UV Light and H_2 Gas Dual Sensing Properties of ZnO/InGaZnO Match-Head Nanorods

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***Abstract*—In this study, ZnO/InGaZnO (IGZO) match-head nanorods (NRs) were fabricated for light/gas dual sensors. A match-head IGZO structure was successfully grown on ZnO NRs. Scanning electron microscope and transmission electron microscope images reveal that amorphous IGZO capsule-like heads were sputtered on the top of crystallized ZnO NRs. Results of X-ray photoelectron spectroscopy spectra indicate that oxygen defects can be generated by the growth of IGZO. Additionally, hydrogen sensing and UV light detection measurements were performed on NRs under various IGZO growth conditions. Results indicate that incorporation of an IGZO match-head on a ZnO NR can functionally enhance hydrogen gas sensing and UV light detection capabilities owing to the increase of trapping states, free carriers, electric fields and surface areas exposed to gas and light. Due to their compact size, steady response and simple fabrication, ZnO/IGZO-based hydrogen gas and UV light dual sensors devices are promising for future environmental monitoring.**

***Index Terms*—ZnO/IGZO match-head, hydrogen gas sensing, UV light, defects, electric field.**

I. Introduction

INFLAMMABLE Hydrogen (H_2) gas and excessive ultraviolet (UV) radiation have recently raised concerns regarding environmental safety [1], [2], and hydrogen gas has been utilized as an ecofriendly clean energy source. However, accumulations of highly concentrated hydrogen gas may be explosive and endanger human safety. UV-A (320 nm-400 nm) light can penetrate the atmosphere and is harmful to skin, potentially inducing skin cancer. Therefore, effective monitoring UV-A radiation and hydrogen gas with a small portable gadget is worthy to investigation. Good sensors have signatures of high sensitivity, rapid response and low manufacturing cost. Semiconductor materials have these characteristics and play a dominant role in current sensing materials. Recently, ZnO nanocomposite-based and IGZO thin film-based gas/light dual sensors with the capability of light detection and gas sensing have been demonstrated, respectively [3], [4]. However, the combination of ZnO and IGZO on light/gas dual sensors has not been clearly reported yet. Furthermore, it is profitable to develop novel ZnO/IGZO hybrid nanostructures to optimize sensing performance. In this study, IGZO match-head/ZnO rod capsule-like nanostructures were fabricated for hydrogen gas/UV-A light dual sensing applications. Analysis results indicate that a match-head IGZO shell structure was successfully grown on ZnO nanorods (NRs) and wrapping ZnO NRs. Moreover, the growth of IGZO match-head shell can enhance both gas and light sensing capability compared with pure ZnO NR-based sensors.

To examine the morphologies and material properties of the nanostructures, multiple material analysis techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and transmission electron microscope (TEM) were performed. Analysis results indicate that an amorphous match-head was successfully grown on top of ZnO NRs. After the formation of the match-head IGZO cap, the sensing chips were measured for hydrogen gas sensing and UV light detection. The sensing measurements revealed that IGZO-capped samples with a sputtering time of 60 minutes had optimized gas sensing and light detection performance. In our previous studies [4], [5], we fabricated ZnO/ZnS core-shell gas/light dual sensing devices and WO_3/ZnO match-head gas/light blocking samples. Compared with WO_3-capped ZnO samples, which had worse sensing behaviors both in H_2 gas sensing and UV photodetection than the ZnO samples without match-head caps, IGZO-match-head cap could enhance both hydrogen gas and UV light dual sensing behaviors. Owing to easy fabrication, rapid response, and compact size, IGZO-match-head/ZnO NRs dual sensors are promising for inflammable hydrogen gas monitoring and hazardous UV light detection.

