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Hydrogen Sensing Properties of Pt/Lanthanum Oxide-Molybdenum Oxide Nanoplatelet/SiC Based Schottky Diode

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Abstract:
An investigation of the electrical and hydrogen sensing properties of a novel Schottky diode based on a nanostructured lanthanum oxide-molybdenum oxide compound is presented herein. Molybdenum oxide (MoO_3) nanoplatelets were grown on SiC substrates via thermal evaporation which was then subsequently coated with lanthanum oxide (La_2O_3) by RF sputtering. The current-voltage characteristics and hydrogen sensing performance (change in barrier height and sensitivity as well as the dynamic response) were examined from 25 to 300°C. At 180°C, a voltage shift of 2.23V was measured from the sensor while exposed to 1% hydrogen gas under a 100 µA constant reverse bias current. The results indicate that the presence of a La_2O_3 thin layer substantially improves the hydrogen sensitivity of the MoO_3 nanoplatelets.

Key words: gas sensor, hydrogen, Schottky diode, nanostructures, lanthanum oxide-molybdenum oxide compound

Introduction

Focus on hydrogen research has grown exponentially over the past decade as it has been proposed as one of the cleanest resources of energy as a fuel [1, 2]. However, the flammable nature of hydrogen gas has raised the need to sense and monitor this substance in concentrations down to the parts per million range for safety concerns in case of leakage.

Schottky diode based sensors using a nanostructured metal oxide sensing layer has shown high sensitivity towards reducing gases (especially hydrogen) [3-8]. The adsorption and dissociation of hydrogen changes the work function of the Schottky contact metal and modulates the Schottky-barrier. Different types of metal oxide materials including RuO_2, ZnO, WO_3 and MoO_3 with unique morphological structures have been examined over the past few years [3-8]. Among these, 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. This implies that 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 [9]. 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 in metal oxides, it is necessary to use materials, in which the equilibrium of oxygen diffusion is constant and minimised.

In this work, we aim to achieve this by depositing La_2O_3 as a highly thermal stable material onto MoO_3 [9]. Many authors have also used this material to dope and improve the characteristics of other oxides (such as TiO_2 and SnO_2) with La_2O_3 for sensing [10, 11]. In this work, we will examine the effect of a thin layer of this material on the hydrogen sensing performance of the MoO_3 nanoplatelet sensor.

Experimental

Nanostructured MoO_3 thin films were deposited on *n*-type 6H-SiC substrates (Tankeblue) using the thermal evaporation deposition technique. Cleaning, dicing and preparation of the SiC substrates, formation of ohmic and Schottky

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contacts [3-8] as well as the MoO_3 deposition method [8] can be referred to our earlier work. The grown MoO_3 thin films were subsequently coated with a 4 nm 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 was used. The chamber was pumped to an operating pressure of 10^{-7} Torr and the substrates were heated to ~300°C. The deposition took place over a period of 16 sec in a mixed Ar/O_2 (4:1) gas using RF power of 25 W. The developed sensor was placed in a multi-channel gas testing system for the electrical and sensing measurements. The experimental set-up and schematic of the nanostructured Schottky diodes has been presented previously [3-8].

Results and Discussions

Fig. 1 shows the SEM micrographs of the La_2O_3 coated thermally grown MoO_3 films comprising of nanoplatelets with dimensions ranging from 2 to 18 µm and thickness of ~200 nm. The nanoplatelets grow in a layer-by-layer structure made of 1.4 nm thick sheets, as observed by Kalantar-zadeh et al. [12]. These platelets provide a high surface area-to-volume available for gas adsorption.

Subsequent analysis of the La_2O_3 coated MoO_3 nanoplatelets by X-ray diffraction (XRD) reveals the crystallographic peaks identifying an orthorhombic structure in the thermally evaporated MoO_3 nanoplatelets [8] (Fig. 2). The stronger peaks at 26° and 39.2° (2θ) is an evidence of the presence of La_2O_3 in the coated films [13].

