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# A Novel Approach to Electronic Nose-Head Design, Using a Copper Thin Film Electrode Patterning Technique

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**Abstract:** Presented in this paper is a process for manufacturing copper electrode patterns on alumina substrates using thin film deposition, spin coating and printed circuit board (PCB) etching techniques. The process was used for the design and manufacture of an array of gas sensors for use in an electronic nose system. This approach was executed in three phases. Firstly a 500nm layer of copper was deposited onto the alumina substrate. Secondly photoresist was applied by spin coating onto the copper layer and finally the PCB etching process was used to achieve the final electrode pattern. Conducting polymer composite materials were deposited onto the resulting electrode patterns producing an array of sensors for vapour detection. The sensor array showed good responses to Propanol at concentrations ranging from 5000ppm to 30000ppm with fast recovery times. The sensor array was slotted into an electronic nose system and an illustrative analysis of the sensor array's ability to discriminate between different solvents was carried out with promising results.

## 1. INTRODUCTION

Existing methods for gas sensor electrode manufacture on alumina substrates include screen-printing[1], thermal evaporation [2, 3] and sputtering[4]. Screen-printing is a commonly used process for laying electrodes on a substrate for electronic nose sensors[5, 6]. Screen-printing is a thick film technology that involves mixing a viscous paste and uses a squeegee to force the paste through the apertures of a stencil screen to form the pattern on the substrate[7]. Once the screen printing is complete it is required to sinter the sample[8]. Thermal evaporation is a process whereby the material to be deposited is placed in a molybdenum boat within a vacuum chamber and a high current is passed through the boat heating the metal until vaporization. A crystal oscillator thickness monitor displays the thickness of material deposited on the substrate. A mask placed over the substrate allows a specific pattern to be created. Sputtering is also an evaporation process whereby the substrate and target material to be deposited are placed in a vacuum chamber. A plasma beam is created in a passive gas such as argon. The ion bombardment is directed at the material to be deposited causing atoms to be propelled towards and bond with the substrate. An example where sputtering

has been used to create electrode patterns on alumina substrates for gas recognition is shown in the literature [4].

Despite the success achieved by these techniques to date they do have their shortcomings in gas sensor electrode manufacture. The thin film coating process is unable to achieve the resolution attainable using PCB fabrication methods. A typical gas sensor electrode gap produced using thin film coating is 5mm[2, 3]. Screen Printing and Thin Film methods require specially designed masks for each new pattern, this may be time consuming and costly. There are several factors that have to be controlled in screen printing to obtain reproducible electrode patterns such as conductor paste viscosity, screen gap, print speed, squeegee and substrate positioning. Any changes in these parameters can seriously affect the dimensions of the electrode pattern [9].

This paper proposes the use of thin film deposition, spin coating and printed circuit board (PCB) etching techniques to manufacture copper electrode patterns on alumina substrates for use in an electronic nose. The electrode patterning technique used in this paper has several advantages over existing techniques. The flexibility of the PCB manufacturing process means that any single-sided electrode pattern is achievable.

The fact that the masks for this process are printed onto acetates means that they are easily replaced, immediate and cost-effective unlike the masks required for other patterning techniques. The versatility of this process allowed for several electrode patterns to be produced with gaps as small as 200microns. This process allows for the production of small easily replaceable sensor arrays to be created. This process was used in the development of a gas sensor array for use in an electronic nose system.

## **2. EXPERIMENTAL**

The five stages of the experimental process were (a) Preparation of the Cu filings, (b) Substrate preparation, (c) Thermal evaporation of a Cu layer onto the alumina substrate, (d) spin coating a layer of photoresist onto the copper-coated alumina substrate and finally (e) electrode patterning using PCB etching techniques. The final step using PCB etching techniques is proportionally the shortest stage that only takes 2 minutes once the mask has been designed and printed.

### **2.1. Preparation of Copper Fillings and substrates**

Cu filings and alumina substrates were prepared using a standard cleaning procedure using– (a) acetone, (b) methanol and (c) deionised water.

