

Gallium Oxide Thin Films from the Atmospheric Pressure Chemical Vapor Deposition Reaction of Gallium Trichloride and Methanol

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The reaction of gallium trichloride and methanol under atmospheric pressure chemical vapor deposition conditions leads to the production of gallium oxide thin films on a variety of substrates. Scanning electron microscopy (SEM) indicated that an island growth mechanism predominated. X-ray photoelectron spectroscopy (XPS) revealed binding energy shifts of 530.6 eV for O 1s and 20.3 eV for Ga 3d. The films were X-ray amorphous. Energy-dispersive X-ray analysis (EDXA) and electron probe microanalysis (EPMA) gave coherent elemental compositions, indicating that a single phase Ga_2O_3 was made, with negligible impurity levels. The films showed little optical reflectance ($\sim 10\%$) and 65–75% total transmission from 400 to 800 nm. Gas-sensing experiments indicated that the films responded best to a reducing gas at 450 °C.

Introduction

Gallium oxide (Ga_2O_3) is a wide band gap semiconductor material,^{1,2} with a host of current and potential applications. It has received attention as a luminescent phosphor,^{3–5} as a compound semiconductor surface passivator,⁶ as a potential deep ultraviolet transparent conducting oxide,⁷ in acid/base catalysis,^{8–10} and as a nanomaterial.^{11–13} Recently, Ga_2O_3 prepared by PVD has received attention as a gas sensor.¹⁴ It has been reported as having a response to oxidizing gases at elevated temperature (>900 °C)¹⁵ and a response to reducing gases at lower temperatures (500 °C).¹⁶

Thin films of Ga_2O_3 have been prepared in a variety of ways. Physical vapor deposition methods such as

magnetron sputtering and electron-beam evaporation have been utilized.^{17,18} Low-pressure chemical vapor deposition of homoleptic gallium alkoxides,¹⁹ gallium tris-hexafluoroacetylacetonate,²⁰ and gallium fluoro-alkoxides has also been conducted.²¹

The production of thin films by CVD affords inexpensive, adhesive reproducible films with low-impurity levels²² and may therefore provide an advantageous method of producing gas sensors. APCVD in particular is of interest because of fast growth rates and high surface coverage.^{23,24} CVD methods are directly compatible with Si micro fabrication technology. In this paper we report the first example of Ga_2O_3 films prepared by APCVD. We also report the first gas-sensing properties of Ga_2O_3 thin films prepared by CVD. This is important as we wish to evaluate whether the generally dense films produced by CVD are compatible with solid-state oxide gas sensors. Typically solid-state oxide sensors are made by screen printing and tend to be very porous.

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Experimental Section

Nitrogen (99.99%) was obtained by BOC and used as supplied. Coatings were obtained on SiO₂-coated float glass. APCVD experiments were conducted on 150 × 45 × 3 mm pieces of glass using a flat-bed cold-walled APCVD reactor. The glass was cleaned prior to use by washing with petroleum ether (60–80 °C) and 2-propanol and then dried in air. A graphite block containing a Whatman cartridge heater was used to heat the glass substrate. The temperature of the substrate was monitored by a Pt–Rh thermocouple. Independent thermocouple measurements indicated that temperature gradients of up to 50 °C cm⁻¹ were observable at 600 °C across the surface of the glass. The rig was designed so that four independent gas lines could be used. All gas-handling lines, regulators, and flow valves were made of stainless steel and were 6.5 mm internal diameter except for the inlet to the mixing chamber and the exhaust line from the apparatus that were 13 mm in diameter. In these experiments three gas lines were used. Gases came directly from a cylinder and were preheated by passing along 2-m lengths of stainless steel tubing, which were curled and inserted inside a tube furnace. The temperatures of all the gas inlet lines were monitored by Pt–Rh thermocouples and Eurotherm heat controllers.

