CHEMICAL ENGINEERING TRANSACTIONS
VOL. 127, 2026
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Laura Capelli, Marzio Invernizzi, Selena Sironi

ISBN 979-12-81206-28-1; **ISSN** 2283-9216
DOI: 10.3303/CET26127022

Gd/SiO_2 Thin Films for Room-Temperature NH_3 Detection

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Ammonia (NH_3) is a widely used industrial gas that poses serious risks to human health and the environment even at low concentrations, necessitating the development of reliable and sensitive detection systems. In this study, Gd/SiO_2 thin films were fabricated via DC magnetron sputtering and investigated as electrochemical sensing materials for room-temperature NH_3 detection. The films were comprehensively characterized by XRD, SEM-EDX, and XPS to assess their structural, morphological, and chemical properties. The results revealed a homogeneous nanogranular morphology and a uniform distribution of oxidized gadolinium species on the SiO_2 substrate. The sensing performance was evaluated by chronoamperometry at a constant applied potential. The Gd/SiO_2 sensor exhibited a stable and reproducible current response over an NH_3 concentration range of 1–60 ppm, with two distinct linear regions. This behavior may be attributed to a change in the sensing mechanism with increasing NH_3 concentration, likely related to the progressive occupation and partial saturation of active adsorption sites, as well as to modifications in surface reaction kinetics. The calculated sensitivities were 0.0179 μA ppm^{-1} (1–15 ppm) and 0.0405 μA ppm^{-1} (15–60 ppm), with a low limit of detection of 0.34 ppm. The improved sensing performance is attributed to enhanced surface reactivity, increased oxygen vacancy concentration, and more efficient charge transfer processes induced by Gd incorporation.

1. Introduction

Ammonia (NH_3) plays a crucial role across a wide range of sectors, including medical applications, refrigeration systems, fertilizer production, integrated circuit manufacturing, water treatment, and the chemical industry (Chua et al., 2021; Shkir et al., 2022; Kumar et al., 2020). Despite its extensive use, ammonia is inherently hazardous. It is a colourless yet highly irritant, flammable, and corrosive gas, representing a significant air pollutant with serious implications for both environmental safety and human health (Li et al., 2018; Lyu et al., 2022). Even at relatively low concentrations (~17 ppm), exposure can cause irritation to the eyes and skin, while prolonged inhalation may result in severe respiratory damage and, in extreme cases, may be life-threatening (Gupta et al., 2020; Singh et al., 2020). In recognition of these risks, the Occupational Safety and Health Administration (OSHA) has established strict exposure limits of 50 ppm over 8 hours and 100 ppm over 4 hours for industrial workers (Kwak et al., 2019). Given these concerns, the development of reliable gas sensors capable of real-time ammonia detection, particularly at room temperature, has become increasingly important for applications in industrial safety, environmental monitoring, automotive emissions control, and medical diagnostics (Boomashri et al., 2022). Various sensing technologies have been explored, including electrochemical, electrical, and optical approaches. Among these, electrochemical sensors (e.g., amperometric and potentiometric types) have attracted significant attention due to their low power consumption, ease of miniaturization, high stability, selectivity, and reproducibility. However, key challenges such as achieving higher sensitivity and faster response and recovery times still remain. To address these limitations, extensive research has focused on the development of advanced sensing materials. Metal oxides (Boomashri et al., 2022; Alkallas et al., 2022; Ştefănescu et al., 2008), hybrid nanomaterials (Stoia et al., 2010), ferrites (Dippong et al., 2021),

Paper Received: 13 April 2026; Revised: 17 May 2026; Accepted: 20 June 2026
Please cite this article as: Cirillo C., Iuliano M., Cirillo C., Navarrete Astorga E., Attanasio C., Sarno M., 2026, Gd/SiO_2 Thin Films for Room-Temperature NH_3 Detection, Chemical Engineering Transactions, 127, 127-132 DOI:10.3303/CET26127022

