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Surface ionisation gas detection: Vertical versus planar readout modes

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ABSTRACT

The work is concerned with the micro-miniaturisation of surface ionisation (SI) gas sensing devices. MEMS microheaters, originally designed for the heating and readout of metal oxide (MOX) gas sensing layers, have been configured to observe SI gas sensor signals. We show that this can be performed in two distinctly different ways. In the first, vertical mode, one of the interdigital platinum (Pt) electrodes on top of the dielectric heater membrane is used as an ion emitting layer while a flat-plate counter electrode, positioned at a short distance above the emitting Pt electrode, is used for the ion current readout. In the second, planar mode, one of the two Pt interdigital electrodes is used as an ion emitter while the second serves as an ion collector. We show that both modes of readout feature ionisation efficiencies orders of magnitude larger than our previously investigated thin-film, flat plate devices. We attribute this first fact to the field enhancement that occurs at the sharp edges of Pt interdigital electrodes. Both modes of readout, however, differ considerably with regard to gas selectivity: whereas in the vertical readout mode a relatively high level of amine selectivity is observed, only a broad-range selectivity is observed in the planar mode. We conclude from this latter observation that the amine-selectivity, which is typical of SI devices, only arises when the surface–adsorbate bond needs to be broken, i.e. whenever analyte ions are forced across an air gap.

1. Introduction

Metal oxide (MOX) gas sensors are widely employed for gas monitoring and alarm applications. Other applications are in the field of electronic nose devices [1–6]. For operation, MOX gas sensors need to be heated to temperatures in the range from 200 to 500 °C. In the past two decades a great deal of work had been devoted to reduce the heating power consumption of such devices [7–10]. Whereas early MOX sensors on ceramic heater substrates consumed heating powers in the order of 1 W per sensor element [11,12], this power consumption could be decreased in the order of tens of milli-Watts using silicon MEMS technologies [7–10]. The latest development in this quest for even lower power consumptions are MOX devices based on single nanowires (SNW). In such extremely miniaturised devices the current flow, that is needed to interrogate the SNW devices, is able to produce a self-heating effect that is large enough to heat the nanowires into the range of temperatures where conventional MOX gas sensors are being operated [13]. In this latter kind of SNW devices the power consumption can be reduced into the level of micro-Watts; i.e. into a range that can be directly supplied by energy harvesting from the environment, i.e. without using batteries [14].

The common working principle of all such sensors are oxidising or reducing surface interactions which alter the concentration of electronic charge carriers in the sub-surface region [1–6,15,16]. In such resistive response (RES) sensors the sensor signal is a change in the in-plane electronic conductivity of the sensing layers. More recently we have shown that MOX sensing layers can also give rise to a surface ionisation (SI) response [17–19]. Surface ionisation is a form of gas response that relies on the adsorption of gas or vapour molecules on heated solid surfaces, the transfer of a valence electron from the adsorbed analytes to the adsorbent solid and the extraction of the ionic surface species towards a collector electrode positioned at a short distance from the ion-emitting surface [20–22]. A striking feature of the SI process is its high sensitivity and selectivity towards hydrocarbons with amine functional groups. This latter property has recently been exploited for realising sensitive, selective and low-complexity sensors for amphetamine-type illicit drugs [23,24].

In the present work we are concerned with the miniaturisation of SI gas sensors using silicon MEMS technologies. In particular, we should like to show that it is possible to produce efficient SI gas sensors from commercially available silicon microheaters, which had been designed to realise conventional RES gas sensors [25]. In the work presented below we show that silicon microheaters fitted

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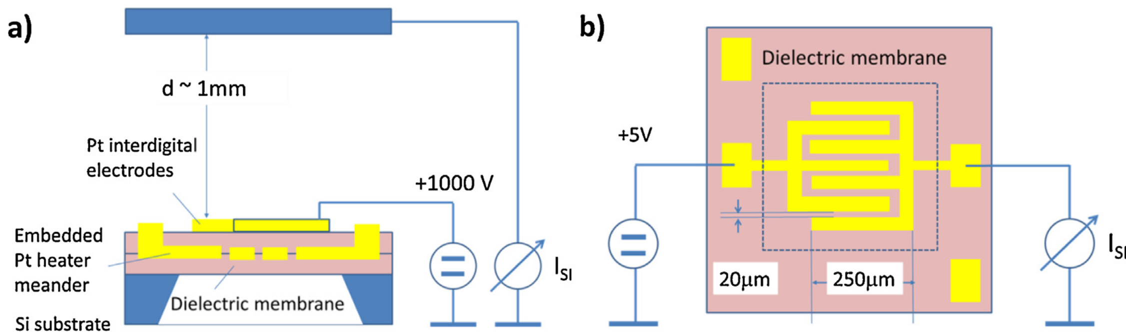

Fig. 1. Vertical (a) and planar (b) readout of the surface ionisation response of MEMS microheater substrates.

with pairs of interdigital platinum (Pt) electrodes can be turned into SI gas sensors and that these can be read out in two different modes with distinctly different gas selectivity properties. In both modes, a very high ionisation efficiency could be observed which is orders of magnitude higher than the emission from our previously used thin-film, flat-plate devices [17–19,23,24] and comparable to SI devices based on single nanowires [26,27].

