Characterization of vertical Au/β-Ga_2O_3 single-crystal Schottky photodiodes with MBE-grown high-resistivity epitaxial layer*

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(Received 17 July 2015; revised manuscript received 31 August 2015; published online 8 December 2015)

High-resistivity β-Ga_2O_3 thin films were grown on Si-doped n-type conductive β-Ga_2O_3 single crystals by molecular beam epitaxy (MBE). Vertical-type Schottky diodes were fabricated, and the electrical properties of the Schottky diodes were studied in this letter. The ideality factor and the series resistance of the Schottky diodes were estimated to be about 1.4 and 4.6×10^6 Ω. The ionized donor concentration and the spreading voltage in the Schottky diodes region are about 4×10^{18} cm^{-3} and 7.6 V, respectively. The ultra-violet (UV) photo-sensitivity of the Schottky diodes was demonstrated by a low-pressure mercury lamp illumination. A photoresponsivity of 1.8 A/W and an external quantum efficiency of 8.7×10^2% were observed at forward bias voltage of 3.8 V, the proper driving voltage of read-out integrated circuit for UV camera. The gain of the Schottky diode was attributed to the existence of a potential barrier in the i–n junction between the MBE-grown highly resistive β-Ga_2O_3 thin films and the n-type conductive β-Ga_2O_3 single-crystal substrate.

Keywords: gallium oxides thin films Schottky diode, ultraviolet photodetector

PACS: 72.20.–i, 73.30.+y, 73.40.Ei, 07.07.Df **DOI:** 10.1088/1674-1056/25/1/017201

1. Introduction

The unique properties of gallium oxide with β-type crystal structure (β-Ga_2O_3) stimulated the study of growth and characteristics of that material in view of new applications. After large-size high-quality melt-grown gallium oxide single-crystal wafers were successfully manufactured, β-Ga_2O_3 has attracted increasing interest as a promising wide band gap semiconductor.[1] β-Ga_2O_3 has a wide band gap of about 4.8 eV, the widest among other oxide semiconductors, such as ZnO (3.4 eV) and SnO_2 (3.6 eV),[2,3] paves the way to deep ultraviolet (DUV) optical applications.[4] In particular, photodetectors with solar-blind sensitivity have attracted significant attention, because they respond only to DUV light, even under sun and room illuminations, which is very suitable for monitoring ozone holes and detecting flames.

In order to develop solar-blind photodetectors, a lot of research work based on β-Ga_2O_3 thin films has been demonstrated.[5,6] However, all the films were polycrystalline because of the unique crystal structure of β-Ga_2O_3, which lacks a suitable heteroepitaxial substrate. The crystalline quality of β-Ga_2O_3 thin films is assumed for direct relationships with photoresponsivity of the photodetectors. The grain boundaries of the polycrystalline thin films act as traps for photogenerated carriers, which results in a long response time. Other than thin-film photodetectors, in order to get a short response time, β-Ga_2O_3 nanostructure photodetectors were reported.[7,8] Better crystalline quality of the β-Ga_2O_3 nanowires and nanobelts resulted in a fast photo-response. However, the fabrication process of nanowire-based device array is still an area in progress. Therefore, to fully develop the potential application of β-Ga_2O_3, photodetectors based on single crystals are needed.

Recently, β-Ga_2O_3 single crystals have become available.[9,10] For vertical-type photodetectors, Schottky contacts and ohmic contacts were formed on the surface and on the back side of the single crystal substrate, respectively. In order to reduce the dark current of the photo-diode, a high resistive layer was usually introduced to form a metal–insulator–semiconductor (MIS) configuration instead of the metal–semiconductor (MS) configuration. Oshima *et al*. fabricated a vertical-type Schottky photo-detector based on undoped n-type β-Ga_2O_3 single crystal.[11] In order to introduce a high resistive layer, the β-Ga_2O_3 single crystal was thermally annealed at 1100 °C for 6 h in ambient oxygen to reduce the oxygen vacancies and decrease the carrier concentration near the surface. Suzuki *et al*. demonstrated an MIS photodiode by sol–gel depositing a high-resistivity β-Ga_2O_3 epitaxial layers on undoped n-type β-Ga_2O_3 single crystal substrates.[12]

Besides the crystalline quality of β-Ga_2O_3 epitaxial layers, presence of donor and acceptor defects, providing suc-

*Project supported by the National Nature Science Foundation of China (Grant No. 61223002) the Science and Technology Commission of Shanghai Municipality, China (Grant No. 13111103700), and the Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20120185300003).

