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SnO₂/NiO Composite Thin Films for Formaldehyde Detection

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Abstract—Formaldehyde (HCHO) is a volatile organic compound that outgasses from textiles and composite wood products, with adverse health effects resulting from prolonged exposure to concentrations of ~ 10 ppb in air. Commercially available HCHO sensors struggle to detect HCHO at such low concentrations. Tin dioxide (SnO₂) / nickel oxide (NiO) polycrystalline composite films have shown sensitivity to ~ 100 ppb via resistance measurements. Here we explore several thin SnO₂/NiO films produced by pulsed laser deposition (PLD), varying preparation parameters including NiO loading and substrate temperature during deposition. These variables are shown to affect both composition and morphology, as characterized by XPS, XRD, SEM, and SEM-EDX. Here we report the response time and sensitivity of these sensor materials to HCHO concentrations from ~ 10 ppb to 1000 ppb at various operating temperatures.

I. INTRODUCTION

Many types of commercial HCHO sensors are available, but few can quantitatively detect HCHO at concentrations below 100 ppb [1]. A recent Health Canada guideline [2] sets the maximum HCHO concentration for short-term (1-hour averaged) and long-term (8-hour averaged) exposure limits at 100 ppb and 40 ppb, respectively. The World Health Organization [3] sets a short-term (30-minute averaged) exposure limit at 80 ppb. There are few affordable sensors that can detect HCHO at these guideline concentrations. There is recent concern regarding HCHO in commercial buildings, driving a desire to improve HCHO sensor technology to meet these exposure levels in an affordable, portable package.

Thin metal-oxide films provide a low-cost class of gas-sensitive materials that can be integrated into a portable electronic gas sensor. HCHO sensors based on nickel oxide (NiO) [4], [5], tin dioxide (SnO₂) [6], [7], and SnO₂/NiO composite films [8] have effectively detected HCHO concentrations from ~ 100 ppb to 1 ppm. We are developing a SnO₂/NiO thin film sensor material to detect HCHO at concentrations ~ 10 ppb, and which can be integrated into a wireless device. Thus, we strive to maximize sensitivity at a modest power consumption.

There have been numerous methods employed in the development of SnO₂/NiO composite films, yet the use of pulsed laser deposition (PLD) has received relatively little attention despite several inherent advantages that are offered by this technique. These advantages include a number of deposition parameters and the ease with which PLD allows for a controlled transfer of the target composition to a thin film [9]. We

have chosen PLD as a thin film preparation technique primarily because it offers a number of independent parameters to tune several film characteristics. These include target composition, substrate temperature, background gas (e.g. O₂ pressure), and deposition time (see Fig. 1).

Here we use PLD to produce a range of SnO₂/NiO films with various NiO loadings and a range of substrate temperatures during deposition. These two parameters affected film composition and morphology, respectively. We then measured a response in electrical resistance of a film upon exposure to HCHO. The most promising candidates for sensing HCHO were prepared with a NiO loading of 20% at a substrate temperature $\sim 250^\circ\text{C}$ during deposition. They exhibited a high sensitivity to ~ 10 ppb with a short response time at operating temperatures achievable with portable electronics.

II. EXPERIMENTAL

PLD is illustrated in Fig. 1. All films were deposited via PLD on alumina (Al₂O₃) using 600 mJ/pulse laser energy at an 8 Hz pulse rate for 20 minutes. Energy fluence at the target was approximately 1.5 J/cm². Oxygen (O₂) pressure during deposition was set at values of 25 mTorr to 400 mTorr for various films, with thickness ranging from 45 nm to 150 nm as determined by profilometry. Substrate temperature was held constant during deposition at temperatures from 150°C to 650°C. After deposition, all films were annealed for 30 minutes at their deposition temperatures in an O₂ atmosphere (400 Torr).

NiO loading (e.g. fraction of NiO in the composite) was controlled by composition of PLD targets, which were prepared by pressing a pellet of uniformly mixed, finely ground powders of pure NiO and SnO₂. Relative NiO loadings of 1%, 2%, 5%, 10%, and 20% were tested. Film compositions were confirmed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (SEM-EDX), and were found to be similar to that of their targets.

