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Hydrogen Sensing Characteristics of Pt Schottky Diodes on ($\bar{2}01$) and (010) Ga_2O_3 Single Crystals

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We investigated the hydrogen sensing characteristics of Pt Schottky diodes on ($\bar{2}01$) and (010) β-Ga_2O_3 bulk crystals. The Pt Schottky diodes on β-Ga_2O_3 wafer exhibited the fast, reversible, and cyclic response upon hydrogen exposure. The maximum value of the relative current change of the ($\bar{2}01$) Ga_2O_3 diode sensor was as high as 7.86×10^7 (%) at 0.8 V, which is slightly higher than that of the (010) Ga_2O_3 diode. The hydrogen responses of both β-Ga_2O_3 diode sensors are believed to result from oxygen and gallium atomic configurations of Ga_2O_3 surfaces for hydrogen adsorption. The Pt Schottky diodes of Ga_2O_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_2O_3 hold great potential for the applications of hydrogen gas sensors with high sensitivity and selectivity.

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Recently, there has been a surge of research interest for the applications of gallium oxide (Ga_2O_3) in high-power devices, solar-blind photodetectors, and gas sensors.[1–3] A large bandgap energy (4.9 eV) of Ga_2O_3 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 Ga_2O_3–based electronic devices to operate at high temperatures due to its low intrinsic carrier concentration. Furthermore, Ga_2O_3 has shown excellent catalytic reactions with various chemicals and gases.[4–8] Beta (β)-Ga_2O_3, the most stable form in different polymorphs in Ga_2O_3, has been widely studied as a reactive oxide layer, which is sensitive to a wide variety of gases. The use of β-Ga_2O_3 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.[9] 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 Ga_2O_3 thin films as gas sensors at high temperatures.[10–12] Trinch et al. first reported the hydrogen response of Ga_2O_3 using a Schottky diode with platinum (Pt) catalytic layer.[13,14] They observed the effective changes in the Schottky barrier height in Pt/Ga_2O_3 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 Ga_2O_3 thin film and Schottky diodes on β-Ga_2O_3 single crystals.[15–18]

It is of great importance to study the hydrogen adsorption on Ga_2O_3 surface in order to understand hydrogen sensing mechanism and improve its hydrogen sensitivity. Jochum et al. found that the hydrogen adsorption on Ga_2O_3 formed OH below 200°C and GaH species above 200°C with Fourier transform infrared spectroscopy.[19] Pan et al. also proposed 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.[20] Their findings also suggested that high temperature would promote the GaH formation on the Ga_2O_3 surfaces owing to surface oxygen vacancies, which make the surface more active for the dissociative adsorption of hydrogen as well as CO_2 and H_2O.[21–25] In this study, we report on the hydrogen sensing performance of Pt/ β-Ga_2O_3 diode sensors and a comparative study of the hydrogen sensing characteristics using ($\bar{2}01$) and (010) β-Ga_2O_3 single crystals.

Experimental

β-phase Ga_2O_3 bulk wafers with ($\bar{2}01$) 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 arcsecs for both β-Ga_2O_3 samples. The dislocation density on the order of 10^3–10^4 cm^{-2} were measured by etch pit measurements. Both β-Ga_2O_3 wafers were Sn-doped with an electron concentration of $\sim 10^{18}$ cm^{-3}. XRC measurements were performed on Jordan Valley QC3 high-resolution X-ray diffraction system with a Cu $K\alpha_1$ X-ray target source ($\lambda = 1.5406$ Å). The fabrication of Pt Schottky diodes started with ohmic contact formation with Ti/Al metals, which were E-beam evaporated on β-Ga_2O_3 and annealed in nitrogen atmosphere in a rapid thermal annealer. Diode sensors were isolated with 200-nm-thick SiN_x layer by plasma-enhanced chemical vapor deposition. Wet etching was performed for window opening of gas sensing area with buffered oxide etchants. 10-nm-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 ($\bar{2}01$) and (010) β-Ga_2O_3 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 Ga_2O_3 bulk wafers having Pt Schottky metal, Ti/Al ohmic metal, and a SiN_x isolation layer. Fig. 2 shows the change in the I–V characteristics of the Pt Schottky diode sensors on (a) (010) and (b) ($\bar{2}01$) Ga_2O_3 wafers