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cessively free electrons and holes, are believed for their direct relationships with photoresponsivity of β-Ga_2O_3 ultraviolet (UV) detectors.[13,14] Molecular beam epitaxy (MBE) is well known to reduce the film impurity levels due to an ultrahigh vacuum environment and high purity source materials. Reproducible doping control and lower unintentional impurity levels in the epitaxial films are achievable by using plasma-assisted molecular-beam-epitaxy (PAMBE).[15,16] In this paper, vertical-type Schottky photodiodes were fabricated by PAMBE growing high resistivity β-Ga_2O_3 thin films on the highly conductive Si-doped β-Ga_2O_3 single crystals. The electrical properties of the photodiodes are analyzed.

2. Experiment

Double-side polished (100) β-Ga_2O_3 single crystal substrates used in this study were fabricated from an Si-doped single crystal ingot grown by the floating zone method.[10] The Si-doped single crystal ingot was an n-type semiconductor with a resistivity of about 9×10^3 Ω·cm at room temperature. The (100) β-Ga_2O_3 single-crystal substrates were about 0.5 mm in thickness. Before high-resistivity homo-epitaxial layer growth, the substrates were cleaned with acetone and methanol.

The β-Ga_2O_3 epitaxial layers were grown in an SVT PAMBE system. A standard shuttered Knudsen cell was used to evaporate gallium (99.9999%) and a mono-atomic oxygen from research-grade oxygen gas (99.998%) was supplied from a radio-frequency (RF) radical cell. The substrates were baked in the growth chamber at 650 °C for 30 min. Oxygen plasma treatment using a pressure of 1×10^{-5} Torr at 650 °C for 30 min was conducted to remove the adsorbates from the substrate surface. On the basis of previous experiments of growth parameters optimization, the oxygen gas flow rate, the input RF power of radical cell, and the temperature of K-cell were maintained at 1 sccm, 300 W, and 940 °C, respectively. An optimized substrate temperature of 760 °C was chosen, and the growth rate was about 50 nm/h. The growth time was fixed at 2 h for all samples, resulting in the gallium oxide layers with thicknesses of about 100 nm as characterized by surface profiler and cross-sectional scanning electron microscopy.

To fabricate a photodiode, a large area of square Ti/Au (∼ 40 nm/240 nm) Ohmic contact (5 mm×5 mm) was first deposited on the back side of the n-type conductive substrate by electron-beam evaporation, and thermally annealed at 850 °C for 30 seconds in ambient nitrogen. The specific contact resistivity is about 3×10^{-2} Ω·cm^2. The contact resistance is about 0.12 Ω, which means good Ohmic characteristics of the Ti/Au electrode after annealing. Then 0.5 mm×0.5 mm square Au (5–10 nm) Schottky contacts were deposited on the surface of the MBE grown β-Ga_2O_3 epitaxial layers through metal mask. The device configuration is illustrated in the insertion of Fig. 1.

The current–voltage (I–V) characteristics of the photodiodes were measured with an HP-4155B semiconductor parameter analyzer. The capacitance of the photodiodes was characterized by a HP-4294A impedance analyzer. A low-pressure mercury lamp with a 254-nm line filters was used as UV light source to evaluate photo-responsivity. The incident light power was calibrated by using a calibrated UV-enhanced Si photodiode.

3. Results and discussion

Figure 1 shows the current–voltage (I–V) curves of the fabricated Schottky diodes at room temperature. Usually, the forward bias I–V characteristics are linear in the semi-logarithmic scale at low forward bias voltages as shown in the insertion of Fig. 1, but deviates considerably from linearity due to the effect of series resistance R_s, the interfacial layer, and the interface states when the applied voltage is sufficiently large. Hence the R_s is a significant parameter in the electrical characteristics of Schottky Barrier diodes, especially in the downward curvature (non-linear region) of the forward bias I–V plots. Except for the R_s, the ideality factor is another significant parameter in both the linear and non-linear region of the I–V plots.

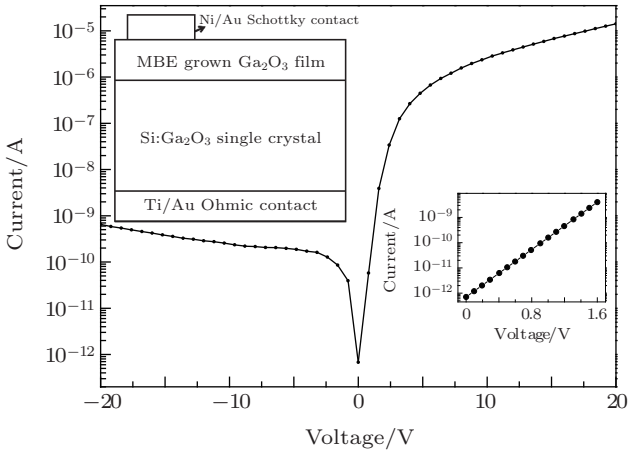


Fig. 1. I–V characteristics of the Schottoky diode. The insertion shows the cross-sectional schematic illustration of the Schottky diode and the I–V characteristics at low forward bias voltages.

