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ARTICLES

Growth and characterization of β-Ga_2O_3 thin films grown on off-angled Al_2O_3 substrates by metal-organic chemical vapor deposition

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Abstract: Beta-gallium oxide (β-Ga_2O_3) thin films were deposited on *c*-plane (0001) sapphire substrates with different mis-cut angles along <$11\bar{2}0$> by metal-organic chemical vapor deposition (MOCVD). The structural properties and surface morphology of as-grown β-Ga_2O_3 thin films were investigated in detail. It was found that by using thin buffer layer and mis-cut substrate technology, the full width at half maximum (FWHM) of the ($\bar{2}01$) diffraction peak of the β-Ga_2O_3 film is decreased from 2° on *c*-plane (0001) Al_2O_3 substrate to 0.64° on an 8° off-angled *c*-plane (0001) Al_2O_3 substrate. The surface root-mean-square (RMS) roughness can also be improved greatly and the value is 1.27 nm for 8° off-angled *c*-plane (0001) Al_2O_3 substrate. Room temperature photoluminescence (PL) was observed, which was attributed to the self-trapped excitons formed by oxygen and gallium vacancies in the film. The ultraviolet–blue PL intensity related with oxygen and gallium vacancies is decreased with the increasing mis-cut angle, which is in agreement with the improved crystal quality measured by high resolution X-ray diffraction (HR-XRD). The present results provide a route for growing high quality β-Ga_2O_3 film on Al_2O_3 substrate.

Key words: β-Ga_2O_3; heteroepitaxy; mis-cut Al_2O_3 substrates; MOCVD

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1. Introduction

In recent years, Ga_2O_3 has gained considerable attention in transparent electrodes, solar-blind ultraviolet detectors, flame sensors and power devices[1–4] thanks to its ultrawide bandgap (4.5–4.9 eV)[5] and high critical breakdown field (8 MV/cm)[6]. Monoclinic crystal β-Ga_2O_3 has the highest thermal stability among the five phases of gallium oxide[7], and its Baliga's figure of merit (BFOM) is 3.8 and 10.14 times that of the third-generation semiconductors GaN and 4H-SiC, respectively[8]. Although homogeneous substrates are the ideal choice for growing β-Ga_2O_3 films, the preparation process for large size gallium oxide wafer is immature and its cost is still expensive when compared with Al_2O_3 substrates. Moreover, the thermal conductivity of gallium oxide is relatively poor, with values of 15.4%, 4.7% and 1.2% for silicon, 4H-SiC and diamond, respectively. Hence, the β-Ga_2O_3 obtained by heteroepitaxy is important for devices that generate amount of heat during operation.

There are several reports about the growth of high-quality Ga_2O_3 on foreign substrates[9]. Ma *et al.* tried to grow Ga_2O_3 on substrates such as $SrTiO_3$(100)[10], epi-GaN/sapphire (0001)[11], MgO(111)[12] and $MgAl_6O_{10}$[13] by using MOCVD. However, these thin films were obtained by heteroepitaxy and have multiple crystal domains, which will affect the transport properties of carriers[14]. Among the different substrates, sapphire substrates are widely studied due to their low cost and smaller lattice mismatch with Ga_2O_3. Substantial effort has been devoted to grow high-quality Ga_2O_3 single crystals on sapphire substrates[15–20]. However, β-Ga_2O_3 and sapphire belong to different crystal phases, and multiple crystal domains will appear because of random nucleation during growth. Using sapphire substrates with off-axis angle, it was shown that the crystallinity of epitaxial β-Ga_2O_3 films can be improved by controlling the crystal domains. Oshima *et al.* have grown Ga_2O_3 on off-axis substrates by HVPE and found that the (310) oriented domains disappeared when off-axis angles beyond 3°[21]. It was also found that the off-angled sapphire substrates can change the growth mode of β-Ga_2O_3 films from six-fold in-plane rotational domain growth to single quadrilateral-domains growth[22].

In this paper, we report β-Ga_2O_3 epitaxial layers on Al_2O_3 substrates with different off-axis angles. The structural properties of β-Ga_2O_3 were studied, and it was found that the surface topography of β-Ga_2O_3 films can be greatly improved by using a buffer layer and off-angled sapphire substrates. The ultraviolet to blue light emission related with oxygen and gallium vacancies was observed and the PL mechanism was investigated.

