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Microfabrication of flexible gas sensing devices based on nanostructured semiconducting metal oxides

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ABSTRACT

Flexible gas sensor devices comprised of heating and transducing elements are produced by directly integrating multilayer polymeric-based platforms and highly crystalline semiconducting metal oxide nanostructures grown via vapour-phase method, as main improvement over other methods for fabricating flexible gas sensors. Thermal simulations and characterizations of the heating element demonstrate these devices provide uniform temperature distribution at the sensing active area, and the electrical properties of the sensing film and electrodes indicate the networked-nanostructures are ohmically connected. Validation of the sensing device shows repeatable and satisfactory responses towards ethanol, demonstrating this fabrication method, with potential in a cost effective production for large-scale applications, is an attractive route for developing next generation of gas sensing devices provided of flexibility and functionality.

1. Introduction

Over the last decade, the interest in sensing technologies based on non-conventional substrates such as plastics, paper or textiles has increased with the idea to introduce these systems to new settings, reducing production cost and adding new functionalities. The availability of flexible sensing technologies, which combine the flexibility of organic materials and the functionality of inorganic materials (e.g. semiconductors), could offer a gateway to breakthroughs in distinct areas, for instance in gas sensors, in which several vapours of industrial, health, law enforcement, and security interest are relevant, and in which wearable, light, cheap, and low power consumption monitoring systems, yet not available in the market, are required [1,2]. In particular, chemo-resistive gas sensors based on semiconducting metal oxides (SMOx) have shown great advantages due to their sensitivity to a number of gaseous species, compact size, simple architecture, and low cost production.

Although flexible materials offer many attractive properties for the fabrication of new microsystems, they also place severe limitations (e.g. thermal and chemical resistance) on the quality of semiconductors that can be integrated onto these materials. To overcome these restrictions various methods for the integration of semiconductors and flexible transducers have been described in the literature, but in general they could be grouped in two approaches: post-transfer (indirect) and direct methods. Post-transfer methods are the most commonly reported and involve the transfer of nanostructured materials (previously prepared at high temperatures) on flexible substrates by drop-cast (wet-transfer method) or by using stamps or soluble glues (dry-transfer methods) [1]. Direct methods, in contrast, are infrequently reported and generally involve the grown of nanostructured materials by hydrothermal processes at relatively low temperatures [3,4] or by thermal oxidation-based processes using catalyst seeds [5].

The literature shows that several SMOx are suitable for chemo-resistive gas sensors (e.g. SnO_2, WO_3, In_2O_3, ZnO, TiO_2, V_2O_5) and recently these SMOx, in the form of quasi-one-dimensional nanostructures (e.g. nanowires, nanotubes, nanorods, nanoneedles), have demonstrated promising sensing properties due to their high surface-area-to-volume ratio [6]. In particular, the literature related to flexible gas sensors report the use of zinc oxide nanostructures, mostly via direct integration approaches [3,4,5,7], whereas materials such as tin oxide, tungsten oxide and indium oxide have been less used, with only few works reporting the use of these materials as thick (SnO_2, WO_3) [8] or thin (InO_x) [9] films integrated via wet-transfer or sputtering method, respectively. Similarly, most of the works on carbon nanofibers [10] and carbon nanotubes [11,12] integrated in flexible devices report the use of post-transfer methods.

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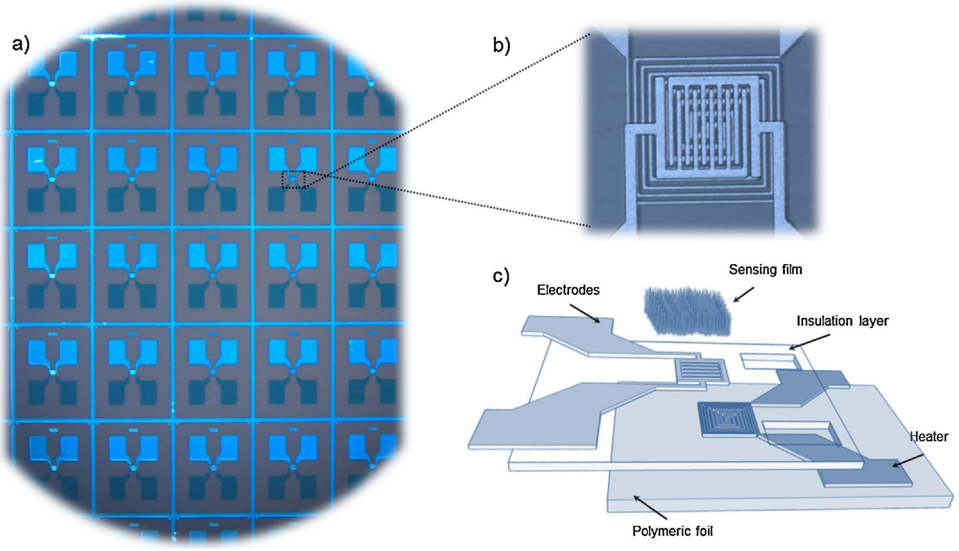

Fig. 1. Optical microscope imaging of the polymeric-based multilayer platforms, including the heating and transducing elements prior to the sensing film integration (a and b), and schematic view of the layers comprising the sensing device (c).

