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Room temperature nitrogen dioxide sensors based on N719-dye sensitized amorphous zinc oxide sensors performed under visible-light illumination

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ABSTRACT

A metal oxide gas sensor working at room temperature has been achieved by impregnating N-719 dye onto an as-sputtered amorphous zinc oxide (ZnO) film. The amorphous ZnO films exhibit a higher electrical conductivity when compared to well-crystallized ZnO films, and the conductivity is further enhanced by sensitization of N-719 dye under visible-light illumination. At room temperature, the dye sensitized amorphous ZnO sensors are exposed to nitrogen dioxide (NO_2) at a concentration ranging from 1.25 to 10 ppm under visible-light illumination. The sensor response is 143% for 1.25 ppm NO_2 and the response increases linearly with the NO_2 concentration. The improvements of gas sensitization are attributed to the enhancement of NO_2 chemisorption and desorption rate by photogenerated electrons under dye sensitization and light illumination. In addition, the effect of humidity on base resistance and sensor response is discussed in detail.

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1. Introduction

Photosensitization phenomenon by organic dyes on wide-band gap semiconductors has been well-known since a dye-sensitized solar cell (DSSC) was developed by Graetzel in the early 1990s [1]. In DSSCs, solar light is not mainly absorbed by the semiconductor but aided by the presence of a dye. Electron–hole pairs are generated in the dye which locates on the surface of wide-band semiconductor electrode under solar light illumination. The electrons then are injected from the dye into the conductance band of the electrode. The role of the dye in DSSC may be extended to the application of semiconductor gas sensors to enhance surface electrical conductance and develop rapid room temperature dye sensitized gas sensor with the help of visible-light illumination.

ZnO is a typical wide-band gap semiconductor, which has been shown to be effective for gas sensors [2–4], electronic devices [5] and electrodes for DSSCs [6]. ZnO was one of the earliest sensing materials that were developed for gas sensor [7]. However, ZnO has not been so widely applied as gas sensing devices when compared with SnO_2, due to its low chemical and thermal stability. In recent years, due to the advancement on the synthesis of controlled ZnO nanostructures, there has been a tremendous interest in developing ZnO based sensors. One of the first research directions is to reduce the working temperature. Much progress has been made either by using new ZnO nanostructures [8,9] or by a combination of hybrid materials, e.g., noble metal-ZnO [10,11] and p–n heterocontact systems [12–15]. To develop ZnO gas sensors that can work at low temperature, it is possible to utilize light illumination to increase carrier concentration in its conductance band and to promote photodesorption. As well known, the adsorbed oxygen on n-type semiconductors (e.g., ZnO) is negatively charged and a built-in-field is formed. Under light illumination with photon energy higher than the band-gap energy, the photogenerated electron–hole pair is separated. As the built-in-field is a result of the adsorbed oxygen, surface gas adsorption/reaction has a significant effect on surface photoconductivity. We demonstrated previously [16] a WO_3 film as a possible sensing element for NO_2 sensors at room temperature under visible-light illumination. The photoconductivity was enhanced by the use of visible-light with a wavelength less than 480 nm, since the photon energy of such light is equivalent or greater to the indirect band-gap energy of WO_3 (2.6–2.8 eV) [17]. As in the case of ZnO, the photon energy should be

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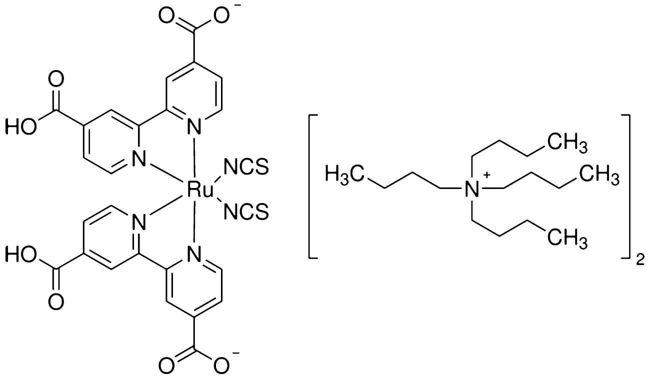

Scheme 1. Molecular structure of N-719 dye.

higher than 3.37 eV, which means the UV light having lambda <370 could be potentially useful for this application [18]. However, UV-sources are power-hungry and expensive, and moreover, they may lead to decomposition of certain materials and gases and therefore result in a change of target gas composition. Compared to UV sources, visible-light sources are inexpensive and environmental friendly. Therefore, it would be very useful to replace the UV radiation by visible-light for gas sensor applications. Some researchers used visible-light to activate ZnO sensors. One method is to develop new ZnO nanostructure, e.g., ZnO nanorod [19]. The second method is to use composite materials, like ZnO-porous silicon [20]. The use of suitable dye molecules, similar to the use of dye sensitizer in DSSCs, is another promising method.

