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Improving the hydrogen gas sensing performance of Pt/MoO_3 nanoplatelets using a nano thick layer of La_2O_3

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ABSTRACT

In this paper, we present how a thin RF sputtered layer of lanthanum oxide (La_2O_3) can alter electrical and improve hydrogen gas sensing characteristics of Pt/molybdenum oxide (MoO_3) nanostructures Schottky diodes. We derived the barrier height, ideality factor and dielectric constant from the measured *I–V* characteristics at operating temperatures in the range of 25–300 °C. The dynamic response, response and recovery times were obtained upon exposure to hydrogen gas at different concentrations. Analysis of the results indicated a substantial improvement to the voltage shift sensitivity of the sensors incorporating the La_2O_3 layer. We associate this enhancement to the formation of numerous trap states due to the presence of the La_2O_3 thin film on the MoO_3 nanoplatelets. These trap states increase the intensity of the dipolar charges at the metal–semiconductor interface, which induce greater bending of the energy bands. However, results also indicate that the presence of La_2O_3 trap states also increases response and recover times as electrons trapping and de-trapping processes occur before they can pass through this thin dielectric layer.

1. Introduction

In recent years, tremendous research focus has been directed into the development of inexpensive, low power and miniaturized gas sensors with enhanced performance. The rise of global concerns such as climate change, environmental sustainability, safety and security has prompted the need for alternative energy transforming systems. Many of these systems incorporate hydrogen and hydrocarbon sensors as one of the crucial elements.

There are currently many different technologies available for hydrogen sensing; among them the semiconducting metal-oxide sensors have shown some of the most promising results. They have attracted widespread commercial interest in a vast range of applications [1,2] and recent advances in nanotechnology has catalyzed the development of many new materials exhibiting enhanced gas sensing performance [3]. These developments have been introduced into new fabrication processes to increase the performance of semiconducting metal-oxide gas sensors.

In previous work, we have investigated the gas sensing performance of different nanostructured metal-oxide including: TiO_2, RuO_2, ZnO, WO_3 and MoO_3 as they were employed in metal/semiconductor junction structures [4–10]. They have shown high sensitivity towards both reducing and oxidizing gases. Among these metal-oxides, MoO_3 has been recognized as one of the most sensitive and extremely volatile materials due to its low melting temperature and low thermal dynamic stability [11–13]. The sensing properties of MoO_3 nanostructures have also been investigated by other research groups [14–20]. In MoO_3, the oxygen vacancies can diffuse from the interior of the material to the surface and vice versa, and the bulk of the oxide has to reach an equilibrium state with ambient oxygen [11]. This is a problem as the oxygen vacancies are the main bulk point defects and play a vital role in the hydrogen gas sensing mechanism. It means that to attain strong sensing properties of MoO_3, it is necessary to use materials, in which the equilibrium of oxygen diffusion is constant and minimized. In this work, we aim to achieve this by depositing La_2O_3 as a highly stable material [21] with a wide band gap of >4.3 eV [22] and relatively high dielectric constant (∼25) [22]. The potential applications of La_2O_3 thin films include dielectric layers in capacitive applications [23], coatings [24], catalysts [25] and gas sensing applications [26–31]. There are also reports showing that La_2O_3 as coating layer can improve the sensing performance of metal-oxide gas sensors by adding additional surface states that exhibit the redox catalytic properties [13,24,26–31].

Therefore, in this work, we will examine the effect of a thin layer of this material on the electrical properties and hydrogen

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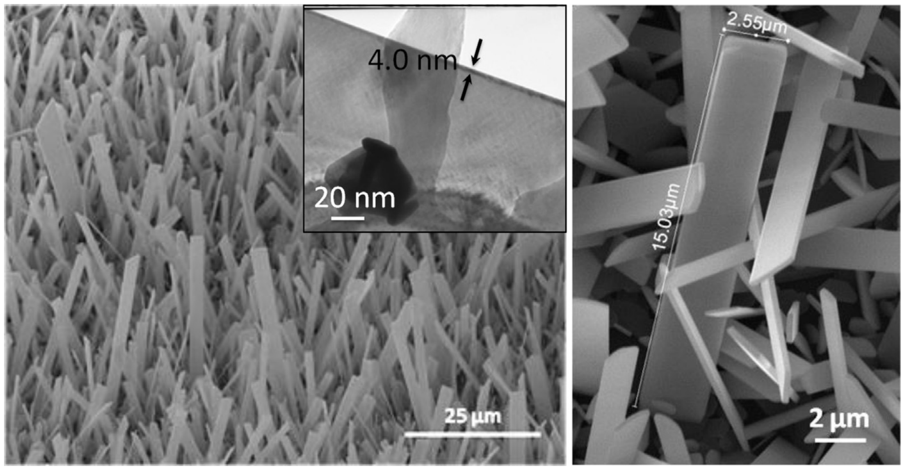

Fig. 1. SEM micrographs of La_2O_3 coated MoO_3 nanoplatelets. Inset: TEM image indicating 4 nm layer of La_2O_3 thin film deposited on the MoO_3 nanoplatelets.

gas sensing characteristics by developing a Pt/La_2O_3 coated MoO_3 nanoplatelets Schottky junction. We will explain how the sensing performance of such a device is linked to the thermionic and Poole–Frenkel conduction mechanisms.