### **2.2. Thermal Evaporation of Cu onto Alumina**

An Edwards coating system E306A was used to deposit the Cu onto the alumina substrates. The Cu was placed into a molybdenum boat and placed between the electrodes. One boat of Cu produces an average thickness of 500nm so to achieve thicker Cu films more than one boat of material is required. A max of four boats can be used during an evaporation process. The vacuum process starts with producing a rough vacuum, which removes most of the air inside the chamber. This process takes approximately 15min or until a vacuum of  $2 \times 10^{-1}$  is produced. The system was then set to high vacuum, which was achieved using an oil diffusion pump. It can take up to an hour to reach the required vacuum of  $1 \times 10^{-5}$  mbar. A large current was passed through the boat and the Cu starts to melt and evaporate. At this stage the shutter was open and the Cu began depositing on the substrate. When the required thickness was reached or

all the Cu in the boat was deposited the shutter was closed and the current was turned off.

### **2.3. Photoresist Deposition**

The copper coated alumina substrate was split into 2”\*2” substrates in preparation for photoresist deposition. A spin coater was used to deposit AZ5214 photoresist. The AZ5214 was used to develop a positive image on the substrate. Using a plastic dropper a layer of the photoresist was smeared over the substrate. The speed of the spin coater was ramped up to 5000rpm for 30 seconds to remove excess photoresist and achieve a thin layer. The spin coater was then ramped up to 7800 for 10 seconds to eliminate the photo resist from the edge of the substrate and then reduced to 0rpm. Subsequently the substrate was removed from the spin coater and cured at room temperature for 24 hours.

### **2.4. Electrode Patterning**

Following the deposition of copper and photoresist onto the alumina substrate, electrode patterning commenced. The desired patterns were drawn in Eagle, a PCB cad package. The designs were then printed onto acetate using a laser printer in preparation for UV exposure. The acetate was placed over the substrate in the UV exposure unit and exposed to UV light for 30 seconds. Subsequently the substrate was removed from the UV exposure unit and placed in Electrolube PDN250ML developer solution for 10 seconds. The substrate was rinsed in water and dipped in etching solution made from SENO 3207 fine etch crystals for approximately 10 seconds, revealing the electrode pattern design. In order to remove the photoresist from the remaining electrode pattern the substrate was re-exposed to UV light with no mask for a further 30 seconds and placed in the developer solution for 10 seconds.

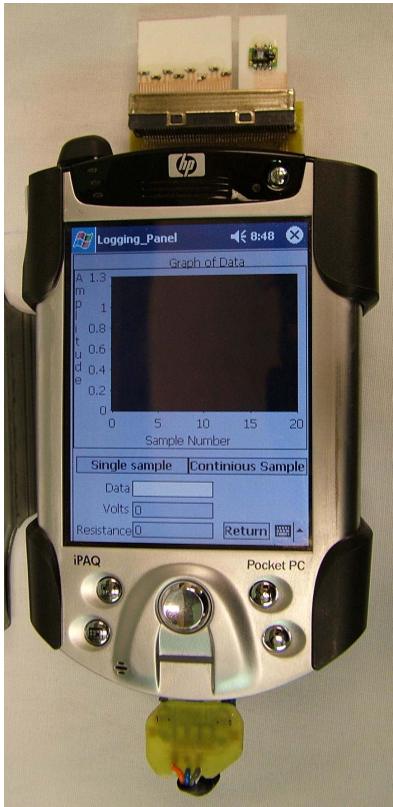
### **2.5. Material Deposition**

Seven polymer-carbon black materials were prepared as described in [10] and deposited between the copper electrodes on the alumina substrate using a drop coating technique. Tab. 1 details the seven polymers deposited.

Sensor 1	PVAc	Polyvinyl acetate
Sensor 2	PEG	Polyethylene glycol
Sensor 3	PEA	Polyethylene adipate
Sensor 4	PVP	Polyvinyl pyrrolidone
Sensor 5	PMMA	Polymethyl methacrylate
Sensor 6	PVB-co-VA-co-VAC	Polyvinyl butyral –co- vinyl alcohol –co- vinyl acetate
Sensor 7	PVB	Polyvinyl butyral
Sensor 8	PEA	Polyethylene adipate