2. Experimental

2.1. Film growth

Crystal β-Ga_2O_3 thin films were grown on *c*-plane Al_2O_3

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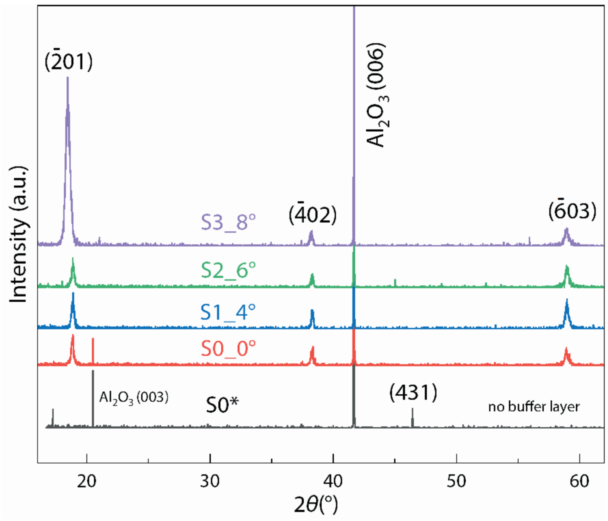

Fig. 1. (Color online) XRD patterns of β-Ga_2O_3 films deposited on *c*-plane Al_2O_3 substrates with different off-axis angles toward <11$\bar{2}$0>.

substrates (Two-inch, single polished) with different off-angles (0°, 4°, 6° and 8°, corresponding to sample Nos. S0-S3) by using MOCVD (Aixtron Ltd) under the same conditions. For comparison, a Ga_2O_3 film (No. S0*) was also deposited without a buffer layer. Trimethylgallium (TMGa, 6N), which was stored in a stainless-steel bubbler maintained at 5 °C, and O_2 (purity, 5N) were used as precursors for gallium and oxygen, respectively. High-purity argon (Ar, 5N) was applied as the carrier gas to deliver TMGa vapor to the reactor chamber by passing through the TMGa bubbler. Prior to growing β-Ga_2O_3 thin films at 960 °C with an O_2/TMGa source flow about 2000 sccm/30 sccm (standard cubic centimeter per minute), a 10 nm thick Ga_2O_3 buffer layer was deposited at 800 °C with an O_2/TMGa source flow about 1000 sccm/5 sccm. During the growth process, an excess oxygen source was used to avoid the formation of a large number of oxygen vacancies in the crystal. Finally, the metal organic source and oxygen cracking efficiency reached 9.5% and 0.7‰, respectively. The chamber pressure was maintained at 100 mbar during the entire growth process.

2.2. Characterization method

The as-grown film thickness was approximately 300 nm with the growth rate about 0.7 μm/h. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to characterize the surface morphology of the samples. HR-XRD and high-resolution transmission electron microscopy (HR-TEM) were carried out to characterize the crystal phase and quality. The room temperature photoluminescence (PL) was measured by using a 213 nm laser as excited source. The PL signal was guided into a monochromator and detected by photomultiplier.

