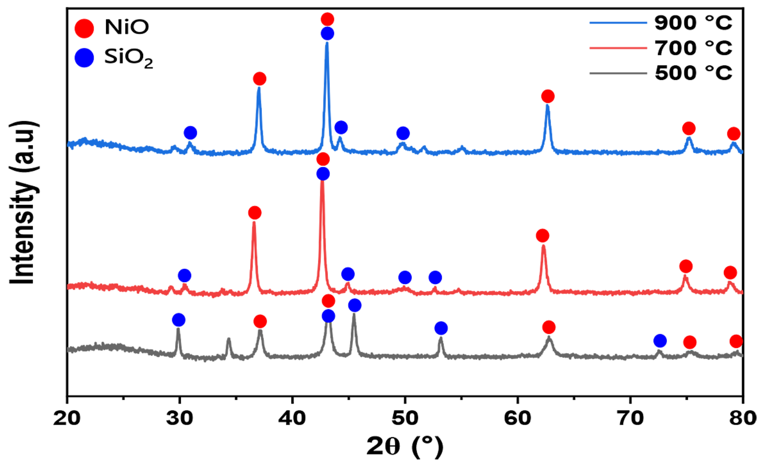

Figure 1. X-ray diffraction patterns of SiO2- NiO nanocomposite films at three calcination temperatures (500, 700, 900 °C). Diffractograms were shifted arbitrarily for better visualization

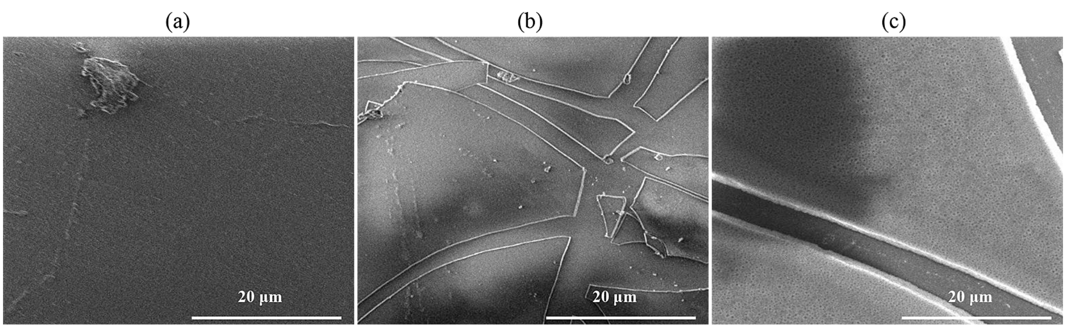

Figure 2. SEM images of SiO_2- NiO nanocomposite films annealed at three temperatures: a) 500 °C, b) 700 °C, and c) 900 °C

Fig. 3 with the help of the FTIR spectra. The spectra show the wavelengths in a range of (460–550) cm^{-1} which corresponds to Si-O-Si vibrations indicating the presence of a silica phase [26]. Such vibrations increase in intensity as the temperature increases. The peaks around (550–600) cm^{-1} are typically associated with the presence of Ni-O [26], indicating the presence of nickel oxide. The shoulder at 1650 cm^{-1} detects an O-H stretching vibration, usually present due to the absorption of water or hydroxyl groups but the vibrations intensity decreases with the increase in annealing temperature. O-H stretching vibrations are generally present in the range of (3000–3500) cm^{-1}[27, 28]. It is within this range where absorption at 500 °C is noticed but which drops down at 700 °C and 900 °C owing to water evaporation and hydroxyl group removal.

MEASURE AND CHARACTERIZE GAS SENSOR PROPERTIES

A thin film of SiO_2-NiO is examined using NH_3 gas. The examination process is carried out at four temperatures: 50, 100, 150, and 200 °C. The examination process is carried out inside a cylindrical chamber with a size of 20 × 60 cm. It is equipped with valves that are directly connected to the NH_3 gas bottle to control the gas concentrations entering the chamber with a heater placed below the sample to control temperature changes as shown in Figure 4. We measure the resistance in the presence of air only, and when the resistance stabilizes, we pump the gas to be tested, where we notice that the resistance changes with the change in testing temperature. Sensitivity means the ability of the thin film to detect small