**Tab. 1.** Materials deposited across electrodes.

### 2.6. Illustrative experiment



**Fig. 1.** Application of resulting sensor design, showing the sensor design inserted into the electronic nose system.

The sensor array was slotted into the e-nose system as shown in Fig. 1. The system was exposed to propanol, acetone, methanol and isopropanol to demonstrate the varying response patterns of the array to each vapour. The e-nose system was set sampling 10 seconds prior to vapour exposure to obtain a

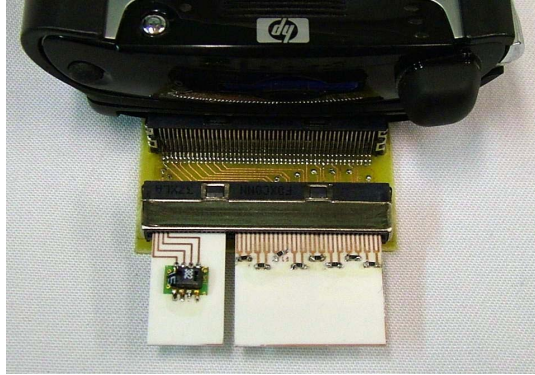
baseline value. 25cm<sup>3</sup> volumes of each solvent were placed into individual glass bottles. The e-nose system was held 1cm above each solvent container for 20 seconds to obtain a response and then moved away from the container to allow the sensors to return to their baseline values. This process was repeated for each solvent.

### 2.7. Controlled exposure of sensor array to propanol

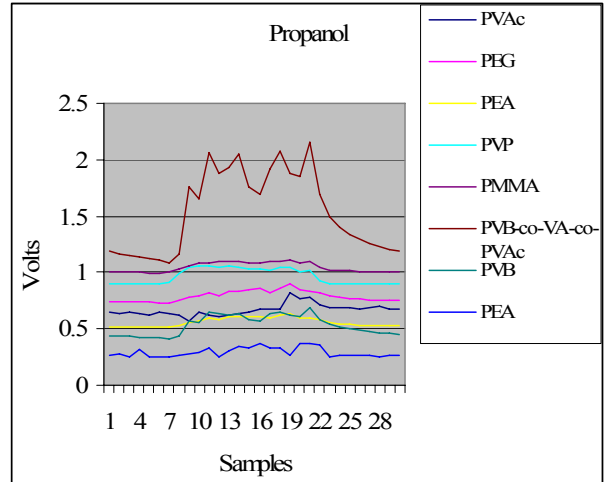
A gas-sampling chamber with mass flow controllers was designed in house and used to examine the response of the sensor array to propanol at concentrations ranging from 5000ppm to 30000ppm. The chamber was flushed for 2minutes prior to exposure to obtain a baseline response to air. The sensors were then exposed to a dynamic flow of the vapour for 1 minute followed by flushing for two minutes to bring the sensors back to baseline. A DAQ card was used to acquire the sensor responses which were recorded by LabVIEW software.

## 3. RESULTS AND DISCUSSION

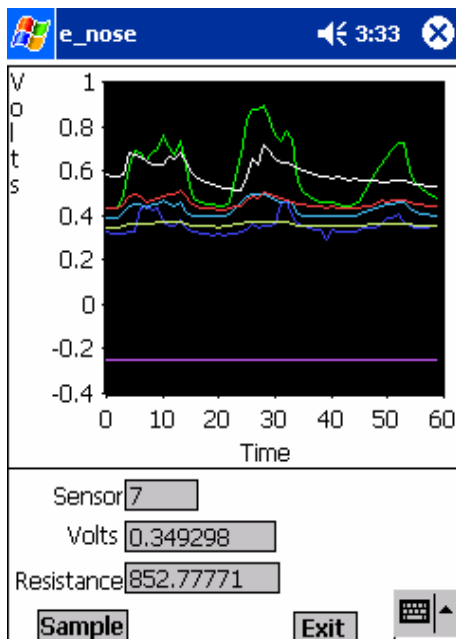
The prototype system is presented in Fig. 1. and Fig. 2. showing the final electrode designs inserted into the electronic nose prototype eliminating the need for solder joints. Fig. 3 shows a screen shot of the LabVIEW software on the PDA displaying the response of the sensor array to propanol, acetone and isopropanol respectively. This experiment was carried out in uncontrolled circumstances to illustrate the ability of the array to produce a signature pattern for each solvent and potentially discriminate between these patterns for solvent identification. The response time which was taken as the time it takes the sensor to reach 90% of max response was between 3-5sec. The recovery times were equally as fast and returned to baseline immediately when the moved away from the solvent. Fig. 4, Fig. 5, Fig. 6, Fig. 7 show the response patterns obtained when exposed to propanol, acetone, isopropanol and methanol respectively. These graphs again clearly demonstrate the ability of the sensor array to produce unique patterns for each solvent in uncontrolled circumstances.



