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High-Quality Schottky Barrier Diodes on β-Gallium Oxide Thin Films on Glass Substrate

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The wide bandgap semiconductor β-gallium oxide with a bandgap of about 4.9 eV is a prime oxide semiconductor candidate for the realization of next generation high power devices.1,2 In the focus of the investigations on gallium oxide is the homoepitaxial growth of high quality gallium oxide layers for the fabrication of unipolar devices such as power rectifiers or power thin film transistors.3-6 Homoepitaxy has been investigated for different crystal orientations like (1 0 0), (0 1 0) and (0 0 1) and different growth techniques like molecular beam epitaxy (MBE)7-12, halide vapor phase epitaxy,12,13,14 metalorganic vapor phase epitaxy (MOVPE),15,16,17 or low pressure chemical vapor deposition.15 A second approach for the realization of conductive gallium oxide thin films is the use of heteroepitaxy using various growth methods, e.g. pulsed laser deposition (PLD),16-22 MBE,7,23 metal organic chemical vapor deposition,24-26 MOVPE27,28 or radio frequency sputtering.26,30 Further, various crystalline substrates including α-sapphire, c-sapphire, r-sapphire, MgO, Si, GaAs, SiC or yttria-stabilized zirconia have been used; epitaxial relationships are reviewed in Ref. 2. The properties of gallium oxide thin films on non-crystalline substrates like glass, however, are much less investigated. So far mainly the structural and optical properties of such thin films have been discussed.16,31,32 Here, we report on the optimization of the structural and electrical properties of β-gallium oxide thin films on quartz glass substrate for the realization of rectifying electronic devices. Such technology could be scaled up to large substrate sizes.

Experimental

The β-gallium oxide thin films were grown by pulsed-laser deposition on quartz glass substrate. The investigated thin films were grown at temperatures between 20°C and 650°C and an oxygen partial pressure of 1 × 10⁻³ mbar. The ceramic target consisted of gallium oxide doped with a fraction of 1 wt% of SiO₂ to increase the conductivity of the thin films. For the optimization of thin film properties we additionally investigated differently fabricated and post-annealed gallium oxide buffer layers. The different buffer layers were either fabricated at room temperature or at 400°C. Further, oxygen partial pressure during growth was 1 × 10⁻³ or 3 × 10⁻⁴ mbar, respectively. Post-growth annealing was performed in oxygen atmosphere at 900°C or 1100°C for 2 h. Subsequently the conductive β-Ga₂O₃:Si layers were deposited. The Schottky barrier diodes (SBDs) were fabricated in a coplanar front-front geometry. The ohmic contacts consist of a thermally evaporated layer stack of Ti/AI/Au with a thickness of each layer of 30 nm. To ensure a good ohmic behavior the ohmic contacts were additionally annealed for 10 min at 500°C in nitrogen ambient.33 The SBDs were fabricated by long-throw or peripheral reactive sputtering of Pt.34 On top of the PtO₂, an additional capping layer of metallic Pt was deposited to ensure an equipotential surface. X-ray diffraction (XRD) was measured with a Philips X’pert with a Bragg–Brentano goniometer. The surface topography was recorded with a Park XE-150 atomic force microscope (AFM) in dynamic non-contact mode. Conductivity measurements were performed in van der Pauw geometry at room temperature. The current-voltage (I-V) measurements were performed in a Süss Waferprober system P200 connected to an Agilent 4155C precision semiconductor parameter analyzer. The measurement conditions, particularly the sweep rate, were the same for all diodes investigated.

Results And Discussion

First, we discuss the structural properties of β-gallium oxide thin films fabricated at an oxygen partial pressure of 1 × 10⁻³ mbar and temperatures ranging between between 20°C and 650°C. In Fig. 1 2θ-ω wide angle X-ray diffraction patterns of these thin films are depicted. For growth temperatures of 20°C and 400°C no diffraction peak is visible which means that these thin films are X-ray amorphous. For growth temperatures of 510°C and higher several different reflections become visible, these thin films are of a polycrystalline nature. The 2θ-ω-scan of the thin film grown at 510°C exhibits the reflection with highest intensity at 30.3°, which can be attributed to reflections at the (1 1 0)-planes of the β-gallium oxide. With increasing growth temperature the intensity of this reflection slightly decreases. Other diffraction peaks with strong intensity of the thin film grown at 510°C belong to the (3 1 3)-planes (at 57.6°) and the (2 0 4)- or (2 2 1)-planes (at 64.3°). With increasing growth temperature the intensity of these reflections decreases. The opposite behavior is found for the reflections at the (2 0 1)-plane. At a growth temperature of 510°C this reflection occurring at 18.9° is not visible. With increasing growth temperature its intensity increases. Concerning heteroepitaxy, a (2 0 1)-oriented growth was reported for β-gallium oxide thin films on c-plane13,35 and a-plane sapphire,26 (0 0 1)-GaN36 and (0 0 1)-ZnO.37