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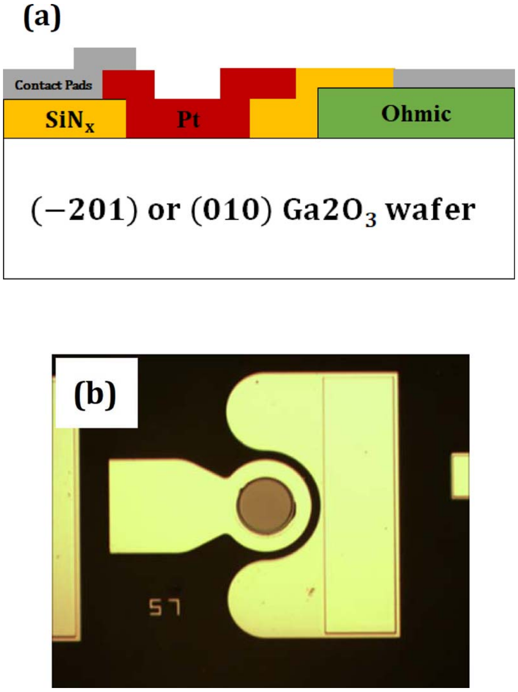

Figure 1. The (a) crossection schematic and (b) optical microscope image of the fabricated Schottky diode with catalytic Pt layer on Ga_2O_3 bulk crystal wafers.

when exposed to 500 ppm H_2 at room temperature. Both Ga_2O_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 (ΔV) was 0.6 V for (010) Ga_2O_3 and 0.5 V for $(\bar{2}01)$ Ga_2O_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_2O_3 surface. The resultant dipole layers at the Pt/Ga_2O_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_2O_3 interface, leading to the decrease in the barrier height and the increase in the forward current.

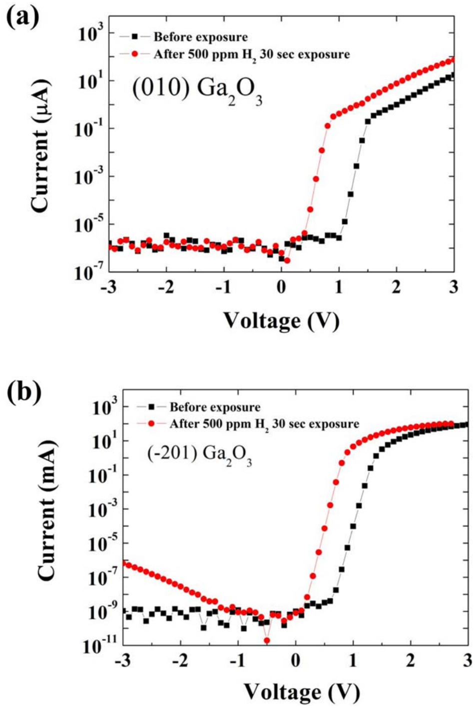

Figure 2. The I–V characteristics of the Pt Schottky diode sensors on (a) (010) and (b) (−201) Ga_2O_3 wafers when exposed to 500 ppm H_2 at room temperature.

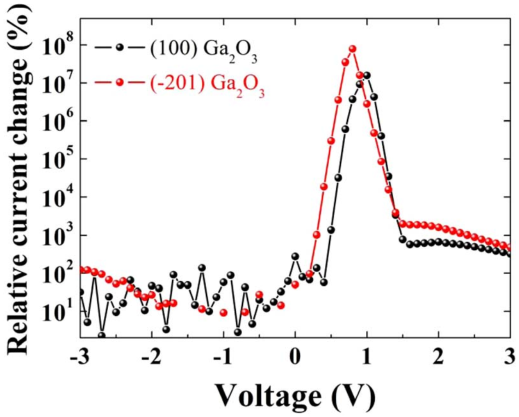

Figure 3. The relative current change as a percentage of the Pt Schottky diode sensors on (010) and (−201) Ga_2O_3 wafers as a function of bias voltage before and after 500 ppm H_2 exposure.