and metal–organic frameworks (MOFs) (Cheng et al., 2021) have all been investigated for ammonia detection. Among these, mixed metal oxide thin films have emerged as promising candidates due to their enhanced catalytic activity and improved sensing performance (Sarno et al., 2019). Their tunable composition and synergistic effects enable improved sensitivity, selectivity, and overall sensing efficiency. In this context, rare-earth-based materials have attracted increasing interest due to their ability to modulate oxygen vacancy concentration and tailor the electronic structure of oxide matrices. Among rare-earth dopants, gadolinium (Gd) is particularly effective in promoting oxygen defect formation, enhancing ionic mobility, and increasing surface reactivity, which are key factors governing gas sensing mechanisms. The incorporation of Gd into oxide matrices significantly modifies their structural, morphological, and optical properties, resulting in a higher density of active sites and facilitating efficient charge transfer during gas adsorption–desorption processes. Gd doping introduces strong interactions between donor levels associated with oxygen vacancies and acceptor levels of Gd, thereby improving overall sensing performance (Das et al., 2024). Furthermore, studies by Hope et al. (2021) have shown that increasing Gd concentration enhances oxygen vacancy density and induces modifications in the cubic symmetry of the host lattice, as confirmed by NMR and EPR analyses. To fabricate high-quality sensing layers with precise control over thickness, morphology, and uniformity, thin-film deposition techniques play a crucial role. In this context, magnetron sputtering represents a highly effective physical vapor deposition (PVD) method for the preparation of oxide-based thin films. The process relies on the ejection of atoms from a solid target through high-energy ion bombardment within a plasma environment. The presence of a magnetic field near the target confines electrons along magnetic field lines, increasing their collision probability with gas atoms and sustaining a highly ionized plasma. As a result, energetic ions continuously strike the target surface, causing the release of atoms that subsequently travel toward the substrate and condense to form a thin film. This magnetic confinement significantly enhances deposition efficiency, directionality, and film uniformity, making magnetron sputtering particularly suitable for the fabrication of electrodes and sensing materials (Colangelo et al., 2024; Iuliano et al., 2024). In this work, Gd-doped SiO_2 (Gd/SiO_2) thin films were synthesized via magnetron sputtering and systematically investigated as sensing materials for ammonia detection at room temperature. Structural and morphological characterizations were performed to elucidate the influence of Gd incorporation on the material properties. Gas sensing measurements demonstrate that the optimized Gd/SiO_2 thin film exhibits enhanced performance toward NH_3, characterized by stable and reproducible responses under ambient conditions. These results highlight the potential of Gd/SiO_2 thin films as effective platforms for ammonia sensing, with promising applications in environmental monitoring and industrial safety.

2. Materials and Methods

2.1 Materials

The Gd source used for the deposition is a 5.08 cm diameter target (99.9% purity) from Testbourne Ltd. The films were deposited on p-doped (100)-oriented silicon (Si) substrates from Crystec GmbH. All other chemicals were supplied by Aldrich Chemical Co. All chemicals were of analytical grade.

2.2 Gd deposition

Gd films were deposited using an ultrahigh vacuum DC diode magnetron sputtering system with a base pressure of 6×10^{-8} mbar. The depositions were carried out at a sputtering power of 135 W and an Ar pressure of 10 µbar, resulting in a growth rate of 0.11 nm/s. The growth rate was determined using a Bruker DektakXT profilometer on patterned films intentionally deposited for calibration purposes.

2.3 Characterizations

The morphology of the electrodes at different stages of preparation was analyzed using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX). The analysis was performed using a TESCAN VEGA LMH (230 V). X-ray diffraction (XRD) measurements were performed by a Bruker D2 Phaser X-ray diffractometer, using CuKα radiation. The chemical composition of the Gd/SiO_2 samples was studied via X-ray photoelectron spectroscopy (XPS) using a Physical Electronics (PHI) VersaProbe II spectrometer equipped with an Al Kα radiation source.

2.4 Gas sensing measurements

The samples were introduced into a gas flow cell, through which dry N_2 and NH_3 gases from commercial cylinders free of water vapor were continuously supplied. The cell was placed inside an environmental chamber to control the operating temperature of the prepared sensors. Initially, N_2 was purged through the system until a stable baseline current was achieved, after which NH_3 gas was introduced. The desired NH_3 concentrations were generated using an automatic gas mixing system consisting of a static mixer and two mass flow controllers:

one connected to an NH_3 cylinder (100 ppm in N_2) and the other to a nitrogen cylinder, while maintaining a total flow rate of 100 sccm. A potentiostat/galvanostat (Autolab PGSTAT302N) was used to record the gas response currents during the electrochemical measurements. The electrochemical sensing performance was evaluated using a Gd/SiO_2-based working electrode via chronoamperometry, where the current response to NH_3 was monitored over time under a constant applied potential (+1.1 V). A schematic diagram of the overall electrochemical gas measurement system is shown in Figure 1.

