Hydrogen Sensing Characteristics of Pt Schottky Diodes on (201) and (010) Ga₂O₃ Single Crystals

Soohwan Jang, Sunwoo Jung, Jihyun Kim, Fan Ren, Stephen J. Pearton, and Kwang Hyeon Baik

1 Department of Chemical Engineering, Dankook University, Yongin 16890, South Korea
2 Department of Chemical Engineering, Korea University, Seoul 02841, South Korea
3 Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, USA
4 Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, USA
5 School of Materials Science and Engineering, Hongik University, Sejong 30018, South Korea

We investigated the hydrogen sensing characteristics of Pt Schottky diodes on (201) and (010) β-Ga₂O₃ bulk crystals. The Pt Schottky diodes on β-Ga₂O₃ wafer exhibited the fast, reversible, and cyclic response upon hydrogen exposure. The maximum value of the relative current change of the (201) Ga₂O₃ diode sensor was as high as 7.86 × 10⁻² (%) at 0.8 V, which is slightly higher than that of the (010) Ga₂O₃ diode. The hydrogen responses of both β-Ga₂O₃ diode sensors are believed to result from oxygen and gallium atomic configurations of Ga₂O₃ surfaces for hydrogen adsorption. The Pt Schottky diodes of Ga₂O₃ wafers did not show any clear response to other gases, such as N₂, CO, CO₂, O₂, CH₄, NO₂, and NH₃. Our finding suggests that the Pt Schottky diodes on β-Ga₂O₃ hold great potential for the applications of hydrogen gas sensors with high sensitivity and selectivity.

Recently, there has been a surge of research interest for the applications of gallium oxide (Ga₂O₃) in high-power devices, solar-blind photodetectors, and gas sensors. A large bandgap energy (4.9 eV) of Ga₂O₃ allows high critical electric field (>8 MV cm⁻¹), leading to making its devices more efficient with small size dimensions. The wide bandgap nature also enables Ga₂O₃-based electronic devices to operate at high temperatures due to its low intrinsic carrier concentration. Furthermore, Ga₂O₃ has shown excellent catalytic reactions with various chemicals and gases. Beta (β) Ga₂O₃, the most stable form in different polymorphs in Ga₂O₃, has been widely studied as a reactive oxide layer, which is sensitive to a wide variety of gases. The use of β-Ga₂O₃ can be a promising alternative in the detection and sensing of hydrogen at high temperatures under harsh conditions, due to its unique hydrogen response as well as chemical and mechanical stability.

Metal oxide thin films and nanostructures for gas sensing applications have been reviewed by Gu et al., especially for hydrogen gas sensing. The surface reactions of oxygen species with hydrogen molecules usually result in the conductivity change of metal oxides. Fleisher et al. investigated the potential applications of Ga₂O₃ thin films as gas sensors at high temperatures. Trinch et al. first reported the hydrogen response of Ga₂O₃ using a Schottky diode with platinum (Pt) catalytic layer. They observed the effective changes in the Schottky barrier height in Pt/Ga₂O₃ diode sensor depending on hydrogen concentrations. Nakaomi et al. also demonstrated highly-sensitive hydrogen gas sensors, which could be operated reliably at high temperatures above 400°C using the field-effect transistors on Ga₂O₃ thin film and Schottky diodes on β-Ga₂O₃ single crystals.

It is of great importance to study the hydrogen adsorption on Ga₂O₃ surface in order to understand hydrogen sensing mechanism and improve its hydrogen sensitivity. Jochum et al. found that the hydrogen adsorption on Ga₂O₃ formed OH below 200°C and GaH species above 200°C with Fourier transform infrared spectroscopy. Pan et al. also proposed their model in their experimental and computational studies that OH and GaH species resulted from the hydrogen adsorption on three-coordinated surface O and on unsaturated Ga atoms, respectively.

Their findings also suggested that high temperature would promote the GaH formation on the Ga₂O₃ surfaces owing to surface oxygen vacancies, which make the surface more active for the dissociative adsorption of hydrogen as well as CO₂ and H₂O. In this study, we report on the hydrogen sensing performance of Pt/β-Ga₂O₃ diode sensors and a comparative study of the hydrogen sensing characteristics using (201) and (010) β-Ga₂O₃ single crystals.

