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 chemoresistors, 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.

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-hexadecanediol. 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.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Average Value using AuMAH (ΔV/ppm)</th>
<th>Average Value using AuHDT (ΔV/ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>1.42 x10^-4</td>
<td>2.50 x10^-4</td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>1.84 x10^-8</td>
<td>7.29 x10^-8</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.06 x10^-9</td>
<td>1.76 x10^-9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>7.38 x10^-5</td>
<td>3.22 x10^-5</td>
</tr>
<tr>
<td>Water</td>
<td>6.0 x10^-9</td>
<td>1.64 x10^-9</td>
</tr>
</tbody>
</table>

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.

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