3. Results and discussion

3.1. Effects of off-axis angles of Al_2O_3 substrates on crystal quality

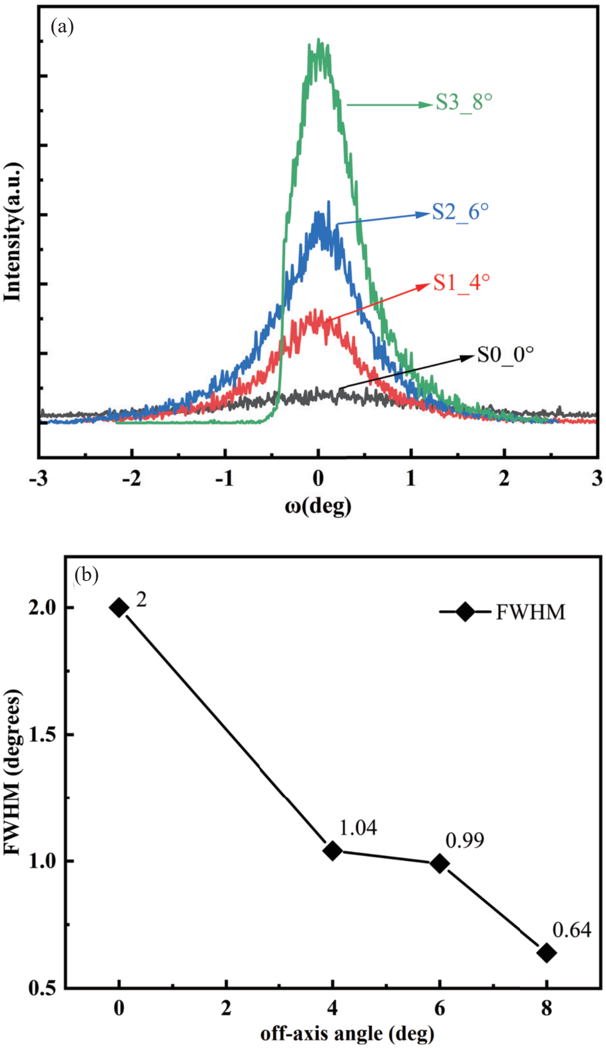

Fig. 2. (Color online) (a) XRD rocking curves of the $(\bar{2}01)$ diffraction peaks of β-Ga_2O_3 films deposited on *c*-plane Al_2O_3 substrates with different off-axis angles toward <11$\bar{2}$0>, (b) FWHM as a function of off-axis angles of Al_2O_3 substrates.

The crystal quality of the gallium oxide thin films grown on sapphire substrates was characterized by HR-XRD in the ω–2θ configuration, as shown in Fig. 1. For the film grown on sapphire substrate (S0*) without a buffer layer, the XRD spectrum shows totally different pattern. By comparing to PDF #06-0529, the appearance of a diffraction peak centered at 46.43° may belong to the δ-Ga_2O_3 domains. Zhuo *et al.* reported that when Ga_2O_3 was first deposited on Al_2O_3 substrates, there were nuclei of various phases[17]. This result also proves that the existence of the buffer layer promoted the growth of β-Ga_2O_3. However, for the films grown on Al_2O_3 substrates with a buffer layer, three sharp diffraction peaks located at 18.45°, 38.29° and 58.95° are observed, which belong to the $(\bar{2}01)$, $(\bar{4}02)$ and $(\bar{6}03)$ planes of β-Ga_2O_3 (compared to JCPDS No. 43-1012). These results show that the obtained gallium oxide films with a buffer layer are pure β-Ga_2O_3 without any other gallium oxide phase. The preferential crystal growth direction is $(\bar{2}01)$ because the arrangement of oxygen atoms in the β-Ga_2O_3 $(\bar{2}01)$ plane is equivalent to sapphire (0001)[15]. Fig. 2 shows the XRD rocking curves at the $(\bar{2}01)$ diffraction peak of the four samples. With the increasing substrates off-axis angles, the XRD peak intensity increases and the full width at half maximum (FWHM) of the $(\bar{2}01)$ diffraction peak is decreased, reaching 0.64° for the film deposited on an 8° off-angled substrate. To illustrate the effect of the buffer layer clearly, β-Ga_2O_3 film without a buffer layer was also grown on

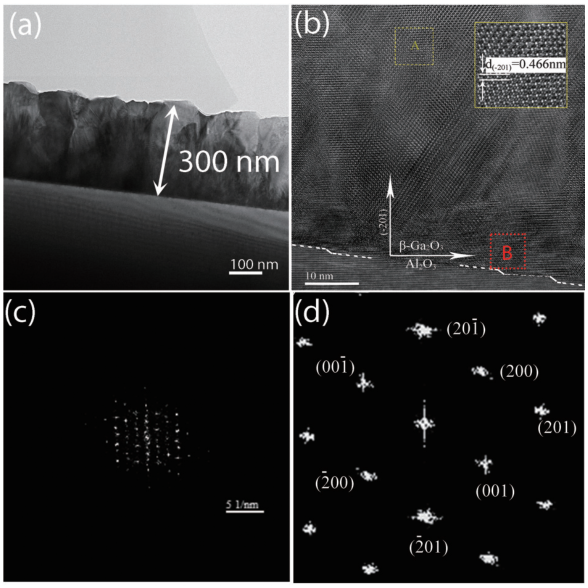

Fig. 3. Cross-sectional TEM of the film deposited on an 8° off-axis sapphire substrate with a thickness of 300 nm. (a) Image of the whole film. (b) HRTEM micrograph of the interface. (c) Selected area electron diffraction (SAED) obtained by Fourier transform of area B. (d) Selected area electron diffraction (SAED) obtained by Fourier transform of area A.

the Al_2O_3 substrate with 8° off-axis angles toward <11$\bar{2}$0>. Very weak X-ray diffraction peak belong to ($\bar{2}$01), ($\bar{4}$02) and ($\bar{6}$03) was observed and the RMS value was 7.5 nm (the RMS value for the film with a buffer is 1.27 nm), from the AFM measurement. (Figures not shown here.) This indicates that the surface topography of β-Ga_2O_3 films grown on off-angled Al_2O_3 substrates can be improved by introducing a buffer layer prior to thick film growth.

