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Regular Article

Sprayed zinc oxide films: Ultra-violet light-induced reversible surface wettability and platinum-sensitization-assisted improved liquefied petroleum gas response

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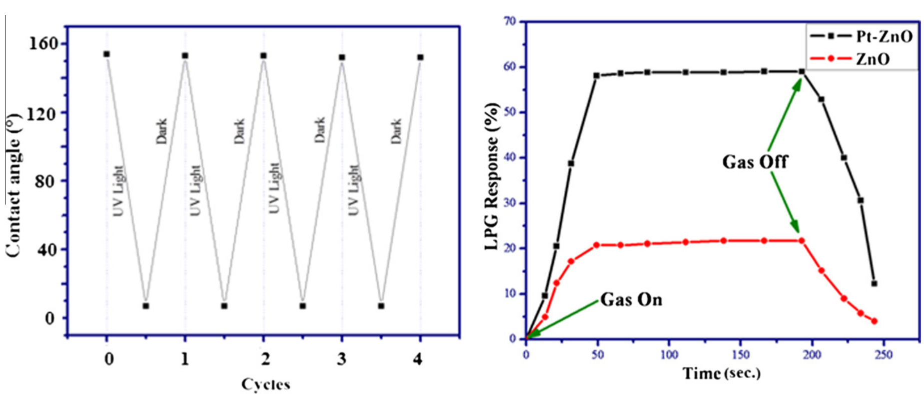
GRAPHICAL ABSTRACT

Effect of UV light irradiation and Pt-sensitization on reversible surface wettability and gas response properties are investigated and reported.



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ABSTRACT

We report the rapid (superhydrophobic to superhydrophilic) transition property and improvement in the liquefied petroleum gas (LPG) sensing response of zinc oxide (ZnO) nanorods (NRs) on UV-irradiation and platinum (Pt) surface sensitization, respectively. The morphological evolution of ZnO NRs is evidenced from the field emission scanning electron microscope and atomic force microscope digital images and for the structural elucidation X-ray diffraction pattern is used. Elemental survey mapping is obtained from energy dispersive X-ray analysis spectrum. The optical properties have been studied by UV–Visible and photoluminescence spectroscopy measurements. The rapid (120 sec) conversion of superhydrophobic (154°) ZnO NRs film to superhydrophilic (7°) is obtained under UV light illumination and the superhydrophobicity is regained by storing sample in dark. The mechanism for switching wettability behavior of ZnO NRs has thoroughly been discussed. In second phase, Pt-sensitized ZnO NRs film has

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Pt-surface sensitization

demonstrated considerable gas sensitivity at 260 ppm concentration of LPG. At 623 K operating temperature, the maximum LPG response of 58% and the response time of 49 sec for 1040 ppm LPG concentration of Pt- sensitized ZnO NRs film are obtained. This higher LPG response of Pt-sensitized ZnO NRs film over pristine is primarily due to electronic effect and catalytic effect (spill-over effect) caused by an additional of Pt on ZnO NRs film surface.

