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SnO₂ functionalized AlGaN/GaN high electron mobility transistor for hydrogen sensing applications

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ARTICLE INFO

Article history:

Received 2 December 2011

Received in revised form

22 March 2012

Accepted 23 March 2012

Available online 1 May 2012

Keywords:

Hydrogen sensor

High electron mobility transistors (HEMT)

Tin oxide (SnO₂)

Annealing

ABSTRACT

In this study, we report on a demonstration of hydrogen sensing at low temperature using SnO₂ functionalized AlGaN/GaN high electron mobility transistors (HEMT). The SnO₂ dispersion was synthesized via a hydrothermal method and selectively deposited on the gate region of a HEMT device through a photolithography process. The high electron sheet carrier concentration of nitride HEMTs provides an increased sensitivity relative to simple Schottky diodes fabricated on GaN layers. The morphology and crystalline properties of the SnO₂-gate, together with the texture of the multilayer films on the device were investigated by SEM, HRTEM, EDS and XRD. The effects of annealing treatment on the crystalline properties of the SnO₂-gate, and gas sensing properties of SnO₂-gated HEMT sensors were studied. The SnO₂-gated HEMT sensor showed fast and reversible hydrogen gas sensing response at low temperature.

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1. Introduction

Hydrogen is a clean, renewable, and sustainable energy carrier for automotive fuel [1] and fuel cells [2] applications. There is great interest in detection of hydrogen sensors for the use in hydrogen-fueled automobiles and with proton-exchange membrane (PEM) and solid oxide fuel cells for spacecraft and other long-term sensing applications. However, hydrogen is a dangerous gas for storage and safety remains a top concern for applications of hydrogen energy. Hydrogen sensors need to be employed for monitoring leakage

of hydrogen storage equipment and fuel tanks for spacecraft and hydrogen fuel cell automobiles. To reduce the power consumption, hydrogen sensors need, if possible, to be operated near room temperature without integrated on-chip heaters or if using a heater to increase the sensor sensitivity, it should consume minimal power. In addition, fast response time is also very important for many hydrogen detection applications [3].

AlGaN/GaN HEMTs show promising performance for use in broad-band power amplifiers in base station applications due to the high sheet carrier concentration, electron mobility in

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the two dimensional electron gas (2DEG) channel and high saturation velocity. The high electron sheet carrier concentration of nitride HEMTs is induced by piezoelectric and spontaneous polarization of the strained AlGa_{0.25}Ga_{0.75}N layer. By modulating the current in the 2DEG channel of the HEMTs through a functionalized gate electrode, HEMT based sensors have been used to detect a variety of gases [4–7].

SnO₂ has been used for detecting CO and H₂ gases at different temperatures [8–10]. The gas sensing properties of the SnO₂-based gas sensors can be improved either by introducing dopants into the SnO₂ [11] or by changing the surface nanostructure of the SnO₂ [12,13] to enhance the sensitivity of the gas sensing. Hamaguchi et al. [14] reported the H₂ gas sensing properties of sensors prepared by fabricating tin oxide nanohole arrays on various electrodes. At 250 °C, the response time and the recovery time of the tin oxide nanohole arrays sensors were about 5 min. Both response and recovery times became much longer as the ambient temperature decreased.

In this work, the gas sensing properties of SnO₂-based sensors were improved neither by doping nor by using the SnO₂ with 1D or 2D nanostructure. A SnO₂ film was used as the gate electrode of HEMT sensor to detect 1% hydrogen at 50 °C.

2. Experimental

2.1. SnO₂-gated HEMT sensor

Fig. 1a shows a schematic cross-sectional view of the AlGa_{0.25}Ga_{0.75}N/GaN HEMT device with SnO₂-gate. The Au-coated gate area was functionalized with SnO₂. The HEMT structure consists of a 2 μm GaN buffer layer, 25 nm Al_{0.25}Ga_{0.75}N layer and 5 nm GaN cap layer. The epilayers were grown by molecular beam epitaxy (MBE) on sapphire substrates. A sheet carrier concentration of $\sim 10^{13}$ cm⁻² and an electron mobility of 1200 cm²/V·s were obtained at 300 K via Hall measurements. 50 × 50 μm² Ohmic contacts were composed of e-beam