2. Experimental

Nanostructured MoO_3 thin films were deposited on *n*-type 6H-SiC substrates (Tankeblue Co.) using thermal evaporation deposition. Cleaning, dicing and preparation of the SiC substrates, formation of ohmic and Schottky contacts as well as the MoO_3 deposition method can be referred to our earlier work [4–9]. The grown MoO_3 thin films were subsequently coated with a thin La_2O_3 layer by RF sputtering. A 99.99% pure La_2O_3 target in a Denton vacuum discovery sputtering system with a distance of ∼15 cm from the substrate was used. The chamber was pumped to an operating pressure of 10^{-7} Torr and the substrate was heated to ∼300 °C. The deposition took place over a period of 16 s in a mixed Ar/O_2 (4:1) gas using RF power of 25 W. The thickness of the La_2O_3 layer was calibrated to 4 nm prior to sputtering using a Spectroscopic Ellipsometer (VASE VB400). The developed sensor was placed in a multi-channel gas testing system for the electrical and sensing measurements and the experimental set-up and schematic of the nanostructured Schottky diodes. The detail of our gas sensing system set-up has been presented previously [4–9].

3. Results and discussion

3.1. Material characterizations

Fig. 1 shows the SEM micrographs of the La_2O_3 coated MoO_3 films comprising of nanoplatelets with dimensions ranging from 2 to 18 µm with a platelet thickness of on average ∼200 nm. The nanoplatelets grew in a layer-by-layer structure made of 1.4 nm thick sheets [32], thus they provide a high surface area-to-volume ratio both internally and externally for gas adsorption. TEM image (inset of Fig. 1) indicates that 4 nm thick layer of La_2O_3 thin films deposited on the MoO_3 nanoplatelets. Analysis of the La_2O_3 coated MoO_3 nanoplatelets by X-ray diffraction (XRD) (Fig. 2) revealed a crystallographic orthorhombic structure. The XRD spectrum of pure thermally evaporated MoO_3 nanoplatelets can be found in Ref. [9]. The stronger peaks at 26° and 39.2° (2θ) evidence the presence of La_2O_3 in the coated films [27,33]. However, the electrical characteristics will identify more evidently the effect of the La_2O_3 layer.

3.2. Electrical characteristics and conduction mechanisms

Fig. 3 shows the current–voltage (*I*–*V*) characteristics of MoO_3 nanoplatelet Schottky diodes with and without La_2O_3 coating at different temperatures up to 360 °C. These temperatures were selected as Comini et al. [34] observed that at operating temperatures higher than 400 °C a strong decrease in conductivity occurs in MoO_3 due to the partial sublimation of the oxide. The La_2O_3 coated diode exhibited nonlinear electrical behavior (Fig. 3a) and also a much higher rectifying voltage at 25 °C as compared to the Schottky diodes without the La_2O_3 coating (Fig. 3b). The augmentation of the electric field localized at the edges of the nanoplatelet morphology can be seen lowering the reverse breakdown voltage of the Pt/MoO_3 *I*–*V* characteristics [9,35]. However, with the addition of La surface states they contribute to increase the defect density and we explain below that the pinning Fermi level is responsible for mutually excluding the localized electric fields from modulating the Schottky barrier. Therefore, we can observe the rectifying and breakdown voltage for the Pt/La_2O_3 coated MoO_3 diodes to be significantly higher than exhibited by the Pt/MoO_3 diodes. However, with respect to increasing temperature, the surface states in the diode with La_2O_3 can eventually recombine with minority carriers and allowing the localized electric fields to contribute and drive the flow of current.

The increase in the rectifying voltage can also be explained in further depth by the theory involving numerous surface traps and their subsequent conduction mechanisms. Semiconductor theory

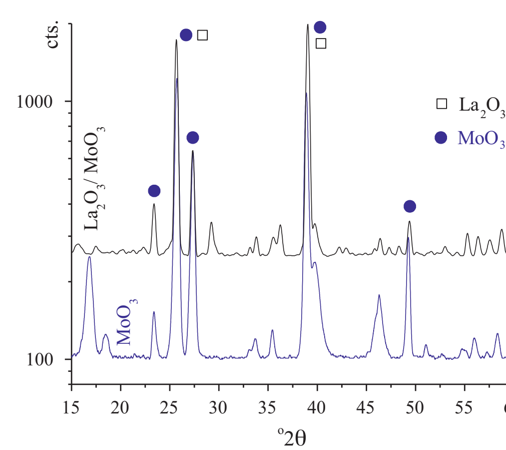

Fig. 2. XRD spectra of the La_2O_3 coated MoO_3 and pure MoO_3 nanoplatelets [9].