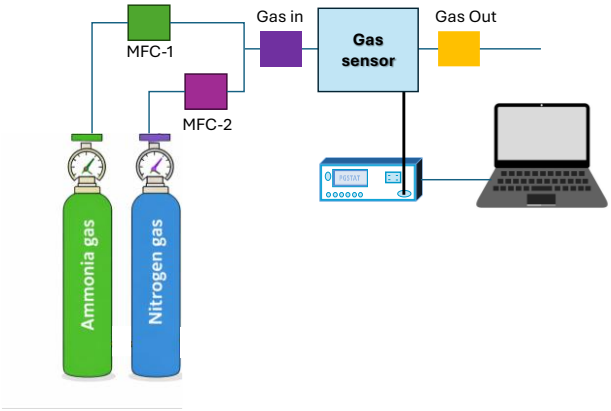

Figure 1: Schematic diagram of the overall electrochemical gas measurement system.

3. Result & Discussion

3.1 Characterizations of Gd/SiO_2

The surface morphology of the Gd/SiO_2 thin films was investigated using SEM, as shown in Figure 2a. The images reveal the formation of a homogeneous nanogranular coating with uniform grain distribution over the substrate surface. EDX analysis confirmed the presence of Si, O, and Gd elements, indicating the successful deposition of the Gd layer onto the SiO_2 substrate. Elemental mapping further demonstrated a uniform distribution of the elements across the film surface, without evident segregation phenomena. The quantitative EDX analysis showed atomic percentages of 60.8 at.% Si, 37.4 at.% O, and 1.8 at.% Gd, while the increased oxygen content suggests the presence of oxidized gadolinium species.

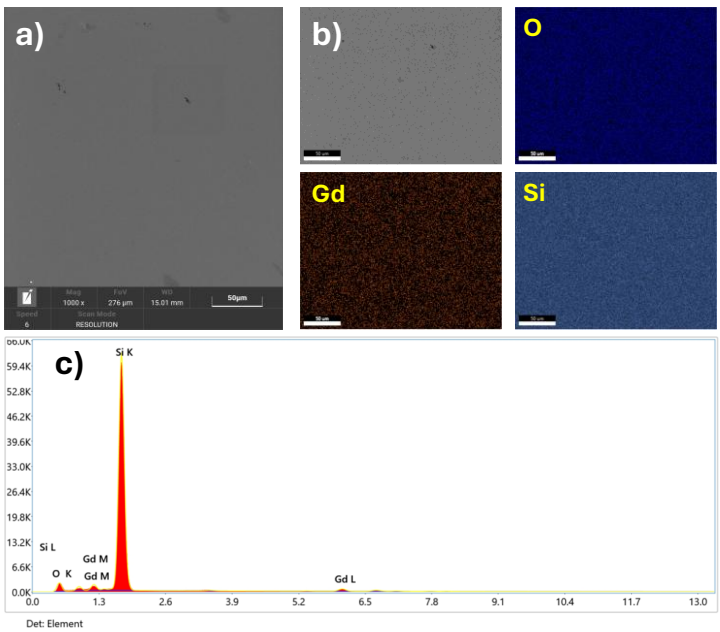

Figure 2: SEM image of the Gd/SiO_2 thin film (a); Elemental mapping of the Gd/SiO_2 thin film (b); and EDX spectrum of the Gd/SiO_2 thin film (c).