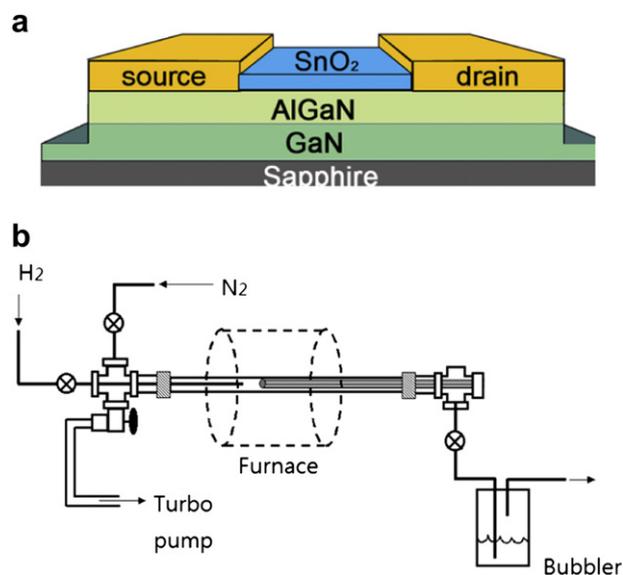


Fig. 1 – Schematic illustrations of (a) AlGa_{0.25}Ga_{0.75}N/GaN HEMT sensor with SnO₂-gate (b) the hydrogen sensing system.

evaporated Ti/Al/Ni/Au and separated from each other by a 20 μm gap using the standard positive resist lift-off process. The Ohmic contacts were annealed at 850 °C for 45 s under flowing N₂. Then, a metal layer consisting of Ti/Au was deposited for interconnections.

The gate area of the sensor was functionalized with a 20 nm of SnO₂ layer through a hydrothermally selective-area deposition method. The SnO₂ gel solution was prepared by adding 1 ml of HCl (40%) and 1 ml of NH₄OH (29%) in 100 ml of SnCl₄ aqueous solution. Then the solution was heated to 95 °C for 15 min. After being cooled to room temperature, the SnO₂ gel solution was spin-coated on the positive photoresist patterned HEMT sample with the gate area opened. To improve the adhesion, the sample was baked at 100 °C for 30 min prior to the standard resist lift-off process using acetone. Then the SnO₂-gated HEMT sample was annealed at 200 °C for 10 min to remove the residue solutions from the SnO₂. The SnO₂ functionalized gas sensor chip was mounted and wire bonded on a chip carrier for hydrogen detection.

2.2. Gas sensing

The system shown in Fig. 1b was utilized for gas sensing. The SnO₂ HEMT gas sensor was bonded to electrical feed-through and exposed to different gas ambients in the test chamber. Initially, the chamber was purged with pure nitrogen until the current reached a steady value. Then, 1% H₂ balanced with N₂ was introduced into the test system. The drain current of the SnO₂-gated HEMT gas sensor was monitored with an HP 4145B parameter analyzer. The temperature of the gas chamber was controlled by the furnace. The drain current for the SnO₂ HEMT gas sensor in nitrogen (I_0) and in the hydrogen-containing environment (I_{gas}) were measured during exposure to on–off cycles, which include sequential introduction of dilute H₂ in N₂ (“on”) and dry N₂ (“off”). The gas sensitivity was determined using the following equation:

$$\text{Sensitivity(\%)} = \frac{I_{\text{gas}} - I_0}{I_0} \times 100\% \quad (1)$$

2.3. Characterization

The high resolution transmission electron microscope (HRTEM) experiments were carried out on a Transmission Electron Microscope (JEOL 2010F). The top-view images of films were observed by a HITACHI S4800 cold field emission scanning electron microscope and energy dispersive spectrometer. XRD studies were carried out with a MAC SCIENCE MXP3 diffractometer.

2.4. Crack analysis

Surface crack density of the SnO₂-gate region was measured before and after annealing using Image J (freeware available from the National Institute of Health at rsbweb.nih.gov/ij/). The length of each crack was approximated with a series of straight lines. The total crack length was normalized against the length of the scale bar in order to convert to a crack length in nanometers rather than pixels. The crack density was computed by taking the number of cracks observed on each

electrode and dividing by the electrode area, determined with a rectangular approximation. This area was normalized against the scale bar size in order to determine the density with respect to the area in 1 cm^2 rather than a number of pixels.