Experimental

β-phase Ga₂O₃ bulk wafers with (201) and (010) crystal orientations were purchased from Tamura Corporation, which were grown by the edge-defined film-fed growth method. The full-widths at half-maximum of X-ray rocking curves (XRCs) were measured to be 65–75 arcsec for both β-Ga₂O₃ samples. The dislocation density on the order of 10⁻¹⁰ cm⁻² were measured by etch pit measurements. Both β-Ga₂O₃ wafers were Sn-doped with an electron concentration of ~10¹⁸ cm⁻³. XRC measurements were performed on Jordan Valley QC3 high-resolution X-ray diffraction system with a Cu Kα X-ray target source (λ = 1.5406 Å). The fabrication of Pt Schottky diodes started with ohmic contact formation with Ti/Al metals, which were E-beam evaporated on β-Ga₂O₃ and annealed in nitrogen atmosphere in a rapid thermal annealer. Diode sensors were isolated with 200-nm-thick SiNx layer by plasma-enhanced chemical vapor deposition. Wet etching was performed for window opening of gas sensing area with buffered oxide etchants. 10-mm-thick Pt film was evaporated on the Schottky contact area. Then, Ti/Au contact pads were deposited for probing and wire bonding. The current-voltage (I-V) curves of Pt Schottky diode sensors on (201) and (010) β-Ga₂O₃ were measured by an Agilent 4155C semiconductor parameter analyzer with different hydrogen concentrations balanced with nitrogen in a gas test chamber.

Results and Discussion

Fig. 1 shows (a) a schematic device crossection and (b) top-view optical microscope image of the fabricated diode sensor on Ga₂O₃ bulk wafers having Pt Schottky metal, Ti/Al ohmic metal, and a SiNx isolation layer. Fig. 2 shows the change in the I–V characteristics of the Pt Schottky diode sensors on (a) (010) and (b) (201) Ga₂O₃ wafers.
Figure 1. The (a) crossection schematic and (b) optical microscope image of the fabricated Schottky diode with catalytic Pt layer on Ga$_2$O$_3$ bulk crystal wafers.

Figure 2. The I–V characteristics of the Pt Schottky diode sensors on (a) (010) and (b) (−201) Ga$_2$O$_3$ wafers when exposed to 500 ppm H$_2$ at room temperature.

Figure 3. The relative current change as a percentage of the Pt Schottky diode sensors on (010) and (−201) Ga$_2$O$_3$ wafers as a function of bias voltage before and after 500 ppm H$_2$ exposure.

Figure 4. The cyclic response curves of the (010) Ga$_2$O$_3$ diode sensor with increasing H$_2$ concentration at the fixed forward bias of 0.8 V upon ambience switching between N$_2$ and different H$_2$ concentration.

when exposed to 500 ppm H$_2$ at room temperature. Both Ga$_2$O$_3$–based diodes exhibited a good rectifying behavior in nitrogen and hydrogen ambience. In the case of hydrogen exposure, the I–V curves clearly shift toward a lower forward voltage, and the forward voltage shift ($\Delta V$) was 0.6 V for (010) Ga$_2$O$_3$ and 0.5 V for (−201) Ga$_2$O$_3$. Upon exposure to hydrogen, the hydrogen molecules decomposes on the Pt layer, and then the adsorption of dissociated hydrogen atoms occurs on oxygen atoms on Ga$_2$O$_3$ surface. The resultant dipole layers at the Pt/Ga$_2$O$_3$ interface induce the reduction of Schottky barrier height (SBH), resulting in the increased forward current. It is believed that the absorbed hydrogen atoms forms electrically polarized layers at the Pt/Ga$_2$O$_3$ interface, leading to the decrease in the barrier height and the increase in the forward current.