According to Cheung's model,[17] the forward current–voltage (I–V) characteristics of a Schottky diode at low forward bias voltages can be expressed by

$$I = I_S \left[\exp\left(\frac{eV_D}{nkT} \right)^{-1} \right], \tag{1}$$

where dimensionless parameter n is called the ideality factor, and $e = 1$ is the electronic charge of electrons, V_D is the voltage applied across the diode, k is the Boltzmann constant, and T is the absolute temperature.

Because of the high resistivity layer in the fabricated diodes, the effect of the diode series resistance R_s cannot be ignored. The voltage V_D across the diode can then be expressed in terms of the total voltage drop V across the series resistor. Thus, $V_D = V - IR_s$. At room temperature, $V_D > 3k_BT/q$ is usually satisfied. Equation (1) becomes

$$I = I_S \exp\left[\frac{eV\,(V - IR_s)}{nk_BT}\right]. \tag{2}$$

Differentiating Eq. (2) with respect to $\ln(I)$ and rearranging terms, we obtain

$$\frac{dV}{d\ln(I)} = IR_s + \frac{n}{\beta}, \tag{3}$$

where $\beta = 1/k_BT$.

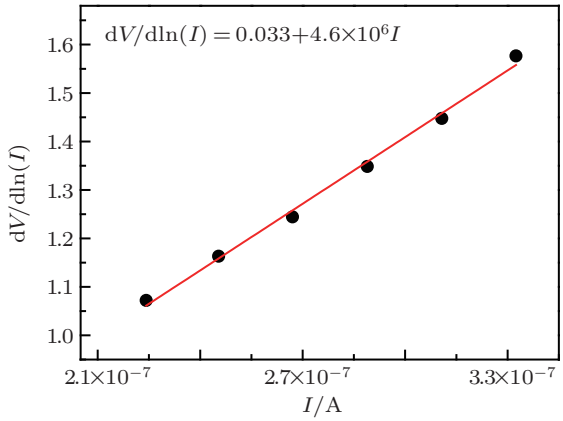


Fig. 2. (color online) Plot of $dV/d\ln(I)$ versus I of the Schottky diode. The insertion shows the linearly fitting result.

Thus, a plot of $dV/d\ln(I)$ vs. I will give R_s as the slope and n/β as the y-axis intercept. The R_s parameter and the ideality factor of the fabricated Schottky diodes were estimated to be about 4.6×10^6 Ω and 1.4 as shown in Fig. 2. The value of ideality factor is greater than unity. Such behavior should be ascribed to the interface states. According to the electric properties of the single crystal substrate, the resistance of the substrate is about 2×10^5 Ω. Hence, the majority of the series resistance R_s results from the highly resistive homo-epitaxial layer.

Figure 3 shows the C–V measurement results at a signal frequency of 1 MHz. A fall in capacitance with the reverse bias voltage in the C–V curve suggests an n-type Schottky contact. The saturation in capacitance at forward bias voltages higher than 7 V indicates the existence of highly resistive homo-epitaxial layer. On the basis of the existence of the highly resistive layer, the capacitance is given by

$$\frac{1}{C} = \frac{1}{C_{sc}} + \frac{1}{C_{film}} + \frac{1}{C_{in}}, \tag{4}$$

where C_{sc}, C_{in}, and C_{film} are the capacitance of the Schottky diode, the capacitance of i–n junction between the n-type substrate and the MBE grown highly resistive thin films, and the capacitance of the highly resistive layer, respectively,

$$C_{sc} = \varepsilon_0\varepsilon_r\frac{S}{d_{sc}}, \quad C_{film} = \varepsilon_0\varepsilon_r\frac{S}{d_{film}}, \quad C_{in} = \varepsilon_0\varepsilon_r\frac{S}{d_{in}}. \tag{5}$$

Here, ε_r, ε_0, d_{sc}, d_{film}, d_{in}, and S are the the relative permittivity of β-Ga_2O_3, which is set at 10, the permittivity of vacuum, which is 8.86×10^{-12}, the thickness of the Schottky diode region, the thickness of MBE grown films, the thickness of the i–n junction region, and the area of the Schottky contacts, which is 2.5×10^{-7} m^2, respectively.