3. Results and discussion

3.1. Morphology and surface crack density

Fig. 2 illustrates a comparison between the surface morphology of the unannealed and annealed SnO_2 -gated devices using plan view SEM images. Comparing the surface morphology of the SnO_2 -gate region between the two samples, the annealed sample contains more surface cracks than the unannealed sample. Additionally, the surface crack density of the SnO_2 -gate region of the samples was measured using Image J and found to be $4.1 \pm 1.4 \times 10^6 \text{ cm}^{-2}$ for the unannealed devices and $11.3 \pm 4.1 \times 10^6 \text{ cm}^{-2}$ for the annealed devices. Such an increase in surface crack density increased

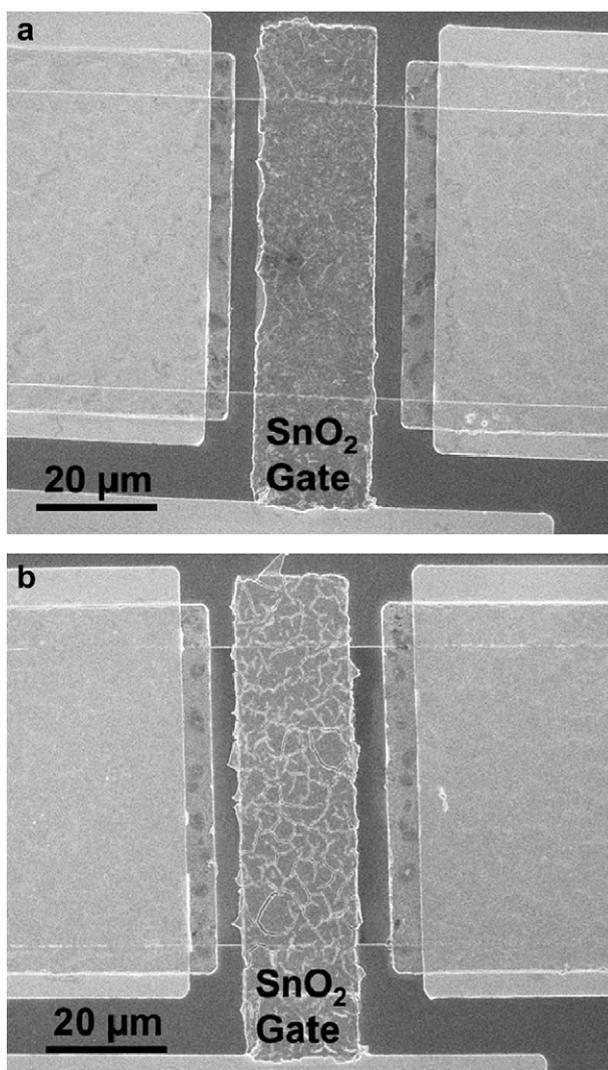


Fig. 2 – SEM images of the surface of the (a) unannealed (b) annealed device.

the surface area for the gas reaction and diffusion to enhance the gas sensing sensitivity.

3.2. Cross-sectional structure

Fig. 3(a) shows the high resolution TEM image of the cross-sectional image of a SnO_2 -gate HEMT device showing the SnO_2 -gate and AlGaIn epilayer. The selected area diffraction (SAD) pattern of SnO_2 -gate is shown in the upper right corner of Fig. 3(a). The SnO_2 -gate appears to be polycrystalline. It shows a discontinuous ring pattern arising from nanocrystallite structures. Fig 3(b) also includes scanning energy dispersive x-ray (EDS) analyses for different layers of the SnO_2 -gated HEMT sensor chip. The upper layer consists of Sn and O elements. There is Al element in the middle layer. The Ga element appears in both the middle and the bottom layers. It confirmed sharp interfaces among SnO_2 , AlGaIn and GaN multilayer structures of the SnO_2 -gated HEMT sensor chip and no intermixing of the layer occurred during the annealing step.

3.3. X-ray analysis

SnO_2 films were coated on the glass and annealed at various temperatures. XRD patterns of these films were investigated to check their crystalline structures. Fig. 4 shows XRD patterns of tin oxide film on glass substrate after being annealed at different temperature (200°C , 300°C and 400°C). The XRD pattern revealed the formation of tetragonal rutile phase in annealed SnO_2 films. The peaks at 2θ values of 38.26° and 78.40° attributed to the (200) and (321) lattice plane reflections of SnO_2 tetragonal rutile crystal, respectively.