Fig. 3 shows the relative current change as a percentage of the Pt Schottky diode sensors on (010) and (−201) Ga$_2$O$_3$ wafers as a function of bias voltage before and after 500 ppm H$_2$ exposure. The relative current change is defined as $(I_{H2} - I_{N2})/I_{N2} \times 100\%$, where $I_{H2}$ and $I_{N2}$ denote diode currents measured in H$_2$ and N$_2$ ambient under different H$_2$ concentration, respectively. The current changes peaked at 0.7–1.0 V for both Schottky diodes. The maximum value of the relative current change was measured to be $7.86 \times 10^7$ (%) at 0.8 V for the (−201) Ga$_2$O$_3$ diode and $1.58 \times 10^7$ (%) at 1.5 V for the (010) Ga$_2$O$_3$ diode. We believe that the sensitivity difference between (010) and (−201) Ga$_2$O$_3$ diodes originate from oxygen and gallium atomic configurations of Ga$_2$O$_3$ surfaces. The SBH changes after exposure to 500 ppm H$_2$ in N$_2$ were measured to be 0.09 eV and 0.27 eV for (010) and (−201) Ga$_2$O$_3$ diodes, respectively. The higher SBH change of (−201) Ga$_2$O$_3$ diode may result from more hydrogen adsorption sites available on (−201) surface owing to the higher density of oxygen dangling bonds. As reported by Jang et al., the density of oxygen atoms is $1.34 \times 10^{15}$ cm$^{-2}$ on the (−201) Ga$_2$O$_3$ surface, which is 1.5 times higher than that on (010) Ga$_2$O$_3$. A larger number of adsorption sites are available for hydrogen atoms on the (−201) Ga$_2$O$_3$ surface, thus forming OH and dipole layers at the Pt/Ga$_2$O$_3$ interface and leading to lowering the SBH. It implies that the understanding of
surface termination and atomic arrangement of oxygen and gallium atoms is important for hydrogen adsorption and the production of Ga-H and OH species for various Ga$_2$O$_3$ crystal planes.

Fig. 4 shows the cyclic response curves of the (010) Ga$_2$O$_3$ diode sensor with increasing H$_2$ concentration at the fixed forward bias of 0.8 V upon ambience switching between N$_2$ and different H$_2$ concentration. The Ga$_2$O$_3$ diode sensors clearly exhibited the fast and repeatable response to various H$_2$ concentrations as well as a full recovery of current level after H$_2$ switching off. Note that the current change of the (201) Ga$_2$O$_3$ diode sensor was about 3.5–4.7 times higher than that of the (010) β-Ga$_2$O$_3$ diode sensor. The response times of both (010) and (201) Ga$_2$O$_3$ diode sensors were measured to less than 2 s to reach 90% of current level of its steady-state value for 500 ppm hydrogen exposure. The forward current increased with a reasonable degree of linearity when H$_2$ concentrations increased from 0.01 to 40,000 ppm.

The electrical response to various gases of the Pt Schottky diodes on (010) Ga$_2$O$_3$ single crystals were measured to investigate the cross-selectivity. As can be seen in Fig. 5, the Pt Schottky diodes on (010) Ga$_2$O$_3$ single crystals did not show any clear response to other gases, such as N$_2$, CO, CO$_2$, O$_2$, CH$_4$, NO$_2$, and NH$_3$. Our finding suggests that the Pt Schottky diodes on β-Ga$_2$O$_3$ hold great potential for the applications of hydrogen gas sensors with high sensitivity and selectivity.

Conclusions

We conducted a comparative study on the hydrogen sensing characteristics of Pt Schottky diodes using (201) and (010) β-Ga$_2$O$_3$ bulk crystals. The Pt Schottky diodes on both β-Ga$_2$O$_3$ wafers exhibited the fast and cyclic response upon the introduction of hydrogen with various hydrogen concentrations. The maximum value of the relative current change was measured 7.86 × 10$^{-4}$ (%) at 0.8 V for the (201) Ga$_2$O$_3$ diode, which is slightly higher than that for the (010) Ga$_2$O$_3$ diode (1.58 × 10$^{-4}$ (%) at 1.0 V). The sensitivity of (010) and (201) Ga$_2$O$_3$ diode sensors is believed to originate from oxygen and gallium atomic configurations on Ga$_2$O$_3$ surfaces. The Pt Schottky diodes of Ga$_2$O$_3$ wafers did not show any clear response to other gases, such as N$_2$, CO, CO$_2$, O$_2$, CH$_4$, NO$_2$, and NH$_3$. Our finding suggests that the Pt Schottky diodes on β-Ga$_2$O$_3$ hold great potential for the applications of hydrogen gas sensors with high sensitivity and selectivity.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2015M3A7B7045185). This present research was also supported by 2018 Hongik University Research Fund.

References