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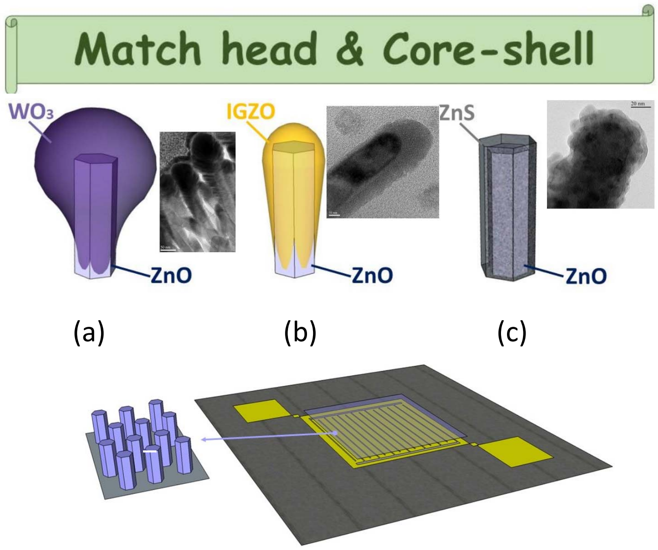

Fig. 1. Illustrations and TEM images of (a) WO_3/ZnO match-head NRs (b) ZnO/IGZO capsule-like match-head NRs and (c) ZnS/ZnO core-shell NRs. (d) ZnO-based nanostructures on a sensing device with two interdigital electrodes.

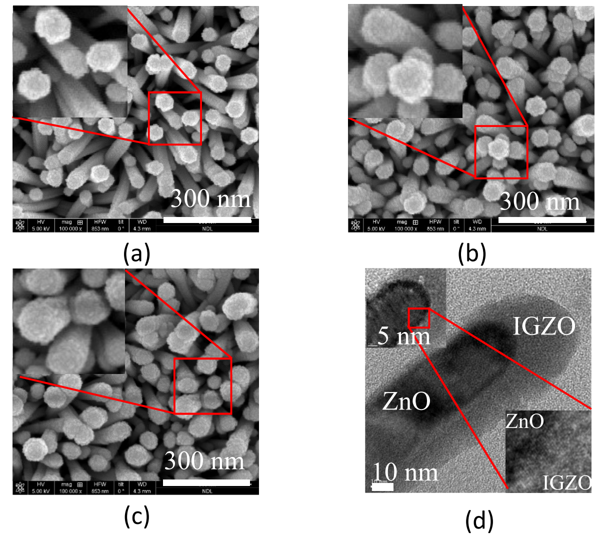

Fig. 2. FESEM images of (a) pure ZnO NRs, (b) ZnO/IGZO NRs with IGZO with sputtering time of 30 min, (c) ZnO/IGZO NRs with IGZO with sputtering time of 60 min and (d) TEM images of ZnO/IGZO NRs with IGZO with sputtering time of 60 min. The enlarged HRTEM image reveals an amorphous IGZO/crystallized ZnO interface in the subfigures.

II. Experimental Details

First, a SiO_2 (250 nm)/Si (525μm) wafer was cut into 2×2 cm^2 samples which were cleansed with ethanol, acetone, and isopropanol. After cleaning, the samples were spin-coated with the seed layer containing the solution prepared by our laboratory [5]. After the NRs were grown on the substrate, the metal film was sputtered on the NRs by RF sputtering to form a match-head structure on top of the NRs. The details of the sputtering process are as follows: The pressure of the chamber was first drawn roughly down to 4×10^{-2} Torr and then finally down to 5×10^{-5} Torr. Then, argon gas was ventilated into the chamber pressure was elevated to 4×10^{-3} Torr. Finally, the target was sputtered with RF power of 100 W. The sensitivity of H_2 gas with the maximum concentration of 300 ppm could be assessed by the generated current, as shown in equation (1).

$$S_{\text{gas}} = [(I_{\text{gas}} - I_{\text{air}})/I_{\text{air}}] \times 100\% \tag{1}$$

The photo sensitivity was measured as follows: UV light sensing measurements were conducted on a sensing chip to examine photo-detection behaviors in a dark room. The wavelength and output power of the light source were 365 nm and 65 mW. Alternation of 30 sec illumination and 30 sec no illumination was performed, and the light detection measurements were analyzed. The light sensitivity was calculated by the change of the generated current between the two electrodes, as shown in equation (2).

$$S_{\text{light}} = [(I_{\text{light}} - I_{\text{dark}})/I_{\text{dark}}] \times 100\% \tag{2}$$