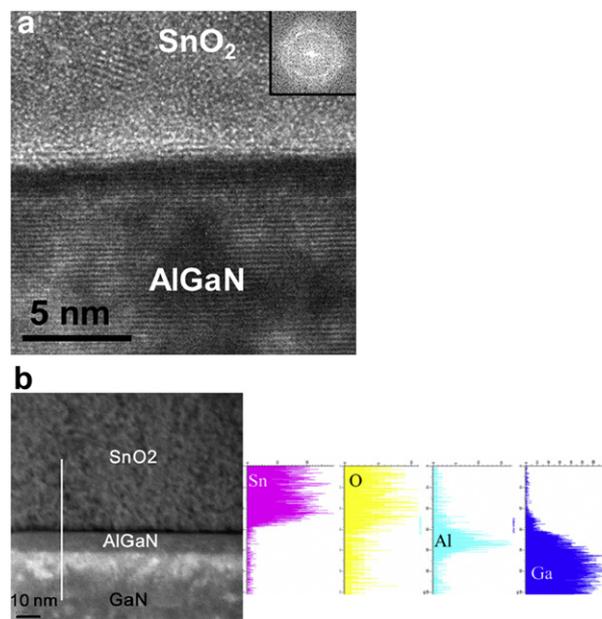


Fig. 3 – (a) High resolution TEM image of the cross section of a device showing the SnO_2 -gate and AlGaIn epilayer (inset diffraction pattern is from the SnO_2 -gate and indicates that it is polycrystalline). (b) EDS analysis with cross-sectional SnO_2 -gated HEMT sensor chip for different layer.

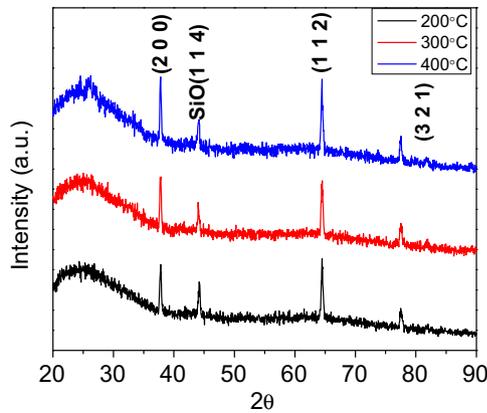


Fig. 4 – XRD patterns of tin oxide films annealed at different temperature (a) 200 °C (b) 300 °C and (c) 400 °C.

The average crystallite size (D) of tin oxide thin film was estimated using the Scherrer equation as follows [15]:

$$d = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where d is the mean crystallite size, K is a grain shape dependent constant (0.9), λ is the wavelength of the incident beam, θ is a Bragg reflection angle and β is the full width half maximum.

The d values of different lattice plane reflections treated at various annealing temperatures are listed in Table 1. As the annealing temperature increased, the sharpness and intensity of the (200) and (321) peaks increased because of the crystalline growth. The average crystallite size was estimated from XRD measurements by the Scherrer equation. The crystallite size was increased slightly from 1.3 nm to 4.2 nm for (200) orientation as the annealing temperature increasing from 200 °C to 400 °C. The crystallite size was increased slightly from 3.1 nm to 5.1 nm for (321) orientation as the annealing temperature increasing from 200 °C to 400 °C. There was a tendency that the crystallite size decreased slightly from 7.8 to 3.7 nm for (112) orientation as the annealing temperature increased from 200 °C to 400 °C.

3.4. Gas sensing properties

3.4.1. Sensing at low temperature

The sensor functionalized with an unannealed SnO₂-gate electrode was not sensitive to the hydrogen. Once the SnO₂

was annealed, the sensors showed different degrees of sensitivity to the 1% H₂ ambient. Fig. 5 shows the time dependence measurements of the hydrogen sensing sensitivity conducted at 50 °C for SnO₂-gated HEMT sensors annealed at different temperatures during the sensor fabrication. The gas ambient was switched between 1% H₂ (in N₂) and pure N₂. The sensitivity for the sensor annealed at 200 °C showed large fluctuations upon the introduction and removal of H₂ gas (Fig. 5a). The signal to noise ratio was poor. Meanwhile, considerable changes in sensitivity were observed when the on and off responses toward H₂ were repeated 2 times. On the contrary, the sensitivity of the sensor annealed at 300 °C increased three times as