Fig. 3 shows the relative current change as a percentage of the Pt Schottky diode sensors on (010) and $(\bar{2}01)$ Ga_2O_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 7.86×10^7 (%) at 0.8 V for the $(\bar{2}01)$ Ga_2O_3 diode and 1.58×10^7 (%) at 1.5 V for the (010) Ga_2O_3 diode. We believe that the sensitivity difference between (010) and $(\bar{2}01)$ Ga_2O_3 diodes originate from oxygen and gallium atomic configurations of Ga_2O_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 $(\bar{2}01)$ Ga_2O_3 diodes, respectively. The higher SBH change of $(\bar{2}01)$ Ga_2O_3 diode may result from more hydrogen adsorption sites available on $(\bar{2}01)$ surface owing to the higher density of oxygen dangling bonds. As reported by Jang et al.,[26] the density of oxygen atoms is 1.34×10^{15} cm^{-2} on the $(\bar{2}01)$ Ga_2O_3 surface, which is 1.5 times higher than that on (010) Ga_2O_3. A larger number of adsorption sites are available for hydrogen atoms on the $(\bar{2}01)$ Ga_2O_3 surface, thus forming OH and dipole layers at the Pt/Ga_2O_3 interface and leading to lowering the SBH. It implies that the understanding of

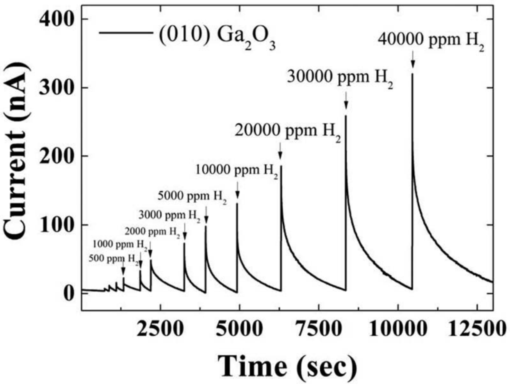

Figure 4. The cyclic response curves of the (010) Ga_2O_3 diode sensor with increasing H_2 concentration at the fixed forward bias of 0.8 V upon ambience switching between N_2 and different H_2 concentration.

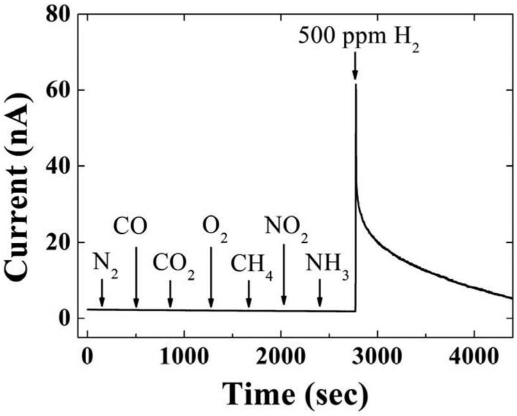

Figure 5. The time-dependent current changes of Pt Schottky diodes on the (010) Ga_2O_3 diode, when exposed to various gas species, including 0.1% CO, 4% CH_4, 10% CO_2, 0.05% NO_2, 2 ppm NH_3, and 500 ppm H_2 in N_2.

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_2O_3 crystal planes.

Fig. 4 shows the cyclic response curves of the (010) Ga_2O_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_2O_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 **$(\bar{2}01)$** Ga_2O_3 diode sensor was about 3.5–4.7 times higher than that of the (010) β-Ga_2O_3 diode sensor. The response times of both (010) and $(\bar{2}01)$ Ga_2O_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_2O_3 single crystals were measured to investigate the cross-selectivity. As can be seen in Fig. 5, the Pt Schottky diodes on (010) Ga_2O_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 at the fixed forward bias of 0.7 V. Pt Schottky diode sensors on Ga_2O_3 wafers showed hydrogen-specific and negligible response to other gas species. This study suggests that the Pt Schottky diodes using β-Ga_2O_3 are highly promising for highly-sensitive hydrogen gas sensors.

Conclusions

We conducted a comparative study on the hydrogen sensing characteristics of Pt Schottky diodes using $(\bar{2}01)$ and (010) β-Ga_2O_3 bulk crystals. The Pt Schottky diodes on both β-Ga_2O_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 7.86×10^7 (%) at 0.8 V for the $(\bar{2}01)$ Ga_2O_3 diode, which is slightly higher than that for the (010) Ga_2O_3 diode (1.58×10^7 (%) at 1.0 V). The sensitivity of (010) and $(\bar{2}01)$ Ga_2O_3 diode sensors is believed to originate from oxygen and gallium atomic configurations on Ga_2O_3 surfaces. The Pt Schottky diodes of Ga_2O_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_2O_3 hold great potential for the applications of hydrogen gas sensors with high sensitivity and selectivity.

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