Figure 2 shows field emission scanning electron microscopy (FE-SEM) images, illustrating the morphology of a typical SnO₂/NiO sensor film with a NiO loading of 20% and a thickness of ~ 50 nm. These PLD films were highly granular and porous. X-ray diffraction (XRD; not shown) only confirmed the cassiterite structure of the SnO₂ phase. NiO was not observed by XRD. However, NiO was quantitatively

Fig. 1. **Pulsed laser deposition.** (a) A photograph of a laser ablation plume; (b) an SnO_2/NiO film deposited on an alumina substrate with pre-fabricated interdigitated electrodes; (c) a schematic illustrating PLD of a composite metal-oxide film.

observed by both XPS and SEM-EDX. For example, XPS and SEM-EDX confirmed that films prepared from a PLD target comprised of 20% NiO had NiO loadings of $20\% \pm 2\%$.

Electrical resistance of composite films was measured in a 1 L flow-through chamber at a flow rate of 500 mL/min while controlling film temperature and gas composition. Trace HCHO in nitrogen (N_2) was supplied from cylinders purchased from Scott Specialty Gases. Mass flow controllers (MFCs) regulated gas flow from an ultra-high purity N_2 cylinder, an ultra-high purity O_2 cylinder, and a trace HCHO/ N_2 cylinder to achieve the desired HCHO concentration while maintaining a constant flow rate of 500 mL/min and constant O_2 concentration of 20%. At a given temperature, the relative conductance response is defined as

$$\frac{(1/R([\text{HCHO}])) - (1/R_{\text{air}})}{1/R_{\text{air}}} = \frac{R_{\text{air}}}{R([\text{HCHO}])} - 1, \quad (1)$$

where $R([\text{HCHO}])$ is the stabilized film resistance after exposure to a known concentration of HCHO, $[\text{HCHO}]$, and R_{air} is the film resistance in simulated dry air (i.e. 20% O_2 ; balance N_2). Response time refers to an average time required for a film's resistance to stabilize after changing the HCHO concentration (generally to or from simulated dry air) at

Fig. 2. **Film morphology.** Field emission scanning electron microscope (FE-SEM) image of a typical SnO_2/NiO film prepared on single-crystal sapphire (e.g. crystalline Al_2O_3) at 250°C and 400 mTorr O_2 , having a thickness ~ 50 nm.

a given temperature. The relative response and response times of SnO_2/NiO films were determined at various concentrations of HCHO in simulated dry air. HCHO concentrations in this study ranged from 12 ppb to 1 ppm, and sensor film operating temperature ranged from 25°C to 550°C .

III. RESULTS AND DISCUSSION

When heated in simulated dry air from 25°C to 550°C , SnO_2/NiO films generally exhibited temperature dependence typical of semiconductors; e.g. $R_{\text{air}}(T) \propto \exp(-aT)$, where T is the film temperature and a is a constant. At a fixed operating temperature, HCHO concentration was cycled between zero (e.g. simulated dry air) and test values at regular intervals. Films with high NiO loadings generally showed larger conductance responses than those with lower NiO loadings. After preliminary measurements on films prepared with NiO loadings from 1% to 20%, we focused our attention on those comprised of 20% NiO.

The time required for resistance to stabilize after exposure to a given concentration of HCHO was inversely proportional to the film temperature during sensing. Figure 3 demonstrates a film's resistance responding to changes in HCHO concentration at 90 minute intervals. This film was deposited at a substrate temperature of 650°C . At a film operating temperature of 300°C or 350°C , its resistance was not stable within 90 minutes of a change in HCHO concentration (e.g. conductance was still drifting upward after 90 minutes exposure to HCHO; still drifting downward after 90 minutes exposure to simulated dry air), as shown in Figs. 3(a) and (b). In general, the cycling time required to reach a stable value at temperatures below 400°C is much greater than 1 hour for films prepared at 650°C . Conversely, the operating temperature required for quasi-realtime HCHO sensing for a film prepared at 650°C is greater than 400°C .

Fig. 3. **Response time.** Conductance vs. time for several cycles of various HCHO concentrations for a typical SnO_2/NiO film prepared at 650°C and 400 mTorr O_2 . HCHO concentration was cycled between test values (90 minutes) and zero (90 minutes) at responding PLD film resistance was measured at film temperatures of (a) 300°C, (b) 350°C, and (c) 400°C.