To explain the role of buffer layer and mis-cut substrate angle, HR-TEM experiments were carried out. As shown in Fig. 3(a), the step is clearly visible along the <11$\bar{2}$0> direction of the Al_2O_3 substrate. The ($\bar{2}$01) plane distance of the epitaxial layer is calculated to be 0.466 nm by performing a Fourier transform on the region selected by the yellow dashed box in Fig. 3(b). As the thickness of the epitaxial layer increases, the atoms are arranged more orderly and most dislocations are successfully constrained in the thin buffer layer. Figs. 3(c) and 3(d) show the SAED patterns of buffer layer near and away the Ga_2O_3 films/Al_2O_3 interface, respectively. The SAED pattern consists of multiple sets of diffraction spots near the interface and became more regular in region A. This indicates that there were other phases of Ga_2O_3 in the initial growth period and the epitaxial layer gradually became pure β-Ga_2O_3 as the film continued to grow. Thus, the great improvement in crystal quality is likely to happen because mis-cut sapphire can inhibit the appearance of the crystal domain by the strong in-plane orientation enhancement[23] and the buffer layer can accommodate most defects.

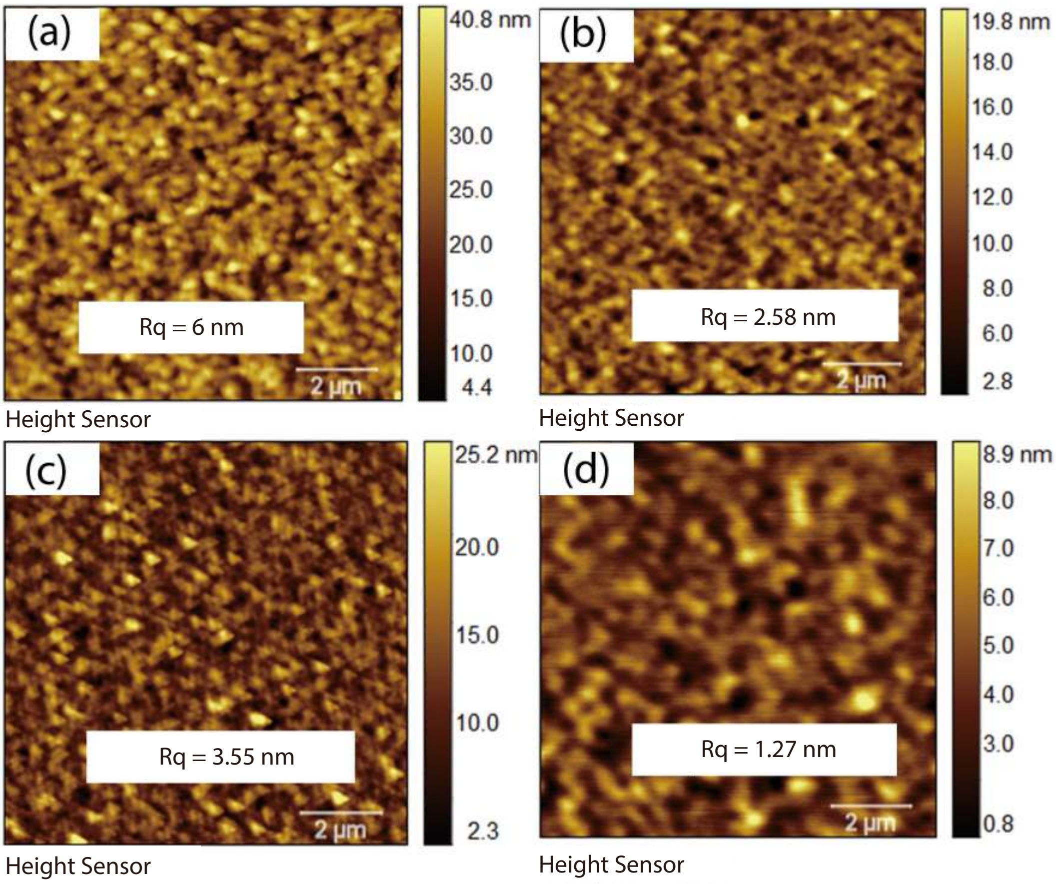

Fig. 4. (Color online) 10 × 10 μm^2 AFM patterns of β-Ga_2O_3 films deposited on (a) 0°, (b) 4°, (c) 6° and (d) 8° off-axis Al_2O_3 substrates. All films were annealed in-situ for 10 min under an oxygen atmosphere.

