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GOLD NANOPARTICLE CMOS SENSOR FOR VOC DETECTION

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Abstract: A novel hybrid system comprising CMOS ASIC chip and two chemoresistors arranged in mono and duo-type ratiometric configurations has been developed. The ASIC chip has been designed to overcome problems associated with discrete chemoreistors, such as temperature dependence of baseline resistance and aging effects; in this work it is used in combination with gold-nanoparticle chemoresistors to demonstrate its advantages. Duo-type configuration (two different materials as fully active elements) was particularly successful in terms of achieving good results in terms of both sensitivity and selectivity.

Keywords: Chemical sensor, Smart sensor; VOC detection

Introduction

Chemical sensors are often challenging to work with because their performance usually depends upon ambient temperature, humidity, and long-term stability/drift. However, using the ratio of two identical/correlated chemical sensors can ameliorate these factors. A low-cost ASIC developed at Warwick [1] allows the integration of thin film chemoresistors in a ratiometric arrangement. The ASIC is designed such that the chemoresistors form two resistors in a non-inverting amplifier circuit. In addition to transducing changes in resistance of the chemoresistors, the ASIC has a temperature controlling circuit which sets their operating temperature. The ASIC was fabricated (via Europractice) through a standard CMOS process. Research on thin film materials comprising of ligand stabilized nano-particle materials has shown that it is possible to modify the physical and chemical properties of these materials and hence control the chemical selectivity [2]. As most odour molecules are usually VOCs, the use of different bifunctional linker molecules with gold nanoparticles allows us to 'tailor' these films to detect specific odours. Three different types of linker molecule were employed to make novel chemoresistors.

Hybrid System Configuration

Figure 1 shows the non-inverting configuration of an operational amplifier. The elements R_p and R_{po} represent the two gold-nanoparticle chemoresistors.

In a standard mono-type arrangement with one active and one passive element: the 'active sensor' is R_p and the 'passive sensor' is R_{po}. The output voltage is directly proportional to R_p/R_{po}. Any common changes to the individual resistors are cancelled as a result of this ratio.

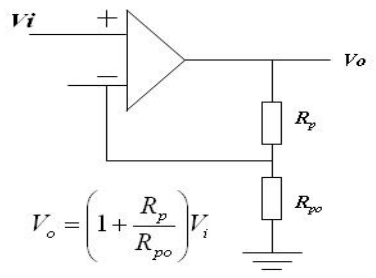

Fig 1. Non-inverting amplifier circuit.

Figure 2 shows a photograph of the final hybrid system with the fabricated ASIC and two chemoresistors wire bonded to it.

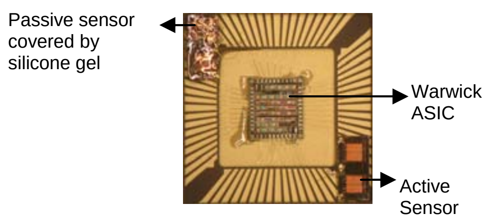

Fig 2. Photograph of the ASIC with the active and passive chemoresistors bonded to it.