Transmittance spectra of the layers grown at different temperatures are depicted in Fig. 1b. The optical bandgap of the X-ray amorphous layers is with values between 4.2 and 4.3 eV significantly lower than the about 5.0 eV of the crystalline layers. For the crystalline layers subbandgap absorption is not observed, the properties of these layers are similar to heteroepitaxial thin films.38 The surface morphology of
the discussed thin films is shown in Fig. 2. The surface of samples grown at 20°C and 400°C consists of a closed smooth gallium oxide layer without a special surface structure. Only a few small holes with a depth of some nm are visible for the layer grown at 400°C. The root mean square surface roughness ($R_q$) of both thin films is with 0.3 nm small compared to heteroepitaxial grown β-gallium oxide thin films. However, the conductivity of these samples was not measurable with the van der Pauw setup used in this study, due to their insulating behavior. For growth temperatures above 510°C the roughness of the thin films is increased and the surface morphology consists of small circular grains. The value of $R_q$ increases with higher growth temperatures and is between 3.1 nm and 4.0 nm. These thin films are conductive and have conductivities between 1 S/m and 2 S/m whereby the largest value is observed for the highest investigated growth temperature of 650°C.

In order to increase the quality of the β-gallium oxide thin films on quartz glass substrate we introduced an undoped gallium oxide buffer layer. From the previous results we chose 20°C and 400°C as growth temperatures in order to obtain smooth buffer layers. The oxygen partial pressure was set to $1 \times 10^{-3}$ and $3 \times 10^{-4}$ mbar, respectively. The thickness of buffer layers was 40–50 nm. Additionally we investigated different post annealing temperatures of the buffer layers to further improve the quality of the conductive β-gallium oxide thin films. The buffer layers were annealed for 2 h at 900°C and 1100°C in an oxygen containing atmosphere. The surface morphology of the differently fabricated buffer layers is depicted in Fig. 3. The surface of the as-grown buffer layers is smooth with $R_q = 0.4$ nm, except for the thin film grown at 400°C and $3 \times 10^{-4}$ mbar, which has a surface with point-like and non-ordered line-shaped hills. The roughness of this thin film is with 5.6 nm much larger compared to the other thin films discussed. The post-annealing of this film decreases the roughness.

Figure 1. (a) XRD 2θ-ω wide angle scans and (b) transmission spectra of β-gallium oxide thin films fabricated at growth temperatures as labeled on quartz glass substrates. The oxygen pressure during growth was $1 \times 10^{-3}$ mbar.

Figure 2. AFM images of the β-gallium oxide thin films fabricated at different growth temperatures on quartz glass substrates. Each image depicts an area of $5 \times 5 \mu m^2$. Below every image the root mean square roughness ($R_q$) and the electrical conductivity are depicted.
slightly to 5.0 nm (900 °C) and 4.7 nm (1100 °C). Nevertheless, these buffer layers were not used for subsequent growth experiments. The thin films with a smooth surface in the as-grown state become rougher due to the post annealing. The annealing at 900 °C induces a surface morphology consisting of small circular grains. The value of $R_q$ is increased compared to the as-fabricated state and varies between 0.9 nm and 1.1 nm, which is still a very good value for a non homoepitaxial grown gallium oxide thin film. A further increase of $R_q$ is caused by the annealing step at 1100 °C with values between 1.8 nm and 5.1 nm. The increase of surface roughness can be explained with an increased size of the grains (Ostwald ripening). The smoothest surface is observed for the thin film grown at 400 °C and $1 \times 10^{-3}$ mbar. Overall, the smallest roughnesses throughout the annealing process were obtained for buffer layers grown at 20 °C and $3 \times 10^{-4}$ mbar (labeled buffer layer A from now on) and 400 °C and $1 \times 10^{-3}$ mbar (labeled buffer layer B), respectively. Buffer layer A and B (as-grown as well as annealed at different temperatures) were used for subsequent growth experiments.

Figure 4 shows XRD 2θ-ω wide angle scans of Si-doped β-gallium oxide thin films fabricated on buffer layers A and B on quartz glass substrates. The diffraction peak with highest intensity of as-fabricated thin films corresponds to the (1 1 0) reflection. Growth on buffer layers annealed at 900 °C leads to an increase of the intensity of the (1 2 0) reflection, especially for buffer layer A. It decreases again for growth on buffer layers annealed at 1100 °C. Again, this effect is more pronounced for buffer layer A. Additionally, various low intensity peaks were obtained for buffer layers grown at 20 °C and $3 \times 10^{-4}$ mbar.