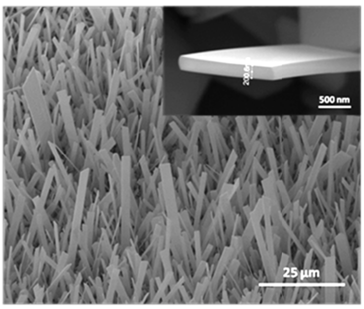

Fig. 1. SEM micrograph of La_2O_3 coated MoO_3 nanoplatelets; (inset: higher magnification).

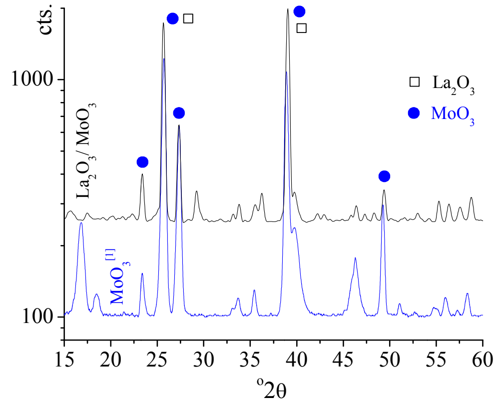

Fig. 2. XRD spectra of MoO_3 [8] and La_2O_3- MoO_3 nanoplatelets.

The change in the current-voltage (*I-V*) characteristics of the sensor was measured in the presence of air and 1% hydrogen from 25°C up to 300°C. Fig. 3(a) shows a plot of the voltage shift as a function of temperature (at 100 µA). The *I-V* measurements from the pure MoO_3 nanoplatelet sensor are shown in Fig. 3(b) for comparison. A maximum voltage shift at 180°C was observed for both sensors indicating an optimal temperature for hydrogen adsorption for sensors based on MoO_3 materials. Both sensors exhibited a significantly larger voltage shift in reverse bias operation than in the forward.

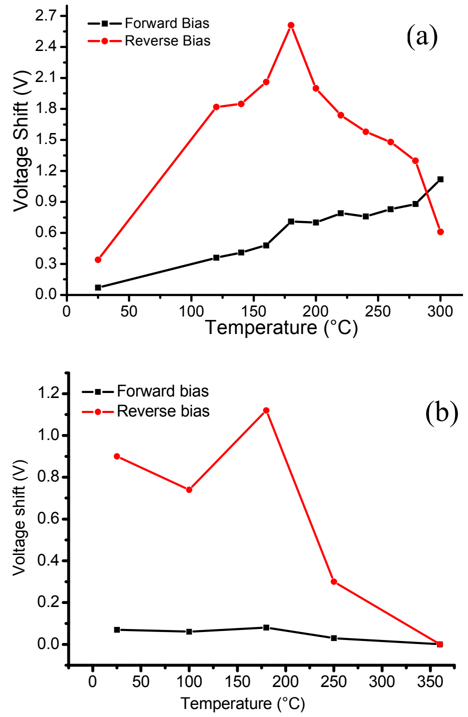

Fig. 3. Plot of voltage shift as a function of temperature towards 1% hydrogen with a constant bias current of 100 µA for (a) La_2O_3-MoO_3 and (b) MoO_3 nanoplatelet based sensors.

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The sensor based on La_2O_3 coated MoO_3 performs significantly better due to the good distribution and coverage of La, which acts as a catalyst. This was also observed by Kim et al. [11] with improved CO_2 sensitivity of lanthanum oxide coated SnO_2 films. The results obtained in the present work suggest that the use of La_2O_3 as a dopant in the base oxide is a useful way to improve the sensitivity, as observed by Zhuiykov et al. [13] with La_2O_3-RuO_2 films, provided that the introduction of La_2O_3 does not lead to a significant change in the orthorhombic structure.