III. Results and Discussion

The three shapes of a ZnO/WO_3 match-head rod, a ZnO/IGZO match-head rod, and a ZnO/ZnS core-shell rod are illustrated as shown in Fig.1 (a), (b), and (c). Moreover, TEM images of the three morphologies of these three nanocomposites were juxtaposed by the three illustrations. The ZnO/WO_3 match-head rod had a round match-head on the top of a NR, as shown in Fig. 1(a), while the ZnO/ZnS core-shell rod had a ZnS shell covering a ZnO rod, as shown in Fig. 1(c). Different from the shapes of the ZnO/WO_3 match-head rod and ZnO/ZnS core-shell rod, the ZnO/IGZO rod resembled two capsules (one inside and one outside), as shown in Fig. 1(b) [6]. Moreover, ZnO-based nanostructures on a sensing device with two interdigital electrodes are shown in Fig. 1(d). To examine surface morphologies, SEM images were taken for ZnO/IGZO match-head NRs, as shown in Fig. 2 (a), (b), and (c). Apparently, with the increase of deposition time, the IGZO NRs match-head became larger, as shown in the top-right corners of Fig. 2 (a), (b), and (c). To further examine the fine nanostructures of ZnO/IGZO nanocomposites, focused ion beam (FIB) microscopy was used to cut a sample and TEM images were taken for a single ZnO/IGZO NR, as shown in Fig. 2 (d).

The TEM image indicates a larger surface area near the top of a ZnO NR with a match-head. The TEM image also shows that a two-capsule structure with a clear border was formed with IGZO wrapping around a ZnO NR. An enlarged high-resolution transmission electron microscopy (HRTEM) image was also taken. The HRTEM image reveals that periodic interval spacing nano-structures can be observed on ZnO NRs, while no periodic interval spacing nanostructures can be seen on the IGZO cap, implying that ZnO had crystallized phases, but IGZO might be amorphous-like.

To further examine the crystallized structures, XRD was used to analyze the ZnO and ZnO/IGZO samples as shown in Fig. 3 (a). Consistent with the HRTEM image as shown in Fig. 2 (d), only ZnO crystallized phases could be observed, while no IGZO crystallized phases could be seen in the XRD patterns. Like the sputtered WO_3 on ZnO NRs, sputtered IGZO may also be amorphous [6].

For oxygen in different chemical states, the peaks of O at 531eV, 532eV and, 533 eV are attributed to

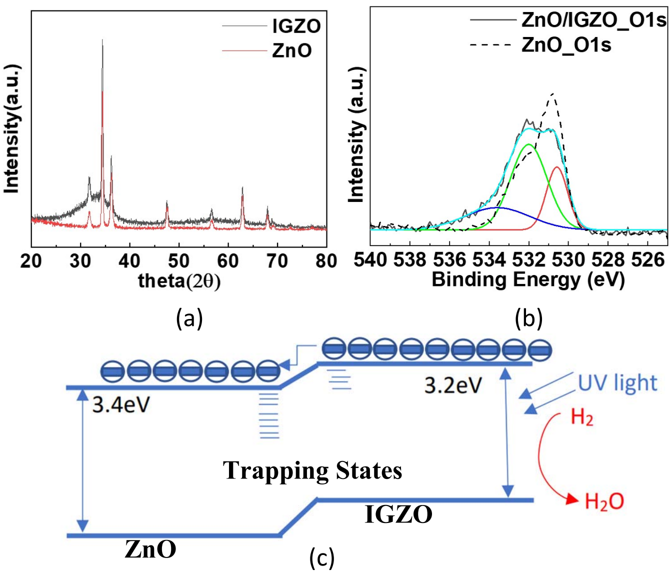

Fig. 3. (a) XRD patterns of ZnO/IGZO and ZnO NRs (b) An XPS spectrum ZnO/IGZO NRs (the aquamarine line deconvoluted into the blue, green, and red lines) and an XPS spectrum of pure ZnO NRs (the dotted line). (c) An illustration of oxygen defects and a high electric field in the depletion region in a ZnO/IGZO band diagram.