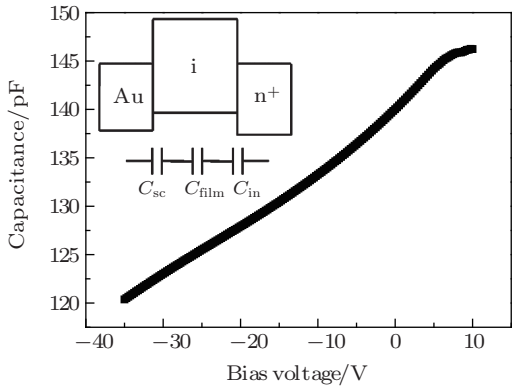


Fig. 3. C–V characteristics of the Schottoky diode. The insertion shows the schematic illustration of band diagram and the equivalent circuit model of the Schottky diode.

The saturation capacitance represents the capacitance of the highly resistive layer in series with the capacitance of the i–n junction,

$$\frac{1}{C_{sat}} = \frac{1}{C_{film}} + \frac{1}{C_{in}}. \tag{6}$$

The thickness of the MBE-grown β-Ga_2O_3 thin films is 100 nm. Then the C_{film} is estimated to be about 222 pF. From Fig. 3, the C_{sat} is estimated to be about 146 pF, which gives C_{in}= 426 pF and d_{in}= 52 nm.

Considering the continuity of the electric field at the interface between the highly resistive layer and the Schottky diode region, the following equations can be obtained:[18]

$$\frac{S^2}{C^2} - \frac{S^2}{C_{sat}^2} = 2\frac{(V_d - V)}{e\varepsilon_r\varepsilon_0 N_{sc}}, \tag{7}$$

$$F = \frac{eN_{SC}}{\varepsilon_0\varepsilon_r}d_{SC}. \tag{8}$$

Here N_{sc} and F are the ionized donor concentration and the electric field in the Schottky diode region, respectively.

A plot of $S^2/C^2 - S^2/C_{sat}^2$ versus bias voltage is shown in Fig. 4. $N_{SC} = 4 \times 10^{18}$ cm^{-3} is deduced from the slope of the fitting of $S^2/C^2 - S^2/C_{sat}^2$ plot. The spreading voltage, V_d= 7.6 V, was estimated from the x-axis intercept of the fitting of $S^2/C^2 - S^2/C_{sat}^2$ plot.

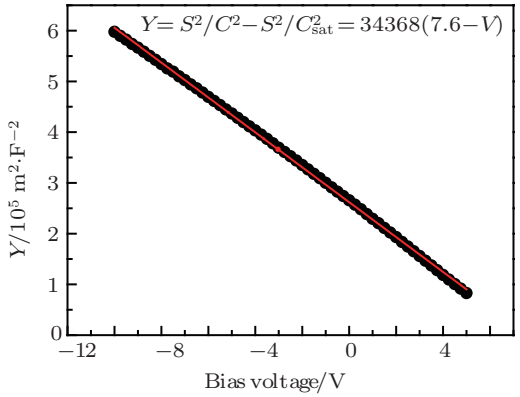


Fig. 4. (color online) Plot of $Y = S^2/C^2 - S^2/C_{sat}^2$ versus V of the Schottky diode. The insertion shows the linearly fitting result.

From Eqs. (5) and (8), at reverse bias voltage of 30 V, $d_{SC} = 28$ nm and $F = 1.8$ MV/cm. The voltage drop across the Schottky diode is about 5 V. The majority reverse bias voltage is applied to the highly resistive homo-epitaxial β-Ga_2O_3 thin films. The breakdown voltage was about 60 V, as shown in Fig. 5. The electric field in the highly resistive homo-epitaxial β-Ga_2O_3 films is about 6 MV/cm. The intrinsic breakdown field is about 8 MV/cm.[1] A little lower breakdown electric field may be attributed to defects in the MBE grown β-Ga_2O_3 thin films. The high ionized donor concentration of $N_{SC} = 4 \times 10^{18}$ cm^{-3} in the Schottky diode region implies high oxygen vacancy in the MBE grown β-Ga_2O_3 thin films. Better epitaxial films with lower oxygen vacancy may result in a higher breakdown voltage.