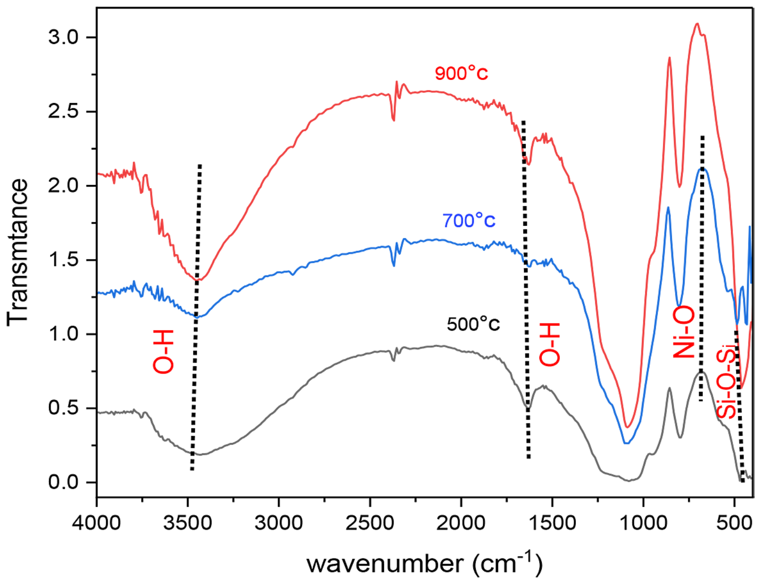

Figure 3. FTIR spectra of SiO_2-NiO nanocomposite films annealed at different temperatures

Figure 4. Gas sensing apparatus

changes in gas concentrations in the surrounding environment and its value can be known through the following equation [29] Equation 2:

$$S\,(\%) = \left|\frac{R_a - R_g}{R_g}\right| \times 100\% \quad (2)$$

where: Ra – is the sensor resistance in dry air and Rg – is the sensor resistance in the gas test.

Figure 5 shows the dynamic sensitivity curves of SiO_2-NiO exposed to NH_3 gas. The film showed high sensitivity in the presence of the gas for samples annealed at 500 °C and 900 °C, but at annealing temperature, of 700 °C showed lower sensitivity because of losing of hydroxyl groups (OH-), which was present at 500 °C and did not form a regular crystalline surface like that found at 900 °C this behavior agrees with FTIR results. Both low and high calcination temperatures provide distinct surface properties that enhance the sensor's interaction with the gas.

Response time is one of the basic requirements in gas sensors devices. Figure 6 shows the film prepared at 900 °C has a distinctive response at 50 °C, which allows a rapid and stable interaction with the gas. Furthermore, the reduction of the response time compared to other films prepared at 500 °C and 700 °C, which shows a faster response with a higher examination temperature, which leads to activation of OH and defects increases the reaction with the gas. Figure 7 shows the thin film prepared at 500 °C a good recovery time using a sensor temperature of 200 °C,

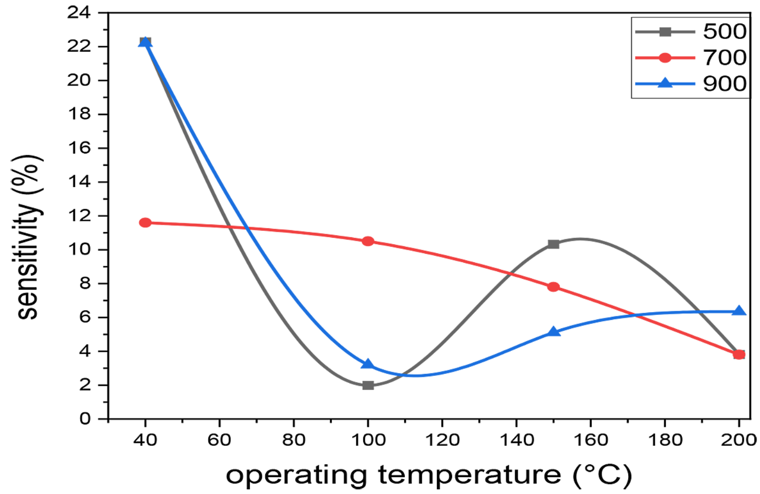

Figure 5. Sensitivity vs. operating temperature of SiO_2-NiO nanocomposite films at the specified temperatures for NH_3 gas. The lines connecting experimental points are the 'eye-guide' only