1. Introduction

Zinc oxide (ZnO), one of the most important semiconducting metal oxide materials, exhibits 3.2–3.4 eV direct band gap energy. It has acquired considerable attention because of its excellent optical, piezo-electrical, chemical, thermal properties and high electrical mobility [1,2]. It has potential applications in wide areas such as optoelectronics [3], solar cells [4] and gas sensors [5]. The wettability, an essential structural property, is governed by chemical composition (surface free energy) and geometrical surface (roughness) of solid materials used therein [6–12]. Superhydrophobic (with water contact angle (CA) > 150°) and superhydrophilic surfaces (CA < 10°) are being extensively investigated due to their importance in industrial applications [13–15]. In recent time, superhydrophobic surfaces have received much attention because of their practical importance in fundamental research as well as in potential applications like lenses, transparent window glasses, cement, and textiles [16]. The control of surface wettability has a broad significance such as anti-fog coating, non-sticking surface, and liquid based semiconductor processing [17]. The control of CA has been used to drive liquid droplets in micro or nano-size channels on biochemical and environmental sensing chips [18]. On the other hand, the liquefied petroleum gas (LPG) has widely been used as fuel for domestic cooking, automobiles, and industrial sector, which is one of the extensively used but highly inflammable and potentially hazardous gases. To prevent major accidents (caused by its leakage), there is a requirement of high sensitivity and low concentration level detection. Alternately, ZnO is the most promising potential material used for LPG sensing application [1]. The noble metals such as gold [19–21], platinum (Pt) [22–24], and palladium [25–27] usually incorporate into metal oxide for improving their gas sensing properties and in this context there are very few reports in literature. There is a need to develop different architectures of metal oxide materials that are sensitive to detect LPG at it's an early stage and even at an ambient temperature too. Several methods have been employed for preparing ZnO such as hydrothermal [28], ultrasonic irradiation [29], sputtering [30], and molecular beam epitaxy [31], in different forms. Compared to these methods, spray pyrolysis deposition (SPD) has several advantages like simplicity, eco-friendly, vacuum-free, and the formation of denser and/or porous films [32,33]. This route provides polycrystalline films and mass production feature. There are several reports on the synthesis of ZnO nanorods (NRs) films by using SPD [34,35]. In this work, for the first time, two aspects were considered; UV-irradiation for changing the surface wettability and Pt-sensitization for enhancing the LPG sensing activity of SPD-deposited ZnO NRs film. The optical properties of ZnO NRs film was studied initially. The surface wettability ZnO films (with and without UV) was studied by measuring the contact angle (CA) values at various surface positions. The rapid transition from superhydrophobic to superhydrophilic nature of ZnO film was recorded on UV light irradiation whose mechanism was thoroughly discussed. The effect of Pt-sensitization on LPG gas sensing response of ZnO NRs film was investigated. The effects of operating temperature and LPG concentration on gas response were analyzed. The transient LPG response was also recorded. The probable model explaining an enhancement in the LPG sensing response was proposed. The LPG response (sensitivity) for Pt-sensitized ZnO NRs film was superior as compared to our previously reported performance value [36].

2. Experimental details

The fabrication of ZnO NRs films was carried out using a method reported earlier [36] discussed in an introduction part. In short, ZnO NRs films were obtained onto a glass substrate by SPD method using 0.3 M solution (methanol: de-ionized water in 2:3 ratio) of zinc acetate. Nearly 50 ml solution was sprayed through a steel nozzle at 675 K temperature. As a part of thermal decomposition of the solution, hazardous fumes generated were expelled out by an exhaust system. The ZnO NRs film so obtained was used for wettability studies. The effect of UV light on wettability was investigated. The UV lamp (Blue Wave Tm 50 AS, medium intensity spot lamp, DYMAX Corporation) with 200–600 nm radiation range and 1000–2000 mW/cm^2 intensity was preferred. The wettability studies were performed using Holmarc Opto-Mechatronics PVT. Ltd. Contact angle measurement instrument. The Pt-sensitization was performed using SPD method onto the ZnO NR surfaces using 0.001 M solution of $H_2PtCl_6{\cdot}H_2O$ aqueous solution (50 ml precursor volume) at 523 K temperature. The spraying area was 16 × 16 cm^2. All depositions were carried out by using Holmarc Opto-Mechatronics PVT. Ltd. spray pyrolysis system (model No. HO-TH-04). In addition to pristine, the Pt-sensitized ZnO NRs film was used for LPG sensing properties. The electrical properties were measured by two probe method using Keithley (6514) electrometer. The ExceLINX interface software was used to record the data. The silver paint was applied at both ends of the testing film in order to make better electrical connections. The copper rods were used for making better electrical connections. To measure gas sensing properties, the test sample i.e. pristine ZnO NRs film was placed in a sealed glass chamber and its air electrical resistivity i.e. R_a was measured. Afterwards LPG gas was injected into the chamber and the resistivity was measured again. After allowing sufficient time for stabilization (saturation), the gas resistivity (R_g) recorded in the presence of LPG gas was obtained. The rest of parameters such as humidity and other gasses, were kept constant. The change in the resistivity of the test sample was only due LPG exposure inside sealed glass testing chamber of the gas sensing system. The used formula for measuring gas response (S) was as follows [37],

$$S = \frac{R_a - R_g}{R_a} \times 100\% \tag{1}$$

The LPG sensing properties were studied using a computer controlled gas sensing testing system.

3. Results and discussion

3.1. Structural analysis

The XRD pattern for pristine ZnO NRs film is as shown in Fig. 1. All peaks in XRD pattern, after matching with PCPDFWIN file