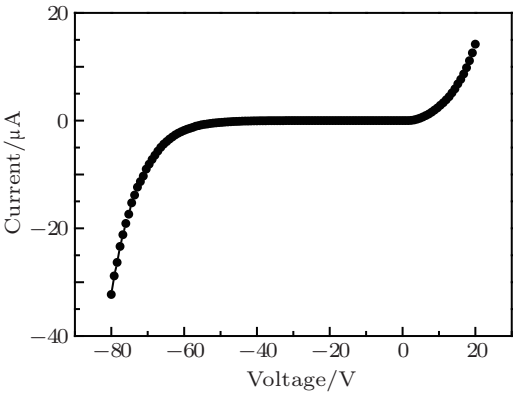


Fig. 5. The reverse breakdown characteristics of the Schottky diode.

When the Schottky diode was irradiated by a low-pressure mercury lamp, a positive direction photo-current under forward bias in addition to a negative direction photo-current under reverse bias was observed. Figure 6 shows the photocurrent of the Schottky diode at reverse bias and forward bias together with its dark current characteristics. The light power density was 13 μW/cm^2. The generation of photocurrent was clearly observed even under reverse-bias condition, which indicates a Schottky barrier photodiode. However the photocurrent under reverse bias is too small (only a few nano-amper) to be used as a UV detector. A large photocurrent was observed under forward biases. For example, a photo-current of 620 nA was detected at 8 V forward bias voltage. Large photocurrent means higher photoresponsivity, but the ratio of photocurrent to dark current is another factor to be considered for UV detectors. The ratio of photocurrent to dark current is very small at 8 V forward bias voltage. Considering all the factors, such as the photoresponsivity, the ratio of photocurrent to dark current, and the operating voltage of the read-out integrated circuit for UV camera, the proper forward bias voltage should be set as about 4 V. The typical measured stable photocurrent and dark current were 59 nA and 1.6 nA at 3.8 V forward bias voltage. The ratio of the photocurrent to dark current is about 36.9. At 3.8 V forward bias voltage, the photoresponsivity $R_\lambda = I_p/P$ is 1.8 A/W, where I_p represents the difference between photocurrent and dark current; P represents the illuminated UV power, which is equal to the UV intensity multiplied by the area of the Schottky diode. The external quantum efficiency $\eta_{ex} = (I_p/q)(P/h\gamma)^{-1}$ was 8.7×10^2%, where q and $h\gamma$ represent the electronic charge of electrons and the energy of the illuminated UV photon, respectively, which implies the existence of internal gain in the Schottky diode. Ideal Schottky diodes do not exhibit gain in essence. In our case, a potential barrier exists at i-n junction between the MBE-grown highly resistive thin film and the n-type conductive β-Ga_2O_3 single crystal substrate as shown in the insertion of Fig. 3. Although the barrier decreases with the applied forward bias, when the bias voltage is smaller than the spreading voltage, the barrier potential still exist in the i–n junction. Under UV light illumination, the resistance of the MBE-grown highly resistive layer decreases because of the photo-generated carriers. Therefore, the barrier height decrease and even diminish at a forward bias. Numerous electrons injected into the highly resistive layer from the n-type substrate in addition to the photogenerated carries produce the large forward current.

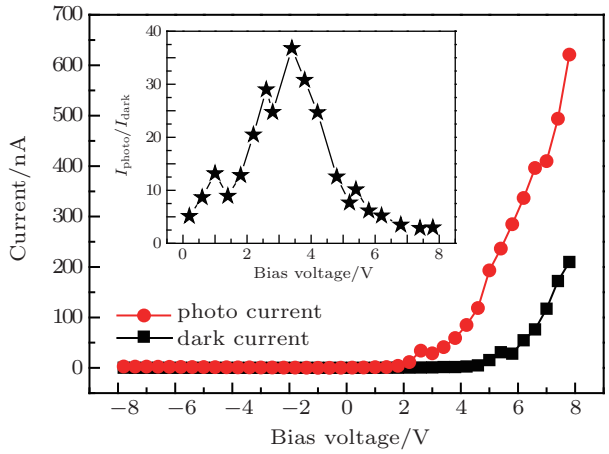


Fig. 6. (color online) Dark current and photocurrent of the Schottky diode. The insertion shows the ratio of photocurrent to dark current of the Schottky diode.

4. Summary

Highly-resistive β-Ga_2O_3 epitaxial layers were grown on conductive Si-doped β-Ga_2O_3 single-crystal substrates by the MBE. Vertical-type Schottky diodes with large photoresponsivity and external quantum efficiency were fabricated. A photoconductive device model with a potential barrier at the i–n junction was proposed to explain the gain of the Schottky diode.

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