Experiments

A study was carried out to sense five chemicals (toluene, propan-1-ol, ethanol, methanol and water) at two different humidities. Two combinations of the chemoresistors used were explored: (a) mono-type devices with chemo-resistors of the *same* film material, but one shielded from the VOCs; and (b) duo-type devices with chemo-resistors of *different* film materials but both exposed to the VOCs. The responses of three different gold nanoparticle linker structures were studied. Linker structures used were: (a) AuMAH: Gold 2-Mercapto-N-[6-(2-mercapto-acetylamino)-hexyl]-acetamide; (b) AuNT: 1,9-nonanedithiol;(c) AuHDT: 1,16-hexa-decanedithiol. Two chemoresistors were selected such that the resistive ratio was as close to unity as possible before exposing to any VOC. The first set of tests were carried out on AuMAH and AuNT sensors at 0% relative humidity (rh) and then at 40% rh. The experiments were first carried out for response to toluene (concentration: 442, 619, 884, 1945, 2918, 4156ppm) and ethanol (805, 1127, 1610, 3542, 7566ppm) at 30°C, and then repeated at 40°C to check for temperature dependence. The flow rate over the sensors was kept at 300 ml/min. The sensors were exposed for 20 min each time, with a 20 min gap between concentrations. The second set of measurements was taken on AuMAH and AuHDT materials with five different chemicals (toluene: 395, 2373, 4321, 2363, 395ppm; propan-1-ol: 276, 1653, 3011, 1653, 276ppm; methanol: 1761, 10567, 19244, 10567, 1761ppm; ethanol: 793, 4758, 8664, 4758, 793ppm; water: 322, 1930, 3514, 1930, 322ppm) at 30°C at 0%rh and then repeated at 40%rh. The flow rate was kept at 400 ml/min.

Results

For the first set of results, it was noticed that at higher temperatures the baseline was more stable. However, the magnitude response decreased for both materials by 10-15%. The AuNT and AuMAH materials gave better results for ethanol than toluene. A reduction in response was also observed at higher humidities. For duo-type tests it was expected that the results for one VOC would be enhanced and for the other one cancelled out. The results obtained showed a reduced response to toluene, but no significant increase in response to ethanol was observed. The response decreased by about 20% at higher humidities and by about 50% at 40°C. The second set of tests was carried out with AuHDT and AuMAH sensors. The AuHDT film has a similar structure to the AuNT film but the linker structure is longer. The AuMAH device favoured response to toluene and propan-1-ol as compared to the other VOCs. The AuHDT sensors gave a large response to toluene, about 80% higher than that obtained with AuMAH. At 40%rh response reduced by half an order of magnitude for AuMAH, but showed slightly higher values for all the chemicals expect water for AuHDT. The average response values obtained for mono-type devices are summarised in Table 1. The most interesting results were achieved with duo-type configuration where a very high response was observed for toluene with a percentage change in the magnitude of voltage output of about 80% at 0%rh and 90% at 40%rh. For methanol, the percentage change in output voltage was about 35% at both relative humidities. Figure 3 shows a typical response to toluene of the device in duo-type configuration.

Table 1. Average values obtained for the two materials at 0%rh in mono-type configuration.

Analyte	**Average Value using AuMAH (ΔV/ppm)**	**Average Value using AuHDT (ΔV/ppm)**
Toluene	1.42×10^{-4}	2.50×10^{-4}
Propan-1-ol	1.84×10^{-4}	7.29×10^{-5}
Methanol	3.06×10^{-5}	1.76×10^{-5}
Ethanol	7.38×10^{-5}	3.22×10^{-5}
Water	6.0×10^{-5}	1.64×10^{-5}

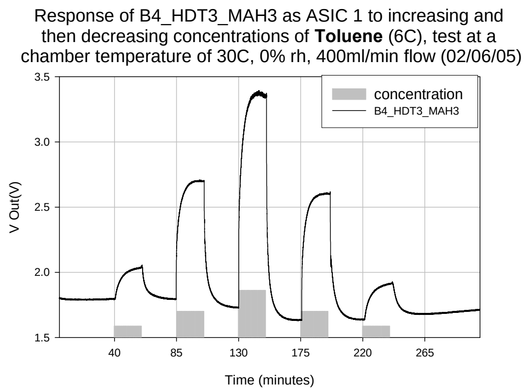

Fig. 3. Typical response to toluene at 30°C with 0%rh in duo-type configuration.

Conclusions

We report on a novel hybrid CMOS-compatible sensor system employing different gold-nanoparticle based chemo-resistive elements as a first step towards complete monolithic smart system implementation. The ASIC chip operates in either mono or duo type configurations. We conclude that duo-type CMOS sensors offer superior performance over conventional single element chemo-resistive VOC sensors.

Acknowledgements

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