

# Antimony oxide thin films from the atmospheric pressure chemical vapour deposition reaction of antimony pentachloride and ethyl acetate

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## Abstract

The reaction of antimony pentachloride and ethyl acetate under atmospheric pressure chemical vapour deposition conditions leads to the production of antimony (III) oxide thin films on glass and gas sensor substrates. Scanning electron microscopy (SEM) indicated that an island growth mechanism predominated. X-ray photoelectron spectroscopy (XPS) revealed binding energy shifts of 20.6 eV for O 2s and 35.4 eV for Sb 4d. The films were X-ray amorphous. Energy dispersive X-ray analysis (EDXA) and electron probe microanalysis (EPMA) gave coherent elemental compositions indicating that single phase  $\text{Sb}_2\text{O}_3$  was made, with negligible impurity levels. The films showed little optical reflectance (~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 400 °C.

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*Keywords:* APCVD; Antimony oxide; Gas sensor

## 1. Introduction

Facile routes to metal oxide thin films are of interest because of the applicability to the microelectronics and gas sensing industries. Antimony oxide ( $\text{Sb}_2\text{O}_3$ ) has received interest as a co-catalyst [1], and as an additive in flame resistant polymers [2]. Additionally it has been used as the base for a new type of glass [3], and has an application within ceramics [4]. Several investigations have been conducted into antimony oxide as a nanomaterial [5–7]. Antimony oxide thin films have received attention. An extensive investigation into the electrical, optical and structural properties of films produced by thermal vacuum evaporation has taken place [8,9]. Additionally investigations by sputtering [10] and spray pyrolysis have also been conducted. Metal organic CVD has been studied using precursors such as antimony butoxide or tri-ethyl antimony

[11] at 600 °C. Aerosol assisted CVD has been investigated using antimony (V) chloride and water [12,13]. It was found in all cases that films of  $\text{Sb}_2\text{O}_3$  were produced, though often in coexistence with  $\text{Sb}_6\text{O}_{13}$ .

Pure antimony oxide has received scant attention for its gas sensing properties [12,14]. A preliminary conference report on the use of a single antimony oxide thin film as a gas sensor suggest a small response to methane gas (resistance decreased by 15%) and some recovery on the removal of the gas. However this report showed a bigger change in resistance of the baseline (25% resistance increase) over a 15 min period than the actual sensor response [15,16]. The production of thin films by APCVD affords inexpensive, adhesive reproducible films with low impurity levels [17], and may therefore provide an advantageous method of producing gas sensors. APCVD has the added benefits of fast growth rates and high surface coverage [18,19]. CVD methods are directly compatible with Si-micro fabrication technology. It is important to evaluate whether the generally dense films produced by CVD are compatible

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with solid-state oxide gas-sensors. Typically solid-state oxide gas-sensors are made by screen-printing and tend to be very porous.

Here we report the first instance of an antimony oxide film being made using APCVD and the first investigation of the gas sensing properties of such a film. Indeed we show that thin film CVD prepared antimony oxide can be a useful gas sensing material for reducing gases such as ethanol.

## 2. Experimental

Nitrogen (99.99%) was obtained from the British Oxygen Company (BOC) and used as supplied. Coatings were obtained on SiO<sub>2</sub> coated float glass. APCVD experiments were conducted on 150 mm × 45 mm × 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 isopropanol 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<sup>-1</sup> 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.

Antimony (V) 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 120 °C by a heating jacket and SbCl<sub>5</sub> 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 later 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 0.3 and 1.0 L min<sup>-1</sup>.

X-ray photoelectron spectra were recorded with a VG ESCALAB 220I XL instrument using a 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 a 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 standardised 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 4-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 interdigitised 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 [22]. Test gasses 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.

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