Gallium(III) chloride (99.99%) was obtained from Aldrich and used without further purification and was placed into a stainless steel bubbler. The bubbler was heated to 150 °C by a heating jacket and GaCl₃ introduced into the gas streams by passing hot nitrogen gas through the liquid. Anhydrous methanol was purchased from Aldrich and used without further treatment. This was preferred over water as the latter gives rise to powdery films. The two components of the system were mixed by the use of two concentric pipes of 6.5 and 13 mm diameter, respectively, the inner pipe being 3 cm shorter than the outer pipe. The concentric pipes were attached directly to the mixing chamber of the coater. Gas flows were adjusted using suitable regulators and flow controllers. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. All of the apparatus was baked out with nitrogen at 150 °C for 30 min before use. Deposition experiments were conducted by heating the horizontal-bed reactor and the bubblers to the desired temperatures before diverting the nitrogen line through the bubbler and hence to the reactor. Deposition experiments were timed by use of a stopwatch and were conducted typically for 1 min. The maximum possible deposition temperature with this equipment was 600 °C. At the end of the deposition only nitrogen was allowed to flow over the glass substrate until the substrate was sufficiently cool to handle (~60 °C). Samples were handled and stored in air. Additional runs were conducted using iron, copper, and silicon wafer substrates and subjected to the same analysis. Deposition temperatures varied from 350 to 600 °C. Nitrogen flow rates were varied between 0.5 and 0.7 L min⁻¹.

X-ray photoelectron spectra were recorded with a VG ESCALAB 220I XL instrument using focused (300-μm spot) monochromatic Al Kα radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging and the binding energies were referenced to an adventitious C 1s peak at 284.6 eV. Depth profiling measurements were obtained by using argon beam sputtering. Electron microprobe analysis was obtained on a JEOL EMA and referenced against gallium and oxygen standards. EDXA was conducted using a JEOL 35-CF instrument. SEM images were acquired on an Hitachi S570 instrument. X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using filtered (Cu Kα₁, λ = 1.5406 Å) radiation in the reflection mode using glancing angle incidence (1.5°). Reflectance and transmission spectra were recorded between 300 and 1150 nm on a Zeiss miniature spectrometer. Measurements were standardized relative to a rhodium mirror (reflectance) and air (transmission). UV–Vis spectra were obtained using a Helios double-beam instrument. Raman spectra were acquired on a Renishaw Raman system 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of

neon. Electrical properties were determined by using a four-probe device. Contact angle experiments were determined by measuring the spread of a 1 μL droplet of water on the film surface and applying a simple trigonometric program.

For gas response, films were deposited onto commercially produced sensor substrates. The sensors consist of a gold track printed on the top of an alumina tile and a platinum heater track printed on the reverse side of the tile. Gold electrodes were formed by laser trimming to produce an interdigitized section with gap and finger widths of 50 μm. Contacts to the devices were formed by spot welding 50 μm-diameter platinum wire to pads of the track material in the corner of the sensor chip. The sensor heater was kept at constant resistance and hence constant temperature by incorporating it into a Wheatstone bridge. Electrical experiments were formed on a locally constructed test rig.²⁵ Test gases were diluted from cylinders of synthetic air (79% nitrogen, 21% oxygen) containing ethanol (100 ppm). The devices were investigated over a variety of temperatures between 400 and 600 °C.

Results

Synthesis and Characterization. Atmospheric pressure chemical vapor deposition (APCVD) reaction of gallium trichloride and methanol led to the production of gallium oxide thin films on a variety of substrates; glass, quartz, aluminum, iron, silicon, and gas sensor. The process was studied across a range of different precursor flow rates and substrate temperatures.

Films would not grow at substrate temperatures lower than 400 °C. Films of uniform thickness were observed at 550 °C and above. The films grown from the reaction of gallium trichloride and methanol appeared colorless and unreflective. Birefringence was observed. The films all passed the Scotch tape test and were resistant to marking with a wet towel and brass stylus but could be marked by a steel scalpel. The films showed no change in their optical properties on storage in air for 3 months.

Compositional analysis was determined by EDXA and EPMA and indicated that the films had the composition Ga₂O₃. The results showed that the films were free of contaminants such as chlorine (typically less than 1 at. %) and were incorporated into the films. In the case of thinner films some breakthrough to the underlying glass substrate was observed; this was corrected for based on a sample of plain glass. Further analysis indicated that all samples had a uniform thickness and composition across the surface in contrast to what has been observed with this experimental setup elsewhere.²⁶ These results show that it is possible to create thin films of gallium oxide with a single stoichiometry, Ga₂O₃.