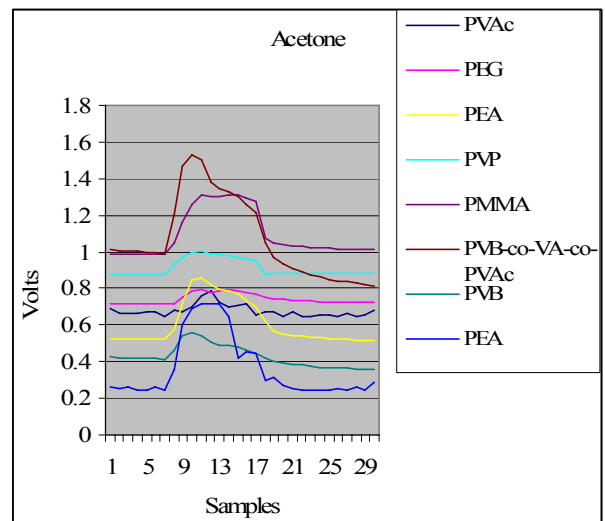
**Fig. 2.** A close up of the design inserted into interfacing electronics.



**Fig. 4.** Response of sensor array to propanol



**Fig. 3.** Screen shot of software on PDA showing the response of the system to propanol, acetone and isopropanol respectively.



**Fig. 5.** Response of sensor array to acetone.

The sensor array was placed in a controlled gas-sampling chamber with mass flow controllers at 25°C. The sensor array showed typical response patterns when exposed to propanol at concentrations from 5000ppm to 30000ppm as shown in Fig. 8. The response of each sensor increased as the concentration of the solvent increased. This corresponds with the transduction mechanism for conducting polymer composites sensors, which is based on percolation theory. The more vapour absorbed into the composite material the more the conducting particles are pushed apart breaking down conducting pathways and increasing the resistance of the material. This in turn causes an increase in voltage dropped across the sensor.

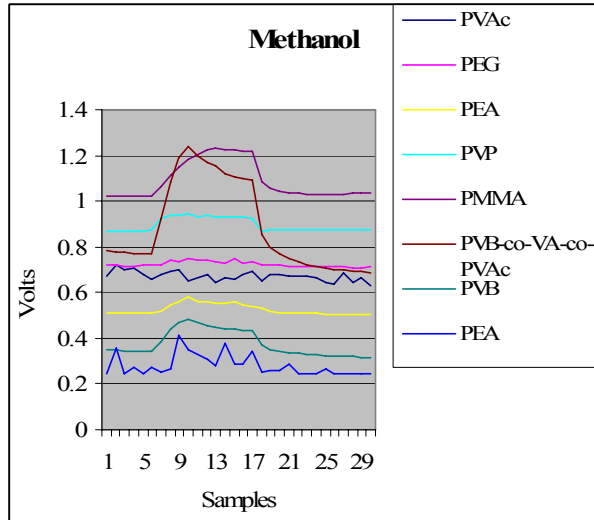


Fig. 6. Response of sensor array to methanol.

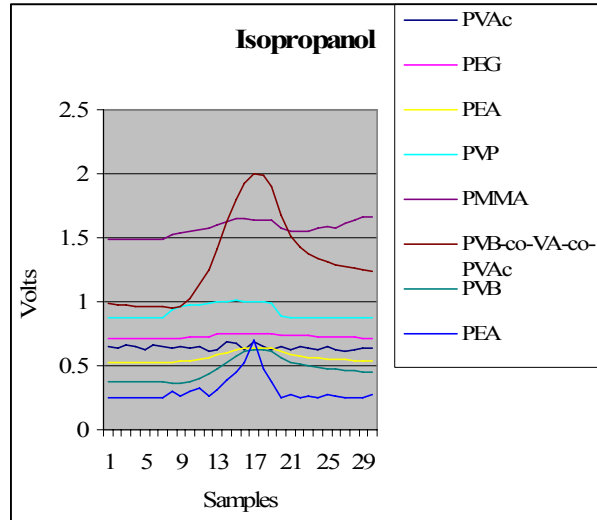


Fig. 7. Response of sensor array to isopropanol.

