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Hydrogen sensitive Schottky diode using semipolar $(1\,1\,\bar{2}\,2)$ AlGaN/GaN heterostructures

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ABSTRACT

In this work, we investigated the hydrogen sensing characteristics of Pt Schottky diodes using semipolar $(1\,1\,\bar{2}\,2)$ AlGaN/GaN structures. First, these diodes showed a large current change of 30 mA at 1 V upon the introduction of 4% hydrogen in nitrogen gas with an accompanying Schottky barrier reduction of 90 meV at 25 °C. Second, their hydrogen detection sensitivity peaked at the zero bias voltage, and slowly decreased with applied bias voltage. Third, they demonstrated stable and reproducible current changes with a reasonable linearity in response to H_2 concentrations from 0.5 ∼ 4% with a step of 0.5%. As such, Pt Schottky diodes on semipolar AlGaN/GaN structures hold great promise for highly-sensitive hydrogen sensors due to their surface polarity and atomic configuration.

1. Introduction

In recent years, hydrogen has received considerable attention due to its potential for alternative energy sources. This has led to extensive studies on the various aspects of commercially viable hydrogen production, particularly in hydrogen-fueled vehicles, aircraft, and fuel cells [1,2]. Unfortunately, such applications have been severely limited due to hydrogen gas-based explosive hazards in the products being developed [3,4]. Also, since hydrogen gas generated from a wide range of industries can be harmful to the environment, the development of highly-sensitive hydrogen gas sensors able to detect even minute amounts of hydrogen has become critically urgent. Thus, quick responsiveness, reliability, improved sensitivity, selectivity, and reliable reproducibility are essential to hydrogen detection if efficiency, affordability and safety are to be achieved in the industry.

Presently, one of the most widely used detection apparatuses is the electrochemical gas sensor which relies on an electrochemical reaction with the electrolyte in the device. Electrochemical gas sensors are advantageous for their reliability and specific gas sensitivity. By contrast, semiconductor-type gas sensors utilize a change in the electrical conductivity of the device when gas is in contact with the semiconductor surface. This, in turn, makes them highly compatible with smart screen and wireless monitoring technologies. For these reasons, gas sensors with catalytic Pd and Pt electrodes had been widely researched based on Schottky diodes, field effect transistors, and metal-oxide-semiconductor (MOS) structures [5–7].

The gallium nitride (GaN)-based materials system is also suitable for use in semiconductor-type gas sensors involving hydrogen sensing. It enables high temperature operations due to low intrinsic carrier concentration, as well as reliable gas detection because of its mechanical and chemical robustness. A wide variety of hydrogen gas sensors based on GaN Schottky diodes, MOS diodes, and AlGaN/GaN high electron mobility transistors (HEMTs) have been developed [8–15]. Song et al. reported Schottky diodes on AlGaN/GaN heterostructures with Pt catalytic metal capable of operating at high temperatures up to 800 °C [11]. According to a recent report by Kim et al., the sensitivity of AlGaN/GaN diodes could be enhanced using Pt nano-networks with a high surface-to-volume ratio [16,17]. Hydrogen gas sensors using nonpolar or semipolar GaN crystal planes are also of great interest because each crystal plane has its own surface atomic arrangement, which shows different reactivity to hydrogen [18,19]. Wang et al. reported that the *c*-plane N-polar $0\,0\,0\,\bar{1}$ GaN Schottky diodes exhibited much higher sensitivity for hydrogen detection than conventional Ga-polar $(0\,0\,0\,1)$ ones, which is consistent with the previous density functional theory noting a much higher affinity of hydrogen to nitrogen in GaN surfaces [20–22]. In this work, we investigated the hydrogen sensing characteristics of Pt Schottky diodes on semipolar $(1\,1\,\bar{2}\,2)$ AlGaN/GaN HEMT structures. We find that Pt Schottky diodes on semipolar AlGaN/GaN structures hold great promise for

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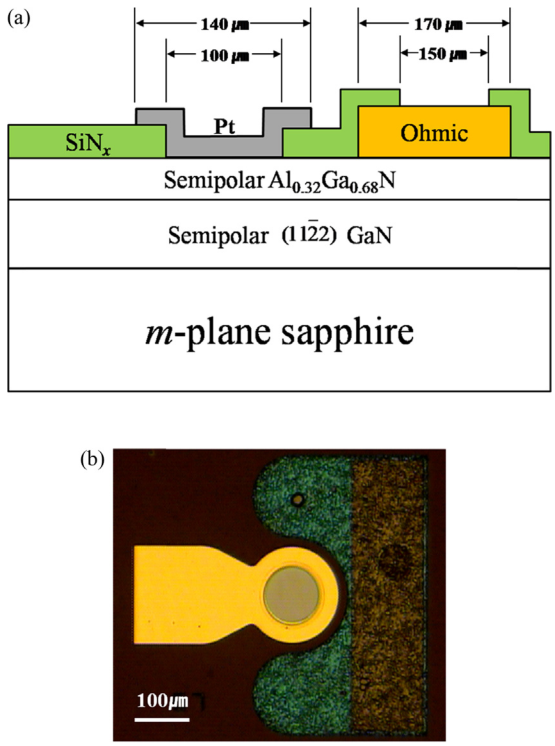

Fig. 1. (a) A schematic cross-sectional view and (b) a top-view image under optical microscope of semipolar (1 1 $\bar{2}$ 2) AlGaN/GaN HEMT sensor with Pt Schottky contact, respectively.