Scanning electron microscopy analysis of the films showed that deposition occurred via an island growth mechanism. The film surfaces consisted of circular particles of gallium oxide ranging from 500 nm to 1 μm in size dispersed across the substrate; a representative sample is shown in Figure 1. There appeared to be no difference in film morphology with substrate. Film thicknesses were measured directly by SEM and gave film thicknesses between 500 nm at 400 °C and 900 nm at 600 °C.

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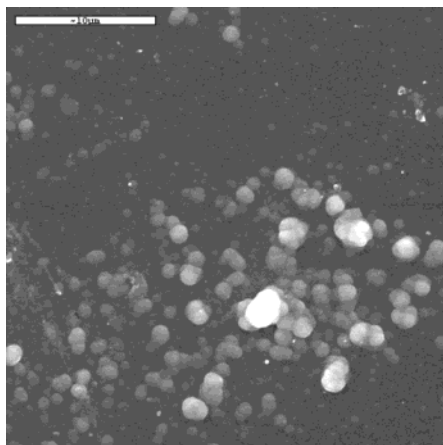


Figure 1. Secondary electron scanning electron microscope image of a gallium oxide (Ga_2O_3) film formed from the APCVD reaction of gallium trichloride and methanol at 600 °C.

All of the films were investigated using Raman microscopy. In all cases no Raman scattering was observed and it is thought that gallium oxide is a poor Raman scatterer. However, Raman spectroscopy indicated the absence of graphitic carbon in the film.

X-ray photoelectron spectroscopy revealed binding energy shifts of 530.6 eV for O 1s and 20.3 eV for Ga 3d, respectively. The XPS peak profiles (Figure 2) are consistent with a single environment for gallium and oxygen. The binding energy shifts are in agreement with previous literature values of 20.3 eV for Ga 3d and 530.5 eV for O 1s.^{27,28}

The optical properties of the films were studied by transmission, reflectance, and UV/visible measurements between 200 and 1100 nm. All samples showed a slight shift in the adsorption edge toward the visible when compared to a plain glass substrate. The films displayed minimal reflectivity (10%) and high transmission (70%). A Tauc plot²⁹ of the UV/visible data indicated that Ga_2O_3 prepared by APCVD on quartz had an indirect band gap of 4.3 eV, comparable to other literature values for Ga_2O_3 of 4.2–4.9 eV.^{1,2}

The gallium oxide thin films prepared by APCVD were X-ray amorphous, as has been seen with previous work carried out on the growth of Ga_2O_3 thin films at 600 °C by low-pressure chemical vapor deposition.^{19,20}

The Ga_2O_3 films were shown to have contact angles for water droplets in the region of 70–80°; this contact

angle was similar to that of plain glass 60–75°. Sheet-resistance measurements indicated that the films were poor conductors at room temperature, typically producing resistivity values in the order of 126000 $\mu\Omega$ cm.

Gas-Sensing Properties. The Ga_2O_3 films were deposited on gas sensor substrates. These films showed an n-type response to ethanol at a variety of temperatures. Gas response was measured as the ratio between R (the resistance when exposed to ethanol) and R_0 (the point immediately preceding the introduction of ethanol). The resistance was measured between the two electrodes of an interdigitized gold electrode structure on an alumina tile. In all cases gas response increased with ethanol concentration; a representative example is shown in Figure 3. The gas response was rapid and a near plateau was reached within minutes of exposure to ethanol. When the ethanol flow was stopped, the response also drops rapidly to near the baseline level and then tails off more slowly to the baseline. Throughout the duration of the experiment the baseline remained stable, showing only a slight downward drift. Some signal noise is evident. Above 60 ppm of ethanol gas the response level remained fairly constant and did not vary to any great extent. Evaluation of response to a gas concentration of 100 ppm of ethanol indicated that the greatest response of R/R_0 at 2.45 occurred at 450 °C (Figure 4); as expected a maximum is reached and then tails off to a plateau. The gas response in the presence of 50% humidity was also evaluated (Figure 5). Addition of humidity into the chamber provokes a slight upward shift in the resistance baseline, which is otherwise relatively flat. The magnitude of the resistance response is similar in dry and humid air.