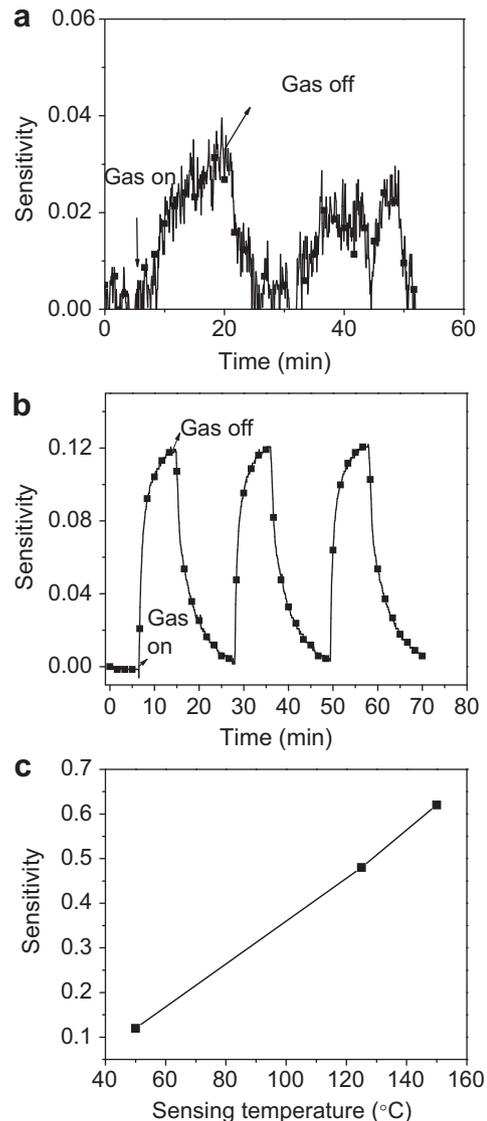


Fig. 5 – Time dependence measurements of the hydrogen detection sensitivity conducted at 50 °C for SnO₂-gated HEMT sensors with SnO₂ annealed at (a) 200 °C (b) 300 °C during the sensor fabrication. The surrounding gas was switched between 1% H₂ in N₂ (gas on) and pure N₂ (gas off). (c) The sensitivity at different sensing temperatures for SnO₂-gated HEMT sensors annealed at 300 °C.

Table 1 – Average crystallite size of SnO₂ annealed at different temperature calculated from different diffraction peaks.

Orientation (hkl)	Annealing temperature		
	200 °C	300 °C	400 °C
(200)	1.3 nm	3.1 nm	4.2 nm
(112)	7.8 nm	3.5 nm	3.7 nm
(321)	3.1 nm	5.1 nm	5.1 nm

compared to the sensor annealed at 200 °C (Fig. 5b). The response and the recovery times at 50 °C for SnO₂-gated HEMT sensor annealed at 300 °C are 4min and 9.5 min, respectively and the response and the recovery time were defined as the time for a sensor to reach 90% of the stable value. The sensor annealed at 300 °C showed no degradation with repeated exposure to hydrogen/nitrogen ambients. The better sensitivity of the sensor annealed at 300 °C was due to an increase of SnO₂ surface contact area, which was consistent with Liu's results in increasing porosity of the SnO₂ layer after annealing [16]. The good sensitivity and reversibility for the SnO₂-gated HEMT sensors annealed at 300 °C were attributed to the larger surface cracks and smaller grain size associated with the high temperature annealing.