Zn-O-Zn (metal oxide), Zn-OH (oxygen defect) and Zn-O-R (organic residue), as shown in Fig. 3 (b) [7]. Compared with pure ZnO NRs as shown in the upper-left subfigure, the Zn-OH component was drastically enhanced with the addition of IGZO match-head. The shallow trapping metastable states related to oxygen defects may be present near the ZnO/IGZO interface owing to OH related species. Based on previous studies [8], [9], these trapping states, as shown in Fig. 3(c), facilitated injection of carriers in the surface region. Based on previous studies [5], [10], oxygen defects were intentionally added or engineered to enhance the sensitivity for specific gases such as O_2, N_2 and H_2. These defect trapping states could function as gas-absorbing and light-harvesting states. For gas sensing behaviors, oxygen defects could donate electrons to the conduction band as the device was exposed to hydrogen gas and these defect states could capture electrons from the conduction band when the device was exposed to the air. Therefore, the hydrogen gas sensitivity could be boosted with these defect states. Additionally, for light sensing behaviors, superoxide anions (O^{2-}) were easier to form around the surface because of these oxygen defect states [4], [11]. More free electron-hole pairs could be generated by the photons and transmitted to the electrodes and hence the light sensitivity increased. Furthermore, high electric fields in the depletion region near the ZnO/IGZO interface could speed up the carrier transition [12]. In addition, a larger surface area with the incorporation of an IGZO match-head could generate larger induced current, due to the larger light absorption or gas reaction area [13].

As shown in Fig. 4, the light current of the sample with IGZO match-heads was much larger than the pure ZnO sample. Moreover, like gas sensing results, the sample with IGZO deposition time of 60 min exhibited the strongest UVA light sensitivity. Since the trapping states near the ZnO/IGZO interface with the carrier transition, the volume carrier density

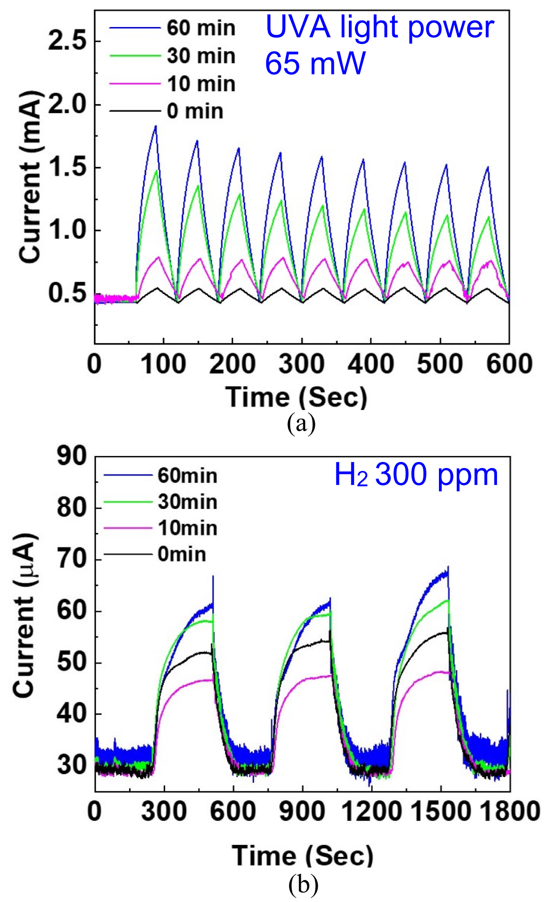

Fig. 4. (a) UV light sensing (b) H_2 gas sensing of ZnO/IGZO samples with various IGZO sputtering time.

may increase. Furthermore, the electric fields in the depletion area in the ZnO/IGZO interface could also strengthen the electric fields and enlarge the current density. Additionally, the sample with IGZO had a larger surface area exposed to light and gas, and the current could increase as the surface area was enlarged. Therefore, the gas/light dual sensitivity could be enhanced.

IV. Conclusion

In this study, ZnO/IGZO match-head NRs were fabricated by hydrothermal and sputtering methods. Morphological observations indicate that IGZO capsule-like heads were successfully sputtered on top of ZnO NRs. XRD patterns and HRTEM images further confirmed the presence of amorphous IGZO and crystallized ZnO. XPS spectra indicated that oxygen defect trapping states could emerge with the growth of IGZO on ZnO NRs and enhance the dual sensing capability. Based on UV light and hydrogen gas sensing measurements, the light/gas dual sensitivity increased with incorporation of IGZO. Oxygen defects could increase the free carriers, and electric field enhancement could enhance the carrier transition speed. Because of their compact size and rapid response, ZnO/IGZO hydrogen gas/UV light dual sensor chips are promising for future hazardous environmental monitoring.

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