In a Schottky diode, the reverse *J-V* characteristic equation is given in eq. (1) [14]:

$$|J_R| \approx A^{**} \cdot T^2 \cdot \exp\left[-\frac{q}{kT}\left(\phi_B - \sqrt{q\xi_m \big/ 4\pi\varepsilon_s}\right)\right] \qquad (1)$$

where A^{**} is the effective Richardson constant, T is the absolute temperature, q is the charge constant, ϕ_{B0} is the barrier height and k is the Boltzmann's constant, ε_s is the permittivity of the material and ξ_m is the enhanced localized electric field in the nanostructure, which is a function of the reverse bias voltage V_R for nanostructured materials [8] as given by eq. (2):

$$\xi_m = \gamma_a \sqrt{\frac{2q \cdot N_D}{\varepsilon_s}\left(|V_R| + \psi_b - \frac{kT}{q}\right)} \qquad (2)$$

where N_D is the density of free carriers and ψ_b is the built in potential. γ_a is the enhancement factor. The magnitude of the enhancement factor can be determined by curve fitting or estimated from the geometry and the dimensions of the nanostructures using models such as sphere on the post [8, 15]:

$$\gamma_a \approx \frac{\xi_\gamma}{\xi_m} \qquad (3)$$

The enhancement of electric field occurs at the edges of the nanostructures as the Schottky diodes are operated under reverse bias. This fundamental phenenomon allows Schottky effect of the lowering of in the barrier height to be amplified into a larger signal that is respectively measured [8]. The addition of the catalytic properties from the La_2O_3 coating may explain why the sensor in Fig 2(a) has significantly higher sensitivity than that of Fig 2(a) over the whole range of temperatures.

Fig. 4(a) shows the dynamic response of the La_2O_3 coated sensor towards hydrogen with different concentrations at 180°C while the sensor was biased at constant reverse current of 100 µA. For comparison, the dynamic response of the pure MoO_3 nanoplatelet sensor is shown in Fig. 4(b) [8]. Table 1 shows the measured voltage shifts of both sensors upon exposure to hydrogen at the different concentrations.

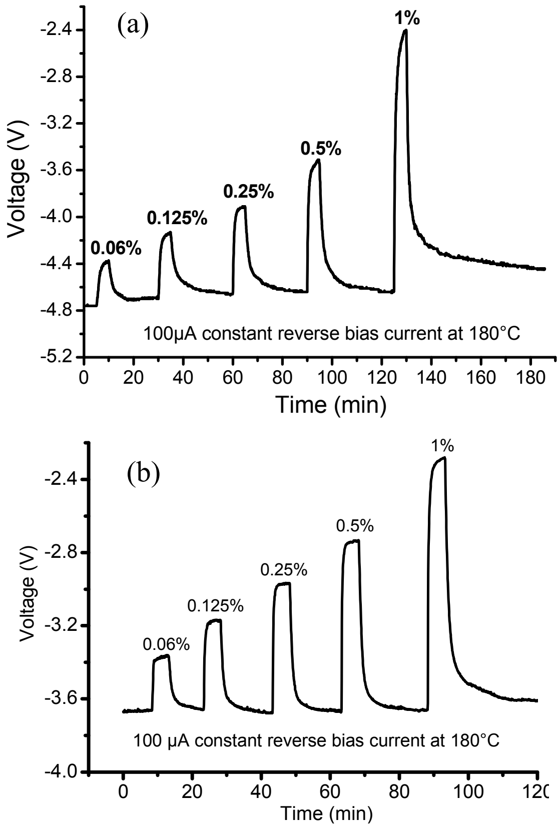

Fig. 4. Dynamic response of the sensors based on (a) La_2O_3-MoO_3 and (b) MoO_3 nanoplatelets towards hydrogen with different concentrations at 180°C.

Tab. 1: Voltage shifts for (a) La_2O_3-MoO_3 and (b) MoO_3 nanoplatelet sensors towards hydrogen with different concentrations at 180°C.

Sensor	Voltage shift (V)				
	0.06%	**0.125%**	**0.25%**	**0.5%**	**1%**
(a)	0.39	0.57	0.75	1.23	2.23
(b)	0.27	0.48	0.70	0.91	1.34

The results from the dynamic performance indicate that the La_2O_3 coated sensor has superior sensing properties towards hydrogen gas and the MoO_3 nanoplatelets provide a high surface area-to-volume platform for the sensor.

Conclusions

In this work, we compared the hydrogen sensing properties of MoO_3 nanoplatelets with and without the coating of a thin layer of La_2O_3.

The structural analysis indicates that the deposited La_2O_3 layer may be amorphous. The hydrogen sensing performance clearly shows significant improvement, demonstrating the important catalytic effect of La_2O_3 in MoO_3 Schottky sensors.

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