Figure 3a shows the XRD pattern of the sputtered Gd thin film deposited on a SiO_2 substrate. A broad band is observed around 2θ ≈ 30°, which can be attributed to the Gd (002) reflection (Hsu et al., 2012). Moreover, a weak diffraction peak is detected at around 2θ ≈ 55°, which can be assigned to the (622) plane of Gd_2O_3 (Ferrara et al., 2008), suggesting partial oxidation of the Gd layer, likely due to exposure to ambient conditions. Within this context, the other diffraction features observed in the pattern can be reasonably ascribed to contributions from the underlying substrate (Iuliano et al., 2024). To further investigate the surface chemical composition and electronic state of the film, XPS analysis was performed. Figure 3b shows the XPS survey spectrum of the Gd/SiO_2 thin film, confirming the presence of Si 2p and O 1s peaks from the substrate, along with characteristic signals corresponding to gadolinium. The high-resolution XPS spectrum of the Gd 4d core level (Figure 3c) provides detailed insight into the chemical state of gadolinium at the film surface. The binding energy position and peak profile of the Gd 4d signal are characteristic of oxidized gadolinium species, indicating that the deposited Gd is predominantly present in the form of Gd–O bonds rather than in a purely metallic state (Dolo et al., 2010). This behavior can be attributed to the high chemical reactivity of gadolinium, which readily undergoes oxidation (Hennings et al., 2007).

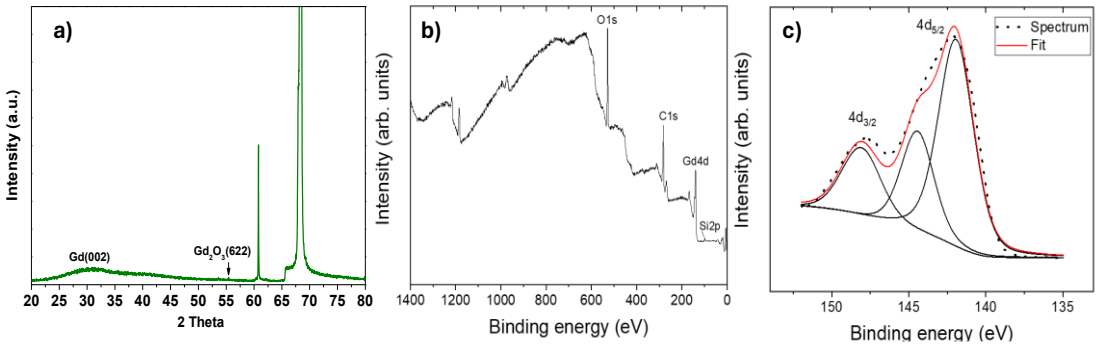

Figure 3: XRD of the Gd/SiO_2 thin film (a), XPS Survey spectra of the Gd/SiO_2 thin film (b); and XPS spectra of Gd 4d (c).

3.2 Electrochemical sensing performance of the Gd/SiO_2

A chronoamperometric technique was employed to evaluate the sensitivity and limit of detection (LOD) toward NH_3 gas using a Gd/SiO_2 electrode. As the NH_3 concentration increased from 1 to 60 ppm, the chronoamperometric current response exhibited a linear increase (Figure 4a). The calibration plot of current versus NH_3 concentration revealed two distinct linear regions: I (μA) = 0.0179 × C + 0.042 in the range of 1–15 ppm, and I (μA) = 0.04052 × C − 0.115 in the range of 15–60 ppm (Figure 4b), with corresponding correlation coefficients of R^2 = 0.92 and R^2 = 0.96, respectively, where C is the NH_3 concentration expressed in ppm. The sensitivity of the sensor was determined from the slope (m) of the calibration curves, while the LOD (S/N = 3) was calculated using the equation 3σ/m, where σ represents the standard deviation of the blank signal. In particular, the blank signal was recorded over multiple chronoamperometric cycles under identical experimental conditions, and the resulting standard deviation was used to estimate the minimum detectable concentration corresponding to a signal-to-noise ratio of 3. The calculated sensitivities were 0.0179 μA ppm^{-1} and 0.0405 μA ppm^{-1} for the low and high concentration ranges, respectively, with an estimated LOD of approximately 0.34 ppm. The enhanced sensing performance, including higher sensitivity and stable response behavior, can be attributed to the large specific surface area, improved adsorption capability, and effective electrocatalytic activity of the Gd/SiO_2 composite toward NH_3 gas. The sensing mechanism is related to the interaction between NH_3 molecules and chemisorbed oxygen species (O^-, O_2^-) on the Gd/SiO_2 surface. Upon exposure to NH_3, these species react with adsorbed oxygen ions, releasing electrons back into the conduction pathway and increasing the measured current. The presence of Gd enhances the density of oxygen vacancies, promoting oxygen adsorption and facilitating charge transfer processes, thereby improving the overall sensing response. Although the selectivity toward interfering gases was not systematically investigated in the present study, the sensing response is expected to be strongly influenced by the specific interaction between NH_3 molecules and the oxygen-related active sites on the Gd/SiO_2 surface. Nevertheless, potential cross-sensitivity toward reducing gases such as ethanol, acetone, CO, or H_2S may occur due to similar surface redox reactions. Future investigations will therefore focus on evaluating the selectivity performance under exposure to different interfering species and humidity conditions in order to assess the practical applicability of the sensor in real environmental monitoring systems.