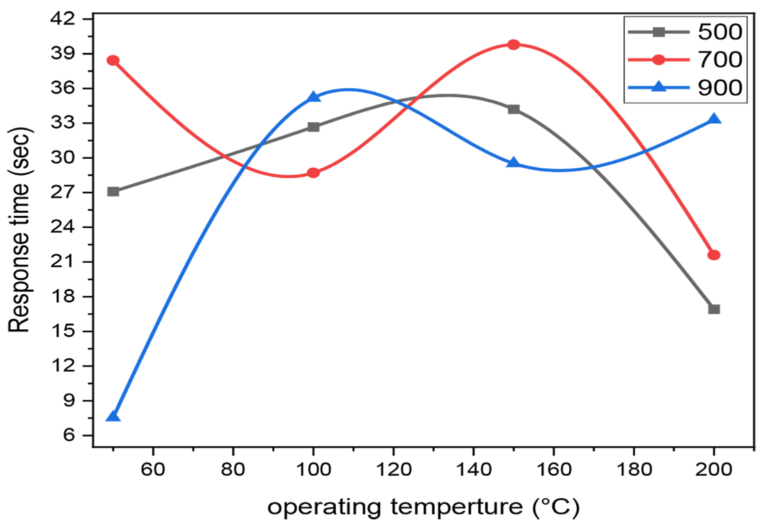

Figure 6. Response time of SiO_2-NiO thin films at different operating temperatures for NH_3 gas. The lines connecting experimental points are the 'eye-guide' only

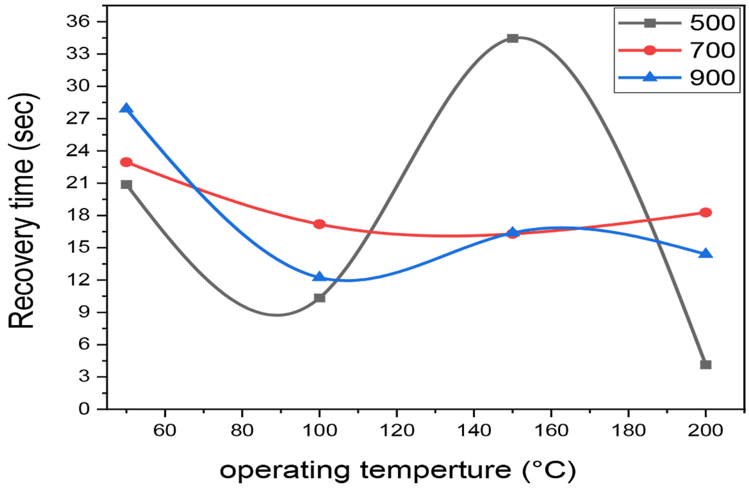

Figure 7. Recovery time of SiO_2-NiO thin films at different operating temperatures for NH_3 gas. The lines connecting experimental points are the 'eye-guide' only