Figure 4 shows conductance and HCHO concentration vs. time for a SnO_2/NiO sensor film prepared at a substrate temperature of 250°C and 400 mTorr O_2 . In Fig. 4, the HCHO concentration was cycled every 30 minutes. This film exhibited an increase in resistance of (a) $\sim 83\%$ at a HCHO concentration of 100 ppb, and (b) $\sim 23\%$ increase at 12 ppb. Such a large change in resistance was common amongst films deposited and annealed at substrate temperatures below 300°C. Remarkably, this film's response time (e.g. that required to reach a stable resistance) at a film temperature of 300°C was shorter than the gas exchange rate of our 1 L chamber. We suspect that a more amorphous and/or granular film morphology is responsible for enhanced sensitivity and decreased response times. This is supported by SEM images, which show an evolution of film granularity with PLD substrate temperature. Higher concentration of oxygen deficiencies in the film - especially partially reduced NiO - might also be responsible for improved performance of films deposited and annealed at lower substrate temperature; however, we have little supporting evidence for this explanation.

Figure 5 shows difference in film resistance (compared to resistance in simulated dry air) vs. HCHO concentration at 300°C, derived from the data shown in Fig. 4. From such a curve, film resistance can be calibrated for a given operating temperature for implementation as a sensor device, having a one-to-one relationship between resistance changes and HCHO concentrations.¹

Films deposited at substrate temperatures below 250°C were also studied. In particular, 3 films were deposited at 150°C that were otherwise prepared exactly the same way as 3 films deposited at 250°C. These 6 films were all deposited on sintered alumina substrates with built-in hot-plates and interdigitated electrodes,² as shown in Fig. 1(b)). The relative response (e.g. percentage change in conductance) and response times of the 150°C films were similar to their 250°C counterparts, but their resistances (e.g. $R([\text{HCHO}])$ and R_{air}) were an order of magnitude higher at a common operating temperature of 300°C.

We also studied films deposited at O_2 pressures from 25 mTorr to 400 mTorr. Film thickness varied slightly with deposition pressure. However, there was no significant difference in relative conductance response when these films were exposed to HCHO concentrations from ~ 10 ppb to 1 ppm.

IV. CONCLUSION

We have shown that HCHO can be detected in simulated dry air at concentrations as low as 12 ppb using SnO_2/NiO films prepared by PLD. In general, a NiO loading of 20% showed a higher HCHO response than lower loadings, and films deposited at a substrate temperature $\sim 250^\circ\text{C}$ showed

¹From the signal-to-noise ratio in Fig. 4 and calibration curve in Fig. 5, it appears that the HCHO detection limit of these PLD films may be well below 12 ppb. Unfortunately our current gas delivery system is unable to reliably source HCHO concentrations below 12 ppb.

²These alumina substrates with built-in hot-plates, platinum temperature sensors, and interdigitated electrodes, were purchased from the Electronics Design Center at Case Western Reserve University.

Fig. 4. **High sensitivity, short response time, and low operating temperature.** Conductance vs. time for several cycles of various HCHO concentrations for a SnO_2/NiO film prepared at 250°C and 400 mTorr O_2 . Concentration was cycled between a fixed concentration (30 minutes) and zero (30 minutes) in an atmosphere of 20% O_2 (balance N_2) at a flow of 500 mL/min. An expansion of the lowest concentrations is shown in a lower panel.

higher response and shorter response time at a lower sensor operating temperature than those deposited at higher substrate temperatures. These materials are promising for affordable low-power realtime applications. Ongoing research involves studying these SnO_2/NiO films in more complicated gas environments,³ possibly followed by further optimization of PLD parameters, is required before these composite SnO_2/NiO thin films can be integrated into sensor devices.

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³For example, it is suspected that these films might show cross-sensitivity to water vapour, CO_2 , alcohols, and other volatile organic compounds.

Fig. 5. **Sensor calibration curve.** Change in resistance, $\Delta R = R([\text{HCHO}]) - R_{\text{air}}(\Omega)$ vs. HCHO concentration at 300°C for a SnO_2/NiO film deposited at 250°C and 400 mTorr O_2 .

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