2. Experimental details

The MEMS heater substrates investigated were supplied by AppliedSensor [25]. These heaters feature a massive silicon frame which supports a suspended dielectric membrane with an embedded platinum (Pt) heater. The top surface of the membrane carries a pair of interdigital Pt electrodes (IDE), which are foreseen to serve as contacts to custom-specific MOX sensing layers. In our experiments we used such substrates in their as-received form without any MOX sensing layer. One or both of the IDEs were used as a surface ion emitting layer. In order to observe SI emission from such an IDE, a grounded counter electrode is needed. As shown in Fig. 1, such a counter electrode can be supplied in either of two forms. In the example shown in Fig. 1a, a flat-plate counter electrode was positioned at a distance of approximately 1 mm above the heated membrane. In this first, vertical readout mode, the counter electrode is at room temperature or slightly above. Electron or ion emission at such a counter electrode is practically impossible and any emission current therefore needs to originate from the heated IDE on top of the heated membrane. In the second, planar readout mode, one of the IDEs is positively biased while the second is at ground potential. As here both IDEs are hot and therefore principally able to emit ions, the same amount of ion current is expected as the bias potential at the IDE pair is reversed.

Heating of the IDEs can be performed by passing a current through the embedded heater meander. Due to the good thermal insulation of the dielectric membrane, temperatures in the order of 500 °C can be attained at the expense of about 50 mW of electrical power input into the Pt heater meander. This attractive possibility, however, could not be exploited yet because of a non-negligible electrical cross-talk between the heater and ion collection circuits. In order to obtain a good SI response, we operated the MEMS devices in a passive heating mode. To this end, the MEMS chips were clued with ceramic solder onto the ceramic heater substrates which had been used in our previous experiments on surface ionisation [17–19].

3. Results

The main distinguishing characteristics of the vertical and lateral readout architectures are electrode distance and temperature of the ion collecting counter electrode as well as nature of the insulator gap (air versus silicon oxy-nitride). The data in the following show that these differences manifest themselves in different forms of the current–voltage characteristics, in differences in the activation energies for the SI emission and in different selectivity properties when easily ionisable molecules are admixed to the ambient air atmosphere.

3.1. Current–voltage characteristics

Whereas IV characteristics in the vertical mode are asymmetric and diode-like, almost fully symmetric characteristics are observed in the planar mode (Fig. 2). In the vertical mode (Fig. 2a), the IV characteristics are asymmetric on account of the fact that, firstly, the hot Pt electrode is able to emit positive ions only and that,

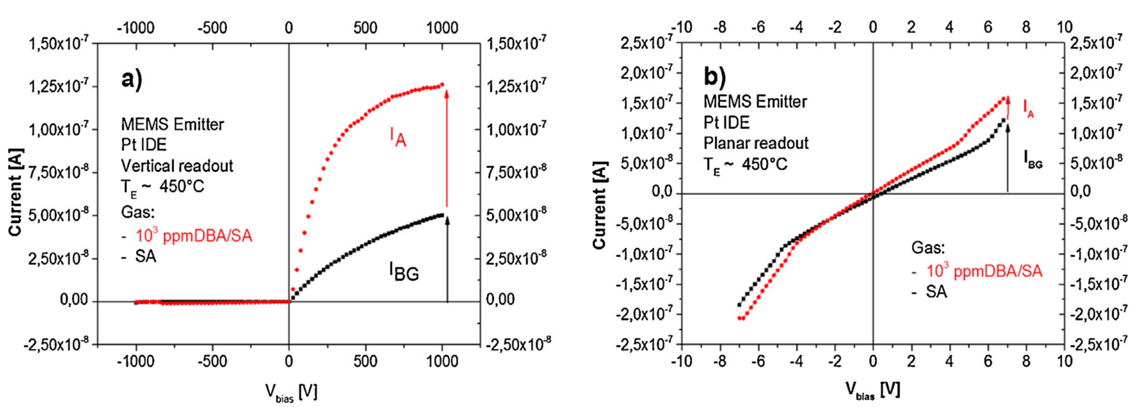

Fig. 2. Current–voltage characteristics as obtained in the vertical (a) and planar readout (b) modes using synthetic air (SA) or SA with an admixture of 10^3 ppm of dibutylamine (DBA) as background atmospheres. I_{BG} is the clean-air background current and I_A the analyte-related ionisation current. The sensor operation temperature in both cases was approximately 450 °C.