Figure 3. AFM images of the differently fabricated undoped gallium oxide buffer layers on quartz glass substrates. Each image depicts an area of $5 \times 5 \mu m^2$. Below every image the root mean square roughness ($R_q$) is shown.
The surface morphology of these thin films is depicted in Fig. 5. The root mean square roughness and the electrical conductivity are depicted below each AFM image. Compared to the thin film grown without buffer layer (first column) the surface of the thin films using a buffer layer is rougher because of an increased grain size. The value of $R_q$ is with 7.2 nm (buffer layer A, second column) and 8.2 nm (buffer layer B, third column) about two times larger compared to the thin film without buffer layer. The electrical conductivity of the respective thin films is considerably higher compared to the layer grown without buffer layer. Growth on annealed buffer layers increases the electrical conductivity even further. The highest value of 890 S/m is obtained for a thin film grown on a buffer layer A annealed at 1100 °C. The film has the highest $R_q$ indicating that the grain size for this particular thin film is largest.

To demonstrate the potential of the investigated $\beta$-gallium oxide thin films on glass substrate for the realization of electronic devices, we fabricated and investigated SBDs on the differently grown thin films. We fabricated PtO$_x$/Ga$_2$O$_3$ SBDs by long-throw or peripheral sputtering.\textsuperscript{40,41} In Fig. 6 room temperature current-voltage characteristics of all sample types are depicted. For better comparability, the current density $j$ is shown instead of the current. The arrows indicate the sweep direction. As reported previously, a large splitting for small currents is visible, which was explained by charging and discharging of the diode capacitance.\textsuperscript{34,37,41} For diodes realized on thin films without buffer layer (labeled Type I, Fig. 6a) the current increases exponentially over more than seven decades before the current flow is limited by the series resistance of the diode. The reverse current is due to the capacitive charging/discharging current. In Fig. 6b diodes on a buffer layer deposited at 20 °C are depicted and are labeled Type A20, Type A900 and Type A1100 (number corresponds to growth/annealing temperature of the buffer). The characteristic of the Type A20 SBD contains regions with comparatively low barrier height as indicated by the excess current observable for low forward bias. Diodes of Type A900 and Type A1100 have a mono-exponential increase of the forward current over more than six orders of magnitude; the slope is highest for Type A900 corresponding to a lower ideality factor compared to SBD Type A1100. Highest forward current density is observed for the Type A1100 diode in good agreement with the electrical transport data discussed above. The reverse current density...
A where the series and parallel resistance of the diode, respectively. The current we used and B1100, respectively. All of the Type B SBDs shown in Fig. 6c exhibits a weak bias dependence for Type B900. As dominant current transport mechanism for Type B1100, a very weak current density is observed for Type B1100. The reverse current density shows a voltage dependence which is strongest for the Type A20 diode. Type B SBDs are fabricated on thin films with buffer layer grown at 400 °C. The growth/annealing temperature is denoted by B400, B900 and B1100, respectively. All of the Type B SBDs shown in Fig. 6c exhibit a mono-exponential increase of the forward current by at least six orders of magnitude. Similar to Type A SBDs, highest forward current density is observed for Type B1100. The reverse current density exhibits a weak bias dependence for Type B1100 and a very weak bias dependence for Type B900. As dominant current transport mechanism for the SBDs we assume thermionic emission. Therefore, we used

\[ I = I_s \left[ \exp \left( \frac{eV - IR_s}{\eta k_B T} \right) - 1 \right] + \frac{V - IR_s}{R_p} \pm I_c, \]  

for the modeling of the current-voltage characteristics. In Eq. 1 \( e \) is the elementary charge, \( V \) the applied voltage, \( T \) the absolute temperature and \( k_B \) Boltzmann’s constant. This model incorporates the voltage dependence of the barrier through the ideality factor \( \eta \), \( R_s \) and \( R_p \) are the series and parallel resistance of the diode, respectively. The current \( I_c \) is the additional charging current. The sign of this current depends on the sweep direction of the measurement. The saturation current \( I_s \) is given by

\[ I_s = A_o A^* T^2 \exp \left( \frac{-\phi^{\text{eff}}_B}{k_B T} \right), \]  

where \( A^* \) is the effective Richardson constant, with a theoretical value of 33.6 A cm\(^{-2}\) K\(^{-2}\) (using an effective mass of \( m^*_e = 0.28 m_{e,0} \), \[ \text{where } m_{e,0} \text{ is the electron rest mass}, A_o \text{ is the contact area and } \phi^{\text{eff}}_B \text{ the effective barrier height of the Schottky diode.} \]