Discussion

Reaction of gallium trichloride and methanol under atmospheric pressure chemical vapor deposition conditions affords thin films of gallium oxide on a range of substrates. The gallium oxide films were found to be of a uniform phase, Ga_2O_3 , regardless of experimental conditions. Faster film growth rates were observed with an increase in substrate temperature, indicating the process is surface-reaction-limited. The choice of substrate appeared not to affect the films in any way—the same Ga_2O_3 composition and island growth morphology was found on quartz, glass, alumina, gold, gas sensor,

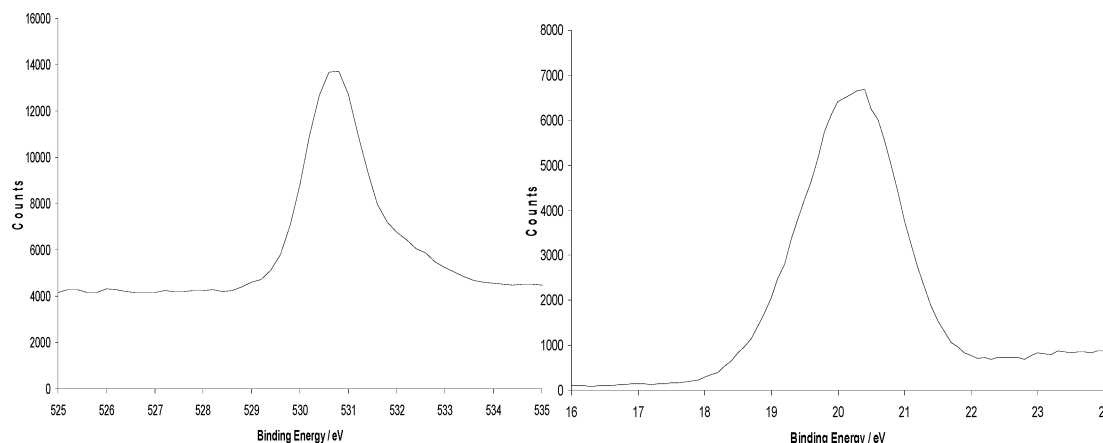


Figure 2. X-ray photoelectron spectroscopy peak profiles for a Ga_2O_3 sample showing on the left the oxygen 1s region and on the right the gallium $2p_3$ region.

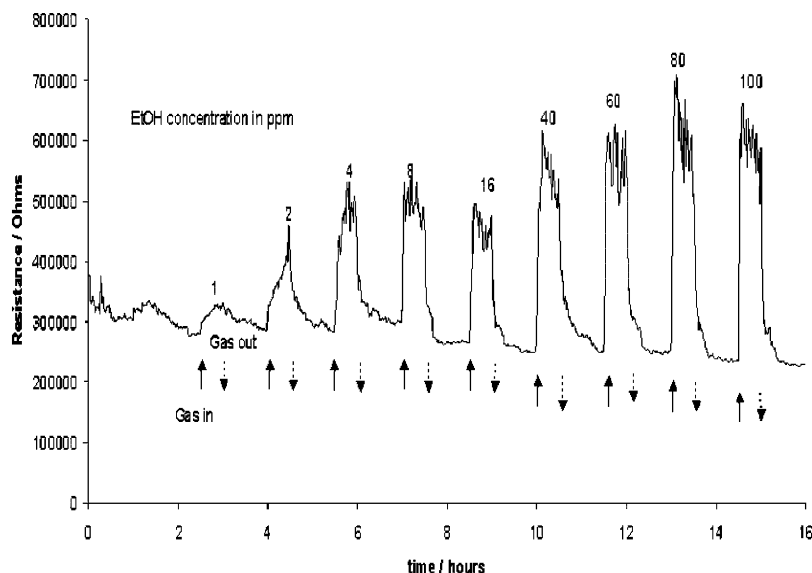


Figure 3. Plot of gas response versus gas concentration for a gas-sensing experiment run at 450 °C. Arrows indicate when the gas flow of ethanol was turned on and off.