3.2. Effects of off-axis angles of Al_2O_3 substrates on β-Ga_2O_3 film surface morphology

Fig. 4 shows the AFM image of β-Ga_2O_3 films deposited

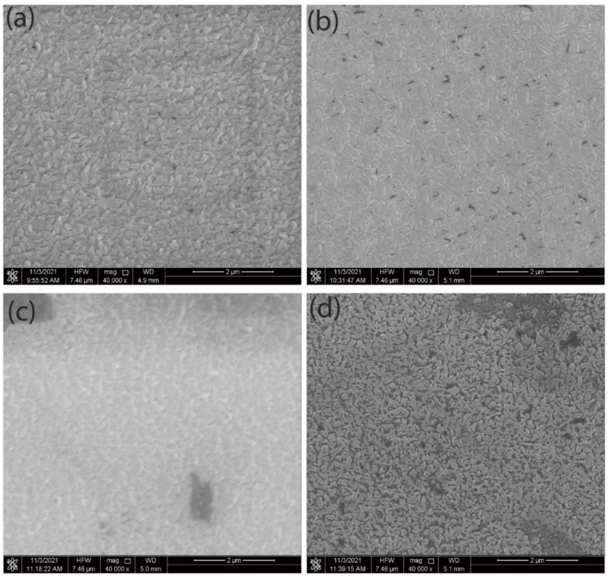

Fig. 5. SEM of β-Ga_2O_3 thin films on Al_2O_3 substrates with (a) 0°, (b) 4°, (c) 6°, and (d) 8° off-angles toward <11$\bar{2}$0>.

on different off-axis Al_2O_3 substrates. The measured surface RMS roughness values of samples S0, S1, S2 and S3 are 6, 2.58, 3.55 and 1.27 nm, respectively. The film deposited on an 8° off-axis Al_2O_3 substrate has the lowest RMS roughness. The RMS value in this work is much lower than the reported values grown on off-angled Al_2O_3 substrates[24]. There are many tiny domains on the surface of the as-grown sample, indicating that the growth changes from a two-dimensional plane growth to a three-dimensional island-like growth pattern. To further reveal the low RMS values of those grown on off-axis sapphire substrates, the surface morphology of β-Ga_2O_3 films was also characterized by SEM, as demonstrated in Fig. 5. The surface domain of the films deposited on mis-cut sapphire substrates seems more closely due to step-flow growth[25] and the film surface shows a corrugated shape, which is the phenomenon of step bunching[26].