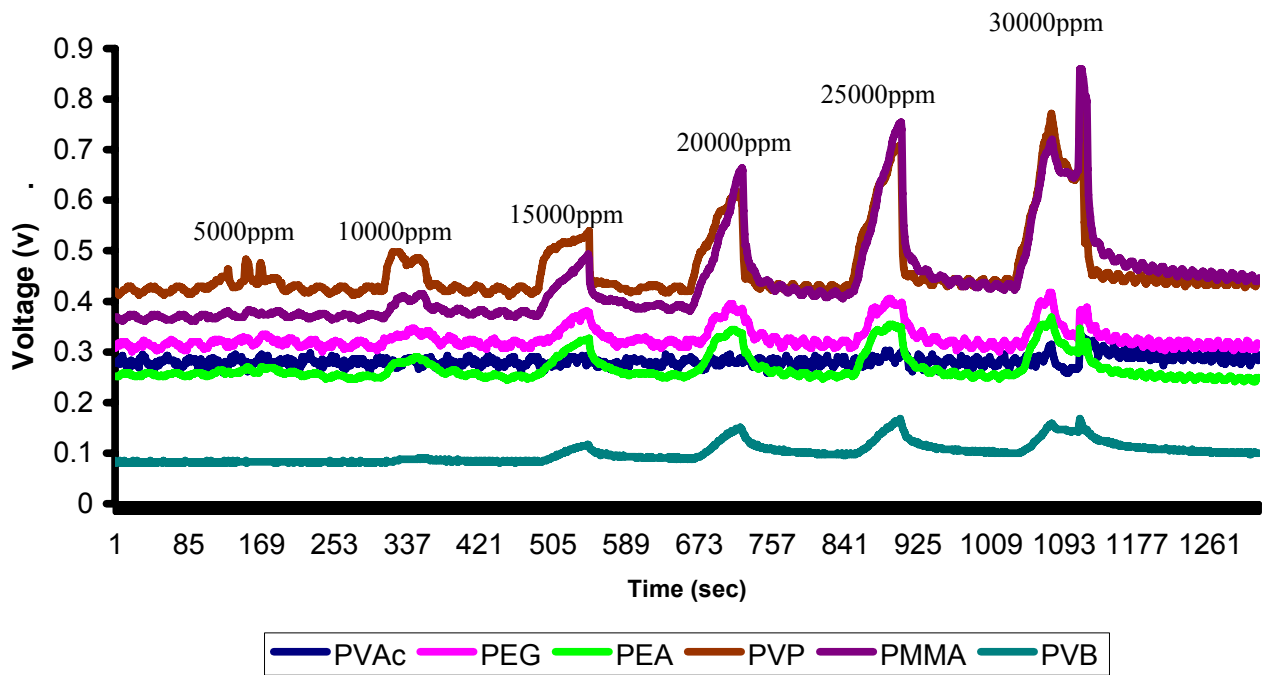


Fig. 8. Response of the conducting polymer composite array to propanol at concentrations ranging from 5000ppm to 30000ppm

#### 4. CONCLUSIONS

A novel electronic nose head has been fabricated using a copper thin film patterning technique and conducting polymer composite materials. This work has demonstrated a method for the design and manufacture of thin film electrodes on alumina

substrates for use as gas sensors in an electronic nose. It has been shown that using the techniques described it is possible to manufacture electrodes that are cost effective, immediate, easily replaceable and reproducible. Using a slot connector also eliminates the need to solder or bond wires onto the copper contact on the substrate allowing for a modular

design. An electronic nose prototype was developed with a conducting polymer composite sensor array capable of producing a signature pattern for four solvents tested in uncontrolled circumstances with almost real time response and recovery times.

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