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Utilizing p-type native oxide on liquid metal microdroplets for low temperature gas sensing

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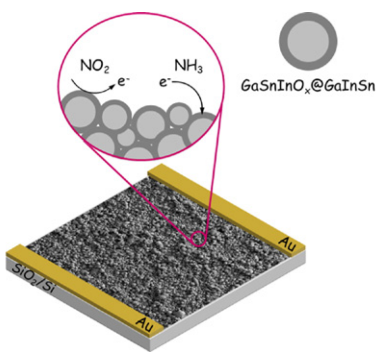
HIGHLIGHTS

- Development of an amorphous p-type oxidized galinstan film confirmed by XRD and Hall effect measurements;
- Sensing performance of oxidized galinstan conductometric devices toward NO_2, NH_3 and CH_4 at low temperatures up to 150 °C;
- Optimal response with a more stable baseline at an operating temperature of 100 °C;

GRAPHICAL ABSTRACT



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ABSTRACT

Liquid metals based on gallium oxidize under ambient conditions to form a native oxide on the surface. Here we take advantage of the semiconducting properties of this oxide layer for gas sensing applications. In particular, the development of gas sensors that operate at low temperatures is an ongoing challenge. Therefore, to address this problem, we fabricated conductometric sensors based on an oxidized liquid metal galinstan layer, and investigated their sensitivity towards NO_2, NH_3 and CH_4 gases. The fabrication of the sensing layer was achieved via a simple approach, involving the sonication of the liquid metal in acetonitrile to produce a solution of micro/nanodroplets and dropcasting it onto a non-conducting alumina substrate at different loadings. The material properties of the developed film were extensively investigated by means of field emission scanning electron microscopy, Raman spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The results confirmed the presence of an amorphous oxide on the surface of the droplets. Hall effect measurements indicated that the oxide film was p-type, which influenced the sensing response towards the different gases. We demonstrated that a physisorption process occurs at 100 °C, leading to a detection limit as low as 1 and 20 ppm for NO_2 and NH_3, respectively.

1. Introduction

Liquid metals have recently received a significant amount of attention due to their interesting physical, chemical, electronic and optical properties [1,2]. The most popular formulation is based on Gallium (Ga) as the dominant element, which is often combined with other

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elements such as Indium (In) and Tin (Sn). For room temperature applications, a eutectic based on GaInSn has gained popularity and is referred to as galinstan, which is an alloy of 68.5% Ga, 21.5% In and 10.0% Sn and importantly is nontoxic [3]. This liquid metal has been employed in an ever-expanding number of applications including microelectromechanical systems (MEMS) [3,4] and coolants [5] to more diverse applications such as a highly deformable liquid-state heterojunction sensors [6], soft matter circuits [7], reconfigurable circuitry [8], liquid metal enabled pumps [9], actuating devices [10,11], plasmonics [12], heavy metal ion sensing [13] and heterogeneous catalysis [14,15].

Ga is quite reactive and easily forms a native oxide on the surface of the liquid metal, which has implications for wetting in the aforementioned applications. However, the semiconducting properties of the native oxide (including Ga_2O_3 and Ga_2O [16]) have been exploited for other types of applications. For example, this oxide has been used as an effective photocatalyst for the degradation of organic dyes [17,18] and is found to be particularly important for the actuation of liquid metals [9–11,19]. For photocatalytic and heavy metal ion sensing applications, it was found that increasing the surface area of galinstan had a profound effect. To achieve this, a liquid galinstan drop was sonicated in water to make a colloidal solution containing micro and nanosized spheres with an oxide coating of Ga_2O_3 that were drop casted onto an inert surface to allow for easy recovery of the photocatalyst [17,18]. Previous work has also shown that liquid metal based on GaIn could be sonicated in ethanol containing a thiol moiety to generate particles from 180 to 600 nm in diameter that, by a careful choice of the ligand, can be reduced below 100 nm [20]. Ga colloids functionalized with acetone, propanol and tetrahydrofuran (THF) have also been obtained via a chemical liquid deposition method [21].