3.3. PL properties of β-Ga_2O_3 films on off-angled Al_2O_3 substrates

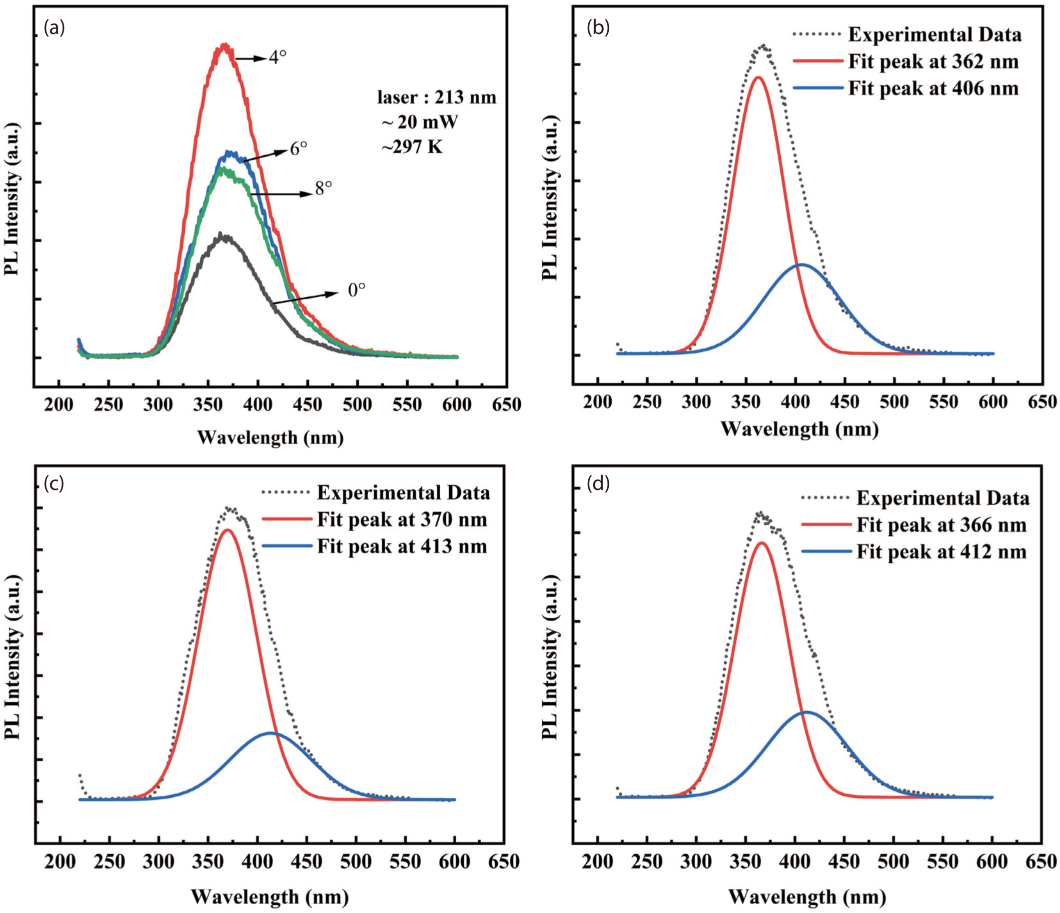

Fig. 6. (Color online) (a) Room temperature PL spectra of all films grown on off-angled Al_2O_3 substrates. The broad emission band from ultraviolet to blue of the β-Ga_2O_3 film deposited on (b) 4°, (c) 6°, and (d) 8° can be divided into two emission peaks near 365 and 410 nm.

PL spectrum is an effective method to investigate the defects of as-grown β-Ga_2O_3 thin films. Fig. 6 shows the room temperature (297 K) PL spectra of β-Ga_2O_3 thin films excited by a 213 nm laser. Compared with the samples grown on the off-axis substrates (S1, S2 and S3), the luminescence of the sample S0 grown on the normal Al_2O_3 substrate is significantly weaker, which is due to the large number of non-radiative recombination centers generated by the crystal domain interface. The PL spectra have a broad emission band from ultraviolet to blue. The broad emission can be divided into two emission peaks near 365 and 410 nm, as shown in Figs. 6(b)–6(d). Varley *et al.* reported that self-trapped holes (STHs) were widespread in β-Ga_2O_3 and localized mainly on a single O atom in the lattice with the shape characteristic of an O 2p orbital[27]. The 365 nm peak is the process of radiative recombination between STHs and electrons to form STEs. This process has a strong electron-phonon coupling effect and local lattice distortion can cause the spectral broadening. The blue emission is overlapped at the UV band tail, which has been widely reported and is suggested to be related to donor-acceptor-pair recombination between V_O donor and V_{Ga} or V_{Ga}–V_O complex acceptors[27, 28]. The radiative recombination luminescence from the conduction band and valence band of β-Ga_2O_3 is not observed in all samples, which is likely to be due to the fast non-radiative transition to the self-trapped energy level. As shown in Fig. 6(a), the PL intensity is the strongest for the S1 sample and decreases with increasing substrate off-axis angles. Thus, the decrease in PL intensity indicates that the density of O and Ga vacancies are reduced. This is in accordance with the improved crystal quality from the XRD measurement.

4. Conclusion

In summary, β-Ga_2O_3 thin films were successfully grown on *c*-plane mis-cut Al_2O_3 substrates. Our results showed that the quality of the β-Ga_2O_3 thin films was improved by step-flow growth, and the FWHM of the $(\bar{2}01)$ plane of the film deposited on an 8° off-angled substrate was 0.64°. It was revealed that the dislocations were mainly blocked by the buffer as observed by TEM measurement. The surface RMS roughness can also be reduced for the β-Ga_2O_3 films deposited on off-axis Al_2O_3 substrates, reaching about 1.27 nm. The β-Ga_2O_3 film had broad light emission from ultraviolet to blue, which was attributed to the oxygen vacancies and gallium vacancies in the films. This vacancy related PL intensity was decreased with increasing off-angle, showing the improved crystalline quality, which was consistent with the HR-XRD results. These findings are helpful for the fabrication of high performance β-Ga_2O_3 devices based on Al_2O_3 substrate in near future.

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