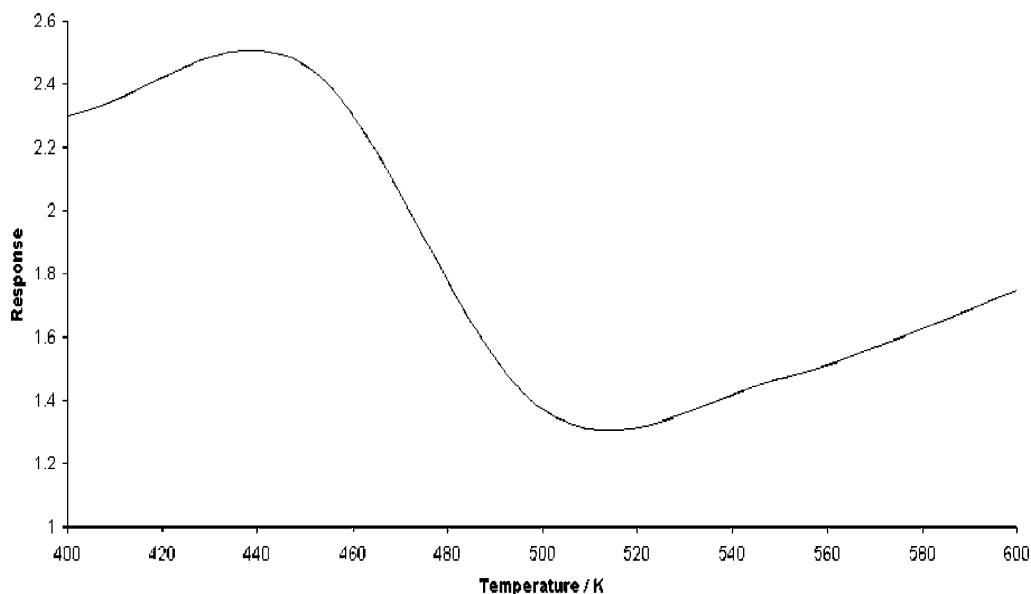


Figure 4. Plot of ethanol response (R/R_0) of the Ga_2O_3 sensor versus sensor operating temperature. The ethanol concentration was kept constant at 100 ppm.

silicon, iron, and aluminum. Notably the same onset temperature of 400 °C for deposition occurred irrespective of substrate, indicating that substrate selective deposition does not occur in the production of Ga_2O_3 films.

The mechanism of reaction was not determined in this study. It is likely that HCl is produced along with CH_3Cl .³⁰ It is not likely that this reaction occurred via an adduct reaction as no material other than product was recovered from the reactor and no evidence of pin-holing was observed in the samples as seen in other works where adduct formation was noted.³¹

The current widely held view of gas sensors³² states that the conductivity of semiconducting oxides in air is determined by the trapping of electrons in surface states associated with surface-absorbed oxygen. If interstitials or oxygen vacancies are immobile in the lattice, then the behavior is described in terms of electron distribution between bulk and surface states. The surface

conductivity is sensitive to small amounts of reactive gas as catalytic surface processes result in a change in the surface coverage of the oxygen surface trap states. If oxygen defects are mobile within the lattice, then the conductivity is determined by the equilibrium between bulk lattice defects and oxygen in the gas phase, and sensitivity to trace reactive gases is lost. A further case for gas sensing can arise where there is a time dependence on the equilibration of lattice and surface states.