There have been several studies reporting on the use of bulk, thin film and nanosized Ga_2O_3 as a material that is suitable for sensing both reducing and oxidizing gases [22–26]. In general, however, these sensors need to be operated at high temperatures, in the 300–1000 °C range. At temperatures above 900 °C they can be used to detect oxygen via perturbation of the bulk-defect equilibrium [23]. Below this temperature, oxygen does not interfere and therefore a variety of gases can be detected [24]. Ga_2O_3 is typically utilized at elevated temperatures in its crystalline form (β phase) as a n-type semiconducting material [25] whose conductivity is based on oxygen deficiencies in the crystal lattice. Its conductivity can also be modified through the introduction of doping species such as Si, Sn and Eu [27]. However, in recent times there have been significant efforts to synthesize materials that can be utilized as gas sensing layers operating at low or room temperature to minimize cost and energy consumption and allow for remote sensing of toxic gases [28–35]. A concern is the monitoring of harmful gases such as NO_2, CH_4 and NH_3, which have detrimental environmental and human impacts if exposure at unacceptable levels occurs from industrial sources, where their use is widespread [34].

In this work, we investigated the use of microdroplets of galinstan, synthesized via sonication in acetonitrile, which form a native amorphous oxide on their surface as a sensing layer for low temperature (below 150 °C) detection of NO_2 and NH_3. Although polycrystalline β-Ga_2O_3 has been reported as having n-type conductivity, a p-type semiconducting behavior was observed from the gas sensing response to both target gases. This was found to be consistent with Hall effect measurements, which showed that the amorphous oxide of galinstan had p-type conductivity and may lead to other interesting applications of this material.

2. Experimental section

Galinstan based conductometric sensors were fabricated by drop casting galinstan dispersion with two different loadings onto cleaned SiO_2/Si substrates (7×7 mm^2) at 70 °C. Drop-casting was repeated 10 times to obtain a film consisting of droplets of oxide coated galinstan (Fig. S1). The dispersion was made by adding either 15 or 120 mg galinstan (Galinstan fluid 4 N, Geratherm Medical AG, Germany) into 5 mL acetonitrile, which was sonicated for 30 min to prepare Sensors 1 and 2, respectively. To obtain the smallest drop size according to the previous work [16] a sonication time of 30 min was chosen. Two Au electrodes with a thickness of ~100 nm and separation of ~1 mm were deposited on top of the dried galinstan films using an Au coater (Leica EM-SCD005 Sputter Coater).

The material properties of the developed films were characterized using field emission scanning electron microscopy (FESEM, Zeiss Sigma VP field emission scanning electron microscope equipped with an Oxford XMax 50 Silicon Drift energy dispersive X-ray detector at 20 kV under high-vacuum), Raman spectroscopy (inVia Renishaw Raman microscope equipped with a 785 nm laser), X-ray photoelectron spectroscopy (XPS, Omicron MultiProbe system using a non-monochromated Mg Kα (1253.6 eV) X-ray source, 300 W), UV–visible

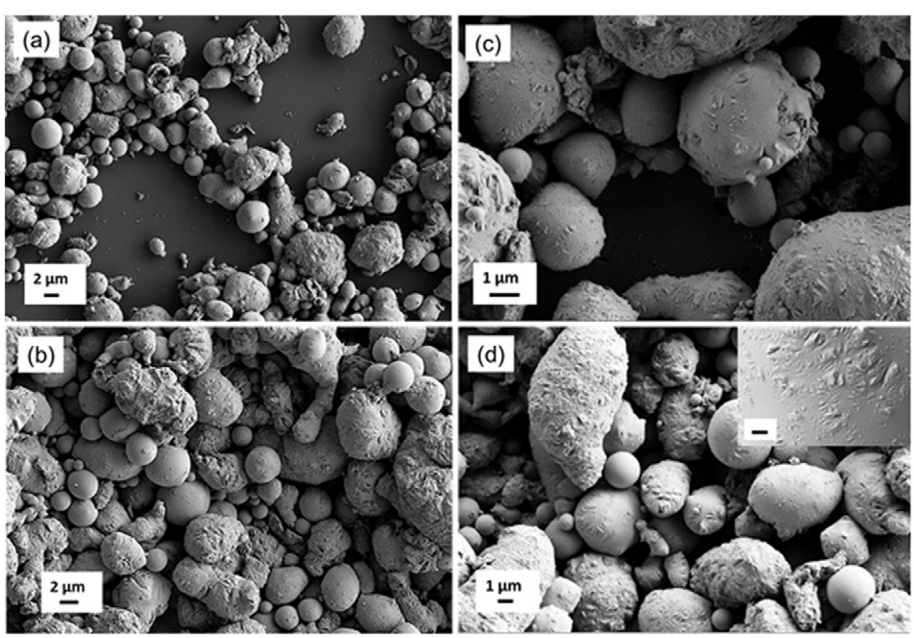

Fig. 1. SEM micrograph of the as-deposited galinstan films in (a), (c) Sensor 1 and (b), (d) Sensor 2 (inset: high resolution SEM image of galinstan droplet skin, the scale bar is 400 nm).