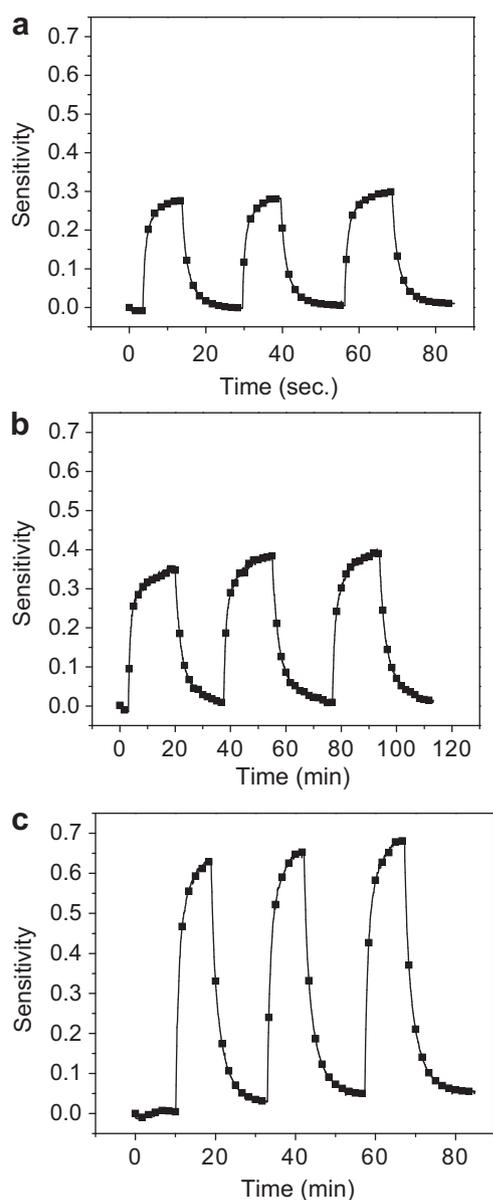


Fig. 6 – Time dependence of the sensitivity at 150 °C for SnO₂-gated HEMT sensors annealed at (a) 200 °C (b) 300 °C (c) 400 °C when the surrounding gas was switched between 1% H₂ in N₂ (gas on) and pure N₂ (gas off) for 3 cycles.

Table 1 shows the grain sizes of SnO₂ annealed at different temperatures based on different crystal orientations. All of them are either smaller or comparable to the space-charge length of SnO₂ (about 6 nm [12]). The small grains of SnO₂ allowed the sensors to be operated in the grain-controlled mode. Wang reported that the sensitivity could be exponentially enhanced when the grain size reduced to a scale comparable to the space-charge length [12]. The grain sizes of SnO₂ sensor annealed at 300 °C were smaller than 6 nm for all (200), (112) and (321) orientations. Sensors were operated in the grain-controlled mode. That may explain why the SnO₂-gated HEMT sensors annealed at 300 °C showed higher sensitivity and sharper response at 50 °C than the sensors annealed at 200 °C. To operate the sensors at 50 °C also helped to minimize the thermal-induced grain size changes to increase the stability and reliability of the sensor.

3.4.2. Operating temperature and annealing temperature

Fig. 5c shows the sensitivity of the SnO₂-gated gas sensor annealed at 300 °C operated at different temperatures. The sensitivity increased as the operating temperature in the testing chamber increased. For polycrystalline SnO₂, grain boundaries contributed most of the resistance and the surface resistivity of the oxide depended on the electron concentration near the surface. By increasing the ambient temperature, more free carriers were generated to reduce the resistivity, thus the sensitivity of the sensor increased. Similar trends were observed for the sensor annealed at 200, 300, and 400 °C. Fig. 6 illustrates the time dependence sensitivity measured at 150 °C for SnO₂-gated HEMT sensors annealed at 200, 300, and 400 °C during the sensor fabrication. When the gas sensing was conducted at 150 °C, all sensors exhibited improved sensitivity. For the sensor annealed at 200 °C, the sensitivity increased and large fluctuations observed for the testing conducted at 50 °C, as shown in Fig. 5(a), was not observed. Among them, the sensor annealed at 400 °C exhibited the highest sensitivity. The sensitivity almost doubled when the annealing temperature increased from 300 °C to 400 °C. Higher annealing temperature (>400 °C) may offer better crystallinity of the SnO₂. However, the Ohmic contact on the AlGaN/GaN would degrade.

4. Conclusion

Tin oxide thin films were fabricated as gates of the HEMT gas sensors and annealed at various temperatures. The annealing temperature exhibits large effect on the hydrogen gas sensing properties of the film. The annealing induced cracks and small grain size of the SnO₂-gate play an important role in the fast and reversible hydrogen gas sensing response at low temperature. After being annealed at a temperature higher than 300 °C, the crystallite sizes of the SnO₂-gate are smaller than the space-charge length of SnO₂ (about 6 nm). Sensors were operated in the grain-controlled mode. Based on the SEM images, the density of the crack is about 0.15/μm² for the annealed sample. We believe that the small crystallite should be the dominant contribution. Such rapid and reversible responses make the SnO₂-gated HEMT gas sensor suitable for practical applications in hydrogen sensing at low temperature.

Acknowledgments

The work at UF was partially supported by the Office of Naval Research (ONR) under contract number 00075094 monitored by Dr. Chagaan Baatar, NSF under contract number ECCS 0901711 monitored by Dr. Yogesh B. Gianchandani. The work at FCU was supported by the National Science Council (NSC) of Taiwan under contract number NSC 100-2628-E-035-003. The authors thank the assistance from the Precision Instrument Support Center of Feng Chia University.

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