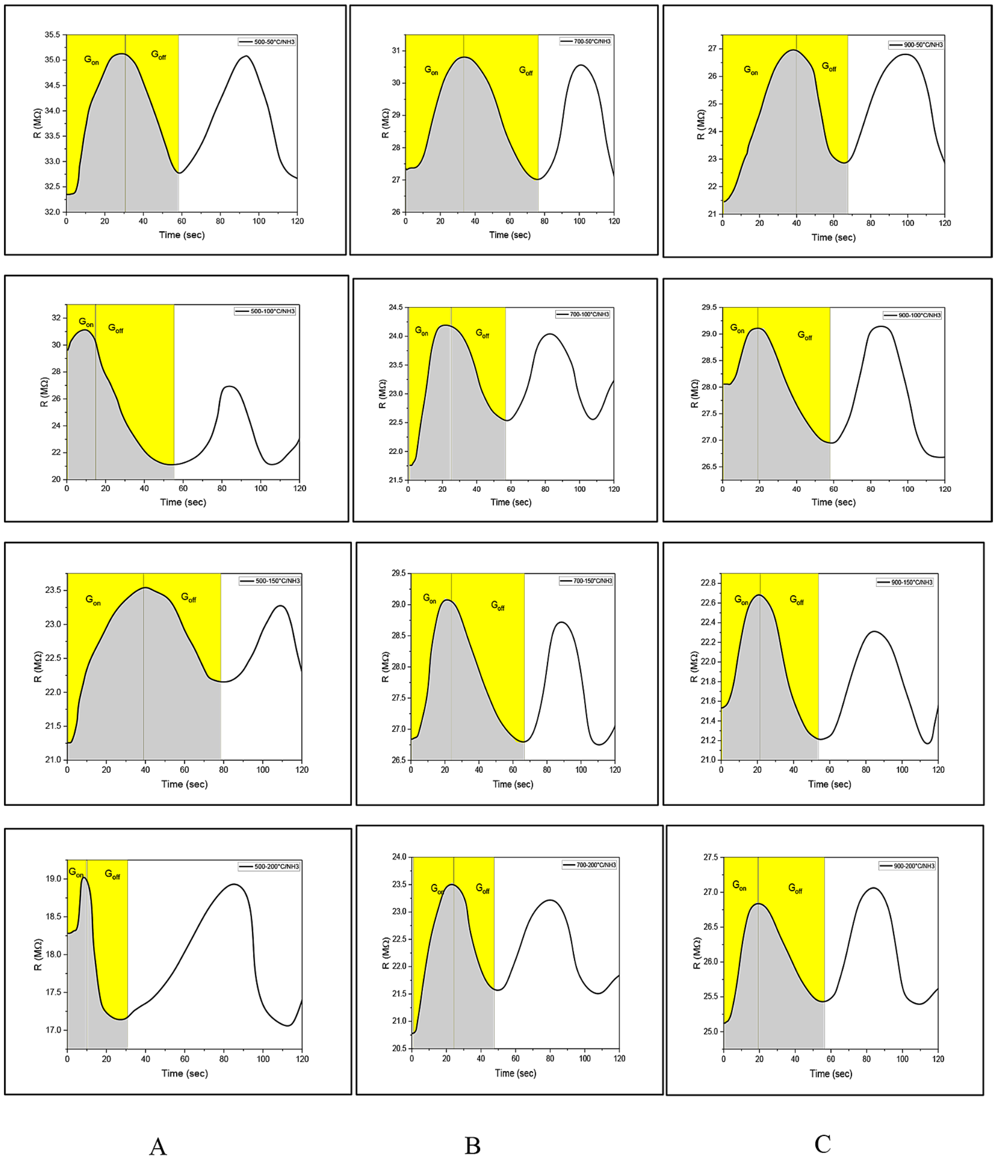

Figure 8. Electrical resistance evolution with time in the presence of NH_3 gas. Annealing and operative temperatures are reported in the figure A – 500 °C, B – 700 °C, and C – 900 °C

compared to films prepared at 700 °C and 900 °C showed a lower recovery time. When examining the resistance of the thin film in the presence of ammonia gas "(Gas-on)", which is a reducing gas, a reaction occurs between the ammonia gas and the NiO in a thin film, where the free electron is reduced by NH_3 gas. This leads to a reduction in the number of free electrons on the membrane surface and an increase in the number of holes as shown in Equation 3, which leads to an increase in the electrical resistance of the thin film as shown in Figure 8 (a, b, and c) we notice the change in electrical resistance with temperature [30, 31], After stopping the gas flow process "Gas-off", we notice a decrease in resistance and return to the original state.

$$(2/3)\ NH_3 + Oo^{\wedge\times} \leftrightarrow H_2O + \\ + (1/3)\ N_2 + 2e' + V\ O^{\cdot\cdot} \qquad (3)$$

In order to provide a comprehensive perspective, this study got a comparable result in performance of the SiO_2-NiO films with recent research results on nanomaterials used in gas sensing [32, 33]. The method used in this research ensures high coating homogeneity and uniformity. Additionally, this method is more cost and time efficient as it does not require expensive equipment or lengthy processing times. The purpose of these comparisons is to highlight advancements in gas sensors and evaluate different fabrication methods in terms of soft film performance [34]. This study offers a suitable material for highly efficient and rapid gas sensing applications, contributing to the development of environmental and industrial gas-sensing technology.

CONCLUSIONS

Using the sol-gel method and spin coating, this study successfully fabricated a hybrid nanocomposite ceramic coating of (SiO_2-NiO). The coating exhibited effective gas-sensing properties. The FTIR and XRD diagram revealed a cubic structure with a high surface area and active groups such as O-H, Si-O-Si, and Ni-O, indicating the high quality of the thin film. The film met all the requirements of good gas sensors. At an operating temperature of 50 °C, the films demonstrated high sensitivity to ammonia gas for thin films annealed at 500 °C and 900 °C. This suggests that both low and high temperatures enhance the surface properties that promote interaction between the sensitizer and the gas. Additionally, the films exhibited good recovery times and response times at high temperatures.

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