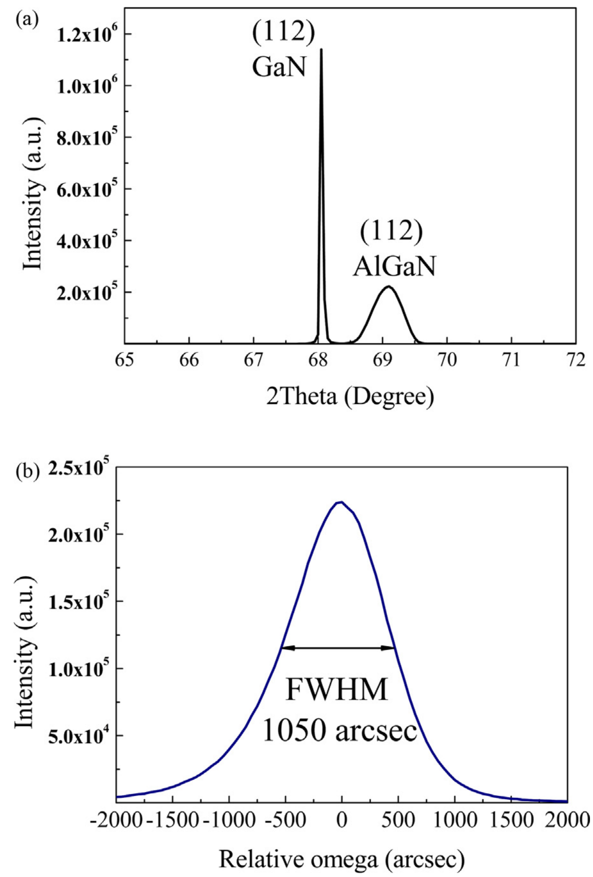

Fig. 2. (a) θ–2θ high-resolution XRD scan for a semipolar (1 1 $\bar{2}$ 2) AlGaN/GaN HEMT structure grown on m-plane sapphire substrates; (b) the on-axis rocking curve of the AlGaN layer with the full width at half maximum of 1050 arcsec.

highly-sensitive hydrogen sensors due to a favorable surface atomic configuration.

2. Experiment

2.4 μm-thick semipolar (1 1 $\bar{2}$ 2) GaN epitaxial films were grown on m-plane sapphire substrates using a high temperature, two-step growth method with an 11 × 2 in. AIX 2400 G3 metal–organic chemical vapor deposition system. Trimethylgallium and ammonia were used as gallium and nitrogen sources, respectively. Prior to growing the seed GaN layer, the sapphire substrate was thermally annealed at 1030 °C in H_2 and NH_3 ambient to remove surface contamination. Semipolar (1 1 $\bar{2}$ 2) GaN films were grown at 1030 °C with a V/III ratio of 1165. The HEMT structure consisted of a 2.4 μm un-doped GaN layer and a 30-nm-thick $Al_{0.32}Ga_{0.68}N$ layer with a doping concentration of 4×10^{18} cm^{-3}. The film surface orientation and crystalline quality of the semipolar (1 1 $\bar{2}$ 2) GaN films were characterized using the high resolution X-ray diffraction (XRD) method.

The Ohmic metal stack of Ti/Al/Pt/Au was deposited by e-beam evaporation, patterned by lift-off, and annealed at 750 °C for 45 s under a N_2 ambient. A 200 nm thick SiN_x passivation layer was formed for diode isolation using a plasma enhanced chemical vapor deposition. The windows for the active sensing area opening were achieved through buffered oxide etchant etching. A 10 nm Pt film was evaporated on the diode's Schottky contact area with the diameter of 100 μm by e-beam evaporation, followed by Ti/Au contact pads for probing and wire bonding. Fig. 1(a) and (b) shows a schematic illustration of device cross-sectional view and a top-view image under optical microscope of semipolar AlGaN/GaN HEMT sensor with Pt Schottky contact, respectively. Current–voltage characteristics for the Pt Schottky diode sensors on semipolar (1 1 $\bar{2}$ 2) AlGaN/GaN HEMT structures exposed to the flammable limit of hydrogen at 1 atm of 4% hydrogen balanced with nitrogen were measured at room temperature in a gas test chamber using an Agilent 4155C semiconductor parameter analyzer.

3. Results and discussion

Fig. 2(a) shows the θ–2θ high-resolution XRD scan for a semipolar (1 1 $\bar{2}$ 2) AlGaN/GaN HEMT structure grown on m-plane sapphire substrates. The AlGaN thickness was estimated to be 30 nm with an Al content of 0.32 for this particular growth condition. Two sharp diffraction peaks at $2\theta = 68.05°$ and 69.1° corresponded to (1 1 $\bar{2}$ 2) GaN and AlGaN, respectively. As can be seen in Fig. 1(b), the full width at half maximum of the on-axis rocking curve was measured to be ~1050 arcsec, indicating a good crystalline and epitaxial quality for the semipolar AlGaN layer formed on the semipolar (1 1 $\bar{2}$ 2) GaN film.

Fig. 3(a) shows current–voltage (I–V) characteristics for the Pt Schottky diode on the semipolar (1 1 $\bar{2}$ 2) AlGaN/GaN HEMT structure before and after exposure to 4% H_2 in N_2 at 25 °C. The Pt Schottky diode exhibited considerable current changes in the sweeping bias range, reaching a change in forward current of more than 30 mA at 1 V. The Schottky behavior gradually shifted to Ohmic-like property with the introduction of hydrogen. This reaction suggests that the H_2 molecules dissociated into atoms on the catalytic Pt film, and formed H-induced dipolar layers, thus leading to a decrease in the effective Schottky barrier height [8–11]. As described in the introduction, it is of special interest here that the nitrogen atoms on the GaN surface along the specific crystal orientations displayed strong affinities for the hydrogen atoms, as reported in the previous literature [18–22]. The authors also reported a large response to hydrogen for the Pt Schottky diode on