When the dye molecules are coated on ZnO surface, the electron–hole pairs can be formed on the surface of the dye. The electrons are injected from the dye into the conductance band of ZnO, which increases the photoconductivity of ZnO. Some dye molecules-ZnO hybrid materials for gas sensors have been previously investigated, for example, porphyrin-ZnO [21], azo-ZnO [22], N3 dye-ZnO [23]. The sensing characteristics of porphyrin-functionalized ZnO nanorods to triethylamine and ethanol were studied [21]. The porphyrin-ZnO nanorods showed a higher response to triethylamine than to ethanol, which made an improvement of selectivity of these two gases. It was previously shown [22] that photogenerated charge transfer took place at the interface between ZnO and azo particles. The most popular dye molecules used in DSSCs applications are metal-complex dyes such as the polypyridyl complex of ruthenium (Ru) [24]. Among the different charge transfer sensitizers, the polypyridyl complex of ruthenium is the preferred choice because of its wide absorption band in the wavelength range of 400–800 nm compared with metal-free organic sensitizers. $[Ru(dcbpyH_2)_2(NCS)_2]$, which is abbreviated as N3-dye was of the first dyes developed for use in DSSCs [25]. N3-dye functionalized ZnO nanoparticles had good response to O_2 and CO [23]. Several modification have been applied to N3-dye and developed N719-dye, as shown in Scheme 1. Two protons of N3 are replaced by a tetrabutylammonium cation group. The N719-dye has maintained a clear leadership in DSSCs and has been highly studied, because of its excellent performance and high efficiency [26]. Gas sensors based on hybrid materials of N719-dye and ZnO have been seldom reported. In this paper, we report that N719-dye can remarkably increase the photoconductivity of amorphous ZnO films. The amorphous ZnO was used since it can be prepared by radio-frequency sputtering at low temperature, even at room temperature. Moreover, The band edge of amorphous ZnO thin films (3.35 eV) is similar to that of crystalline ZnO (3.37 eV) [27]. The room temperature sensing characteristics of the dye sensitized amorphous ZnO films to NO_2 were enhanced by visible-light illumination.

2. Experimental methods

In this work, 400 nm thick amorphous ZnO (designated as a-ZnO in this paper) films were prepared on commercial Al_2O_3 substrates equipped with Au interdigital electrodes using radio-frequency (r.f.) sputtering technique in an argon atmosphere with a sintered ZnO target. The sputtering was performed at ambient temperature and a working pressure of 2 Pa. Prior to sputtering, the substrates were ultrasonically cleaned in isopropanol for 5 min. During sputtering, the distance between the substrate and the target was set to 80 mm and the r.f. power was maintained at 200 W. The thickness of the films was measured using an optical profilometer (nj-HP 105, NanoJura, France) on samples sputtered on glass substrates.

To get hybrid materials of dye-metal oxide, a-ZnO and well-crystallized ZnO films were immersed in an ethanolic solution of 3.0×10^{-4} M N719-dye at room temperature for 12 h, and then dried in air. The samples were directly subjected, without any prior treatment, for surface morphology characterization by scanning electron microscopy (SEM, Philips XL20). The phase structures of the samples were measured by grazing incidence X-ray diffraction (GI-XRD) using Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) was performed to analyze chemical compositions of the films using VG ESCALAB 220 iXL system with an Al K_α monochromatic X-ray source. The UV–vis spectra of Al_2O_3 substrate/a-ZnO film/N719-dye sensitized a-ZnO film were obtained using an integrating sphere (Labsphere model RSA-PE-19 reflectance spectroscopy accessory) attached to a Perkin–Elmer Lambda 19 UV/VIS/NIR spectrophotometer. The measurements were carried out at room temperature in the wavelength range of 300–800 nm in air. Since the a-ZnO films are deposited on rough alumina substrates, the absorption of the different samples has been extracted from their diffuse reflectance R in Kubelka–Munk units as $F(R) = (1-R)^2/2R$ [28].

A blue bulb made of 18 LEDs (Omnilux, wavelength = 480 nm) was installed in a plastic chamber, in front of the sensors. The distance between the bulb and the sensor was fixed at 45 mm. Light intensity at the position of the sensor was measured by means of a photodiode (Thorlabs, FDS100) and estimated to be 0.37 W/cm^2. The blue light illuminations and electrical resistivity measurements were performed inside the chamber [16]. The sensors were connected to a home-made system to measure electrical resistivity of the gas sensors. The moisture level of reference air was controlled by mixing dry and wet air (obtained by bubbling in deionized water at 25 °C) and was fixed at 50% unless further specified. The total flow rate of reference air was 500 mL/min. When the sensor resistance was stable in air (R_{air}), 100 ppm NO_2 in air was introduced into the chamber with a flow rate ranging from 6.25 to 50 mL/min. In this work, the flow rates of reference air and diluted NO_2 were modulated by mass flow controllers. After the sensors were exposed to NO_2 for 15 min, the resistance in NO_2 (R_{NO2}) was determined. The response of the gas sensor was defined as $(R_{NO_2} - R_{air})/R_{air}$.

To investigate the influence of the relative humidity (RH) of air on sensor properties, quartz crystal microbalance (QCM) tests were performed. 400 nm a-ZnO films were also deposited on gold electrode of the QCM by r.f. sputtering and then immersed in N-719 dye solution using the same process parameters for the films on Al_2O_3 substrates. The change of the crystal frequency to its initial value was taken as an indication of adsorption or desorption of gas molecules.

3. Results and discussion

3.1. Microstructural characterizations

The color of as-sputtered a-ZnO film is transparent dark yellow, which indicated that the as-sputtered film was amorphous [29].

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