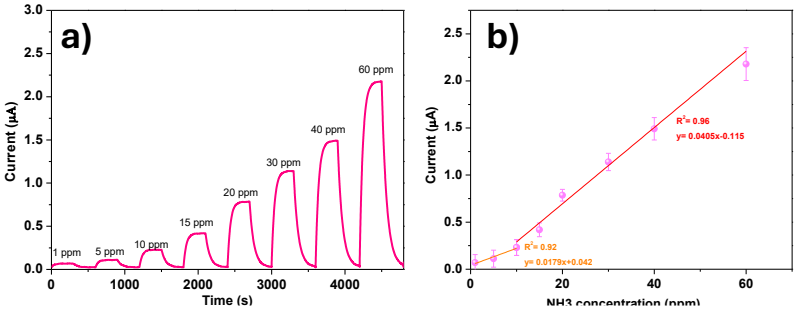

Figure 4: Chronoamperometric response to NH_3 (1–60 ppm) (a), Calibration plot with two linear ranges (b).

3.3 Repeatability test

The operational stability of the Gd/SiO_2 film was evaluated through a repeatability test by performing five consecutive measurement cycles under controlled conditions, during which the sample's current response was recorded (Figure 5). Chronoamperometric measurements were carried out at a constant applied potential of 1.1 V, while the sensor was exposed to a fixed ammonia concentration of 60 ppm.

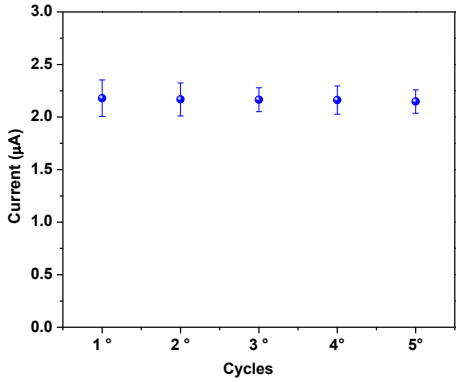

Figure 5: Repeatability test of Gd/SiO_2 film at 60 ppm NH_3 under chronoamperometric conditions (1.1 V) over five consecutive cycles.

The analysis of the data reveals that the current remains nearly constant throughout all five cycles, with no noticeable drift, instability, or signal degradation. This behavior indicates that the material preserves a stable response even after repeated exposure to the target gas under identical operating conditions. The high reproducibility of the current values obtained in successive cycles demonstrates the reliability of the device.

4. Conclusions

In this study, Gd/SiO_2 thin films were successfully fabricated via DC magnetron sputtering and evaluated as electrochemical sensors for ammonia detection at room temperature. Structural and morphological analyses confirmed the formation of a homogeneous nanogranular coating with uniformly distributed gadolinium, predominantly in oxidized form, contributing to enhanced surface activity. The electrochemical measurements demonstrated that the Gd/SiO_2-based sensor exhibits a stable and reproducible response to NH_3 in the concentration range of 1–60 ppm. The presence of two linear response regions highlights the capability of the sensor to operate effectively across both low and moderate concentration ranges, with a low detection limit of 0.34 ppm. The improved sensing performance can be attributed to the synergistic effects of Gd incorporation, which enhances oxygen vacancy density, surface reactivity, and charge transfer processes. The results confirm that Gd/SiO_2 thin films represent a promising platform for room-temperature ammonia sensing.

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