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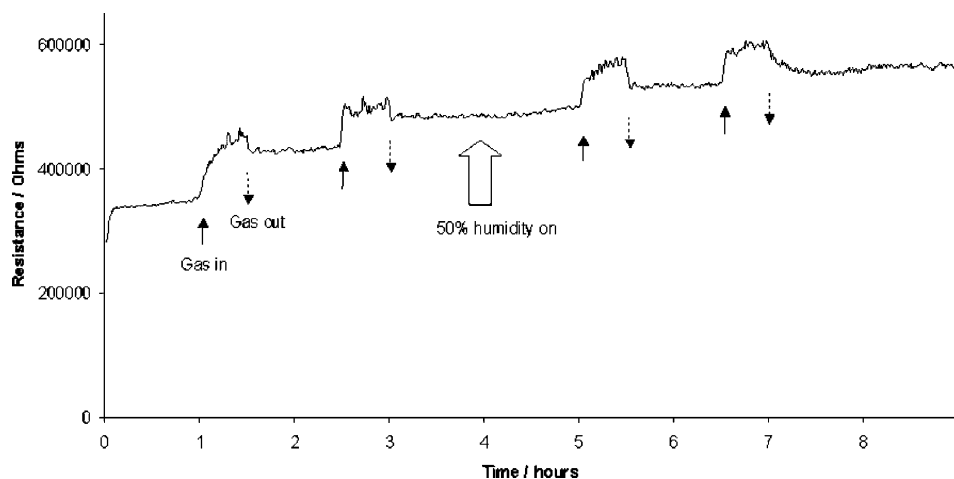


Figure 5. Resistance of a Ga_2O_3 sensor on exposure to ethanol in dry air and air of 50% humidity. The first two peaks are gas responses to ethanol (40 ppm) in dry air and the second two responses to ethanol (40 ppm) in 50% humidity.

Conductivity time dependence can also be observed as a result of lattice defect migration, which alters the potential and thus the charge carrier distribution near the surface. Due to a micro-structural effect, part of the conductivity is gas-sensitive due to modification in surface reactions, while the conductivity contributed by the bulk is not gas-sensitive.³³ If the films are especially thin (hundreds of nanometers), then dense films such as those produced by CVD methodology may produce high-quality gas sensors.

For the Ga_2O_3 sensors made here the change in resistance is due to changes in oxygen trap sites in response to the catalytic oxidation of ethanol. This is not due to absorption, as we would expect to see a marked change in the gas-sensing response on the introduction of humidity into the gas chamber. At the temperatures used oxygen defects within Ga_2O_3 must be low. The gas response for the Ga_2O_3 sensors to ethanol was biggest at 450 °C where R/R_0 was 2.45. For all samples the gas response increased with gas concentration as expected, although the signal appeared to saturate at around 60–100 ppm of ethanol gas. Humidity did not have as pronounced an effect as has been seen with other types of metal oxide sensors.³⁴ This is probably because the surface-absorbed water is not associated with the same surface state as the surface-absorbed ethanol. This is particularly useful as SnO_2 , the most widespread material in use, as a gas sensitive resistor shows a large change in resistance with relative humidity.³⁴ This makes SnO_2 unsuitable for a range of purposes.

The response peak shape for all samples was quite “square”; this indicates that some of the resistivity change is a result of contributions from the bulk of the material as indicated above. As dense films have relatively fewer adsorption sites than porous films, they will saturate quicker. This is likely to be a contributing factor to the square response and also ties in with the

maximum of response. Previous work has examined the gas-sensing properties of PVD-prepared gallium oxide films in the presence of gases such as methane and carbon monoxide.^{15,16} At higher temperatures (>600 °C) methane gas is readily sensed; an example result indicates that the R_0/R value for a sensor prepared by sputtering to 5000 ppm methane in dry air is 40 at 700 °C. Conversely, at 600 °C the R_0/R value for 5000 ppm carbon monoxide is around 5. Values for R_0/R for APCVD-produced films range between 1 and 2.45 for gas concentrations between 1 and 100 ppm. Despite the bulk contribution to the resistance due to the density of these films they are still responsive sensors. For functional devices they show a maximum R/R_0 response at 450 °C. This is significantly lower than the sputtered material (700 °C). Such a lowering of maximum response temperature is important as sensor devices are often required to work in remote/hostile environments and run off of a battery; hence, lower maximum temperatures require less energy.

Conclusion

Reaction of gallium trichloride with methanol under APCVD conditions affords clear films of gallium oxide on a variety of substrates. The films show good surface coverage, adhesion, and uniformity. Gallium oxide films of a single phase were obtained. These were colorless in appearance and had low electrical conductivity at room temperature. The response to reducing gas (ethanol) by APCVD-prepared gallium oxide gas sensors was evaluated. It was found that there was a significant gas-sensing response which was most pronounced at 450 °C.

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