Despite potential advantages of gas-phase methods, for direct growth of nanostructures on different substrates, these methods have not been reported for the fabrication of flexible gas sensors yet. Current advances in CVD and its variants, such as aerosol assisted CVD [13], provide the possibility to overcome the temperature restrictions for the integration of nanostructures, either via appropriate selection or design of precursors [14] or by the utilization of chemically active solvents to transport these precursors [15], and recently aerosol assisted CVD has been adapted to integrate nanostructures on fragile silicon-based MEMS platforms [16].

Here, we report the fabrication and characterization of flexible gas sensing devices comprised of heating and transducing elements, which, in addition, incorporate highly crystalline tungsten oxide nanostructures directly integrated via aerosol assisted CVD.

2. Sensor fabrication

2.1. Processing steps

Polymeric transducing platforms were fabricated on a commercial high heat resistant polyimide foil (Upilex-S, 125 μm, UBE). Fabrication started with the surface activation of a 4 in. polyimide foil wafer in oxygen plasma to promote adherence of the metallic layers (ALCATEL AMS 110, 600 W, 3 min). Subsequently, patterning of a double loop heater was achieved using a reversible photoresist layer (AZ 5214E, 1.7 μm) followed by the deposition of a Ti/Pt (25 nm/250 nm) layer via sputtering (ALCATEL 610); the use of a reversible photoresist, providing negative wall angles of the pattern, improved the lift-off process of the metallic layers. Platinum was selected as heating material for its good properties and its linearity between electrical resistance and temperature. Then, an insulation layer was formed onto the heater by spin coating (4500 rpm, 40 s) of a solution of polyimide precursorpolyamic acid (U-Varnish, UBE), which afterwards was cured to accelerate the imidization reaction at 350 °C following the temperature pattern suggested by the manufacturer. This thermal process ensures obtaining the parameters reported by the manufacturer, including the long-term heat resistance and low outgassing. Opening of the heater contacts was achieved by dry etching with oxygen plasma (ALCATEL AMS 110, 600 W, 8 min), and the electrodes of Ti/Pt (25 nm/250 nm), with a gap of 5 μm, were patterned by lift-off following the same procedure used to structure the heater. Finally, tungsten oxide nanostructures were grown at 350 °C on the top of the electrodes via aerosol assisted CVD of tungsten hexacarbonyl (40 mg, $W(CO)_6$, Sigma–Aldrich, ≥97%) dissolved in methanol (10 ml, Sigma–Aldrich, ≥99.6%) [17]. Briefly, the adjustment of conditions for growing tungsten oxide nanostructures from $W(CO)_6$ involved a screening of deposition temperatures, solvents and solution concentrations; it is worth noting that in this work, $W(CO)_6$ was used as AACVD precursor due to its lower decomposition temperature [18] compared to tungsten hexaphenoxide $W(OPh)_6$ (the precursor studied in our previous works) [16]. A shadow mask was used during the deposition process, in order to protect the contacts and confine the film deposition to the electrode area. Fig. 1a and b shows the processed wafer and a single element prior to the sensing material deposition, and Fig. 1c depicts the layers comprising the whole device. Bending of the device, before and after AACVD deposition, showed no visible detachment of the Ti/Pt layers or the tungsten oxide films, indicating the layers comprising the structure have relatively strong adherence to the polymer; the reliability of sputtered Ti/Pt layers on polymeric foils to circular bending has also been demonstrated recently [19]. After deposition, the structures were annealed in air at 375 °C for 1 h, and then fixed on a TO-8 package to facilitate the characterization steps.

2.2. Simulation and characterization

Electrothermal simulations of the heaters were carried out using the Joule Heating and Thermal Expansion model of COMSOL Multiphysics 4.3a, and the electrical characterizations, for both heaters and sensing film, were achieved using an electrometer (Keithley 2400) controlled by Labview.

The cross section of the device, the morphology of the sensing film and its elemental composition were examined using Scanning Electron Microscopy (SEM and EDX – Carl Zeiss, Auriga Series, 3 kV), and the sensing material structure using X-Ray Diffraction (XRD – Bruker, AXS D8-Advance, Cu Kα radiation operated at 40 kV and 40 mA).

Gas sensors were tested in a continuous flow test chamber provided of mass flow controllers (Brooks 5850E) to regulate the mixture of pure synthetic air and ethanol (C_2H_5OH, Praxair, 100 ppm) [20]. The sensors were exposed to ethanol and subsequently the