For each diode type we have plotted the effective barrier height versus the ideality factor (Figs. 6d–6f). For SBDs of Type I a linear decrease of the effective barrier height with increasing ideality factor is observed. This is typical for Schottky diodes with lateral fluctuations of the barrier potential and in accordance with Tung’s theory and the empirical investigations of Schmittdorf et al. An increasing ideality factor means that the barrier height potential fluctuations increase which results in a decrease of the effective barrier height. The homogeneous barrier height, obtained by extrapolating the data to \( \eta = 1.03, \) is 1.61 eV for Type I diodes. In tendency, the ideality factors of diodes on buffer layer B are slightly higher. The \( (\phi^{\text{eff}}_B, \eta) \)-plots of the three diode types are very similar, the homogeneous barrier height is between 1.51 eV and 1.59 eV. For Type B400 diodes the spread is very small and indicates that the reproducibility is highest among all the different diode types. Diodes on as-grown buffer layer A have different \( (\phi^{\text{eff}}_B, \eta) \) dependencies than diodes on annealed buffer A resulting in a rather large spread of the homogeneous barrier heights that range between 1.12 eV and 1.45 eV. Further, a notable spread is seen. Lowest effective barrier heights and highest ideality factors are observed for Type A20 SBDs. The biggest spread in the data is observed for Type A900 diodes (best and worst parameter pairs are deduced for this type). Overall, all of the Type A SBDs are inferior to Type I and B diodes for which the ideality factor and barrier height correspond to values obtained for SBDs on heteroepitaxial \( \beta \)-gallium oxide thin films, e. g. on c-sapphire substrate.
Finally, we compare the properties of the PtO$_x$/Ga$_2$O$_3$ SBDs on glass to similarly fabricated SBDs on heteroepitaxial thin films$^{34}$ and single crystalline material. Figure 7a depicts current-voltage characteristics of Schottky contacts on bulk and heteroepitaxial material together with a characteristic of a Type I diode. Highest rectification of 4.9 $\times$ 10$^7$ and lowest series resistance of 390 $\Omega$ are obtained for the diode on the Ga$_2$O$_3$ single crystal. The ideality factor is with 1.09 lowest and the effective barrier height is with 1.94 eV highest among the three diode types. The characteristics of the SBDs on the heteroepitaxial thin film and on the Ga$_2$O$_3$ on glass are similar, which is also reflected in the parameters deduced. The rectification is 1.2 $\times$ 10$^5$ and 5.8 $\times$ 10$^5$, the ideality factor 1.34 and 1.39 and the effective barrier height 1.46 eV and 1.43 eV for the heteroepitaxial SBD and the SBD on glass, respectively. For both, the series resistance is in the order of 10 k$\Omega$. From the plot, again a similar behavior of the PtO$_x$/Ga$_2$O$_3$ SBDs on glass substrate and c-plane sapphire is observed. This implies that PtO$_x$/Ga$_2$O$_3$ diodes on glass are a viable alternative to SBDs on heteroepitaxial thin films. This might be interesting for the development and fabrication of low-cost solar-blind photo detectors on Ga$_2$O$_3$ and its ternary alloys.

Conclusions

In summary, the growth of silicon-doped β-gallium oxide thin films on glass substrate is promising for applications in active electronic devices. For growth temperatures below 510°C the fabricated thin films are X-ray amorphous, non-conductive and have an optical bandgap which is with 4.2 – 4.3 eV significantly below the optical bandgap β-gallium oxide ($E_g \approx 4.9$ eV). For growth temperatures of 510°C and larger the thin films become polycrystalline, conductive and have optical band gaps close to 5.0 eV. The structural and electrical properties of the thin film grown at 650°C were optimized using differently grown and annealed β-gallium oxide buffer layers. The thin films grown on buffer layers fabricated at 20°C and annealed at 1100°C exhibit highest conductivity of 890 S/m. Overall the grain size of thin films on buffer layers increased resulting in higher conductivity but higher surface roughness as well. This leads to higher forward currents of SBDs but also to increased reverse current compared to diodes on thin films without buffer layers. Nevertheless, the properties of the SBDs reported is similar to SBDs on heteroepitaxial material and present therefore a viable alternative for e.g. the fabrication of photo detectors. Besides traditional doping strategies, the variation of the electrical properties of the thin films due to differently treated buffer layers provides additional freedom for device design.

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