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Growth properties of gallium oxide on sapphire substrate by plasma-assisted pulsed laser deposition

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Abstract: Gallium oxide was deposited on a *c*-plane sapphire substrate by oxygen plasma-assisted pulsed laser deposition (PLD). An oxygen radical was generated by an inductive coupled plasma source and the effect of radio frequency (RF) power on growth rate was investigated. A film grown with plasma assistance showed 2.7 times faster growth rate. X-ray diffraction and Raman spectroscopy analysis showed β-Ga_2O_3 films grown with plasma assistance at 500 °C. The roughness of the films decreased when the RF power of plasma treatment increased. Transmittance of these films was at least 80% and showed sharp absorption edge at 250 nm which was consistent with data previously reported.

Key words: wide bandgap; gallium oxide; oxygen radical; pulsed laser deposition; plasma

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1. Introduction

Gallium oxide (Ga_2O_3) has recently attracted attention from the science community due to its interesting properties such as good thermal stability, high dielectric constant, and wide bandgap[1]. Ga_2O_3 has five polymorphs: α, β, γ, δ, and ε[2]. Of its many forms, β-Ga_2O_3 receives the most attention from researchers because it is the most stable form of Ga_2O_3. β-Ga_2O_3 has been reported for making devices such as light-emitting diodes[3], ultraviolet (UV) detectors[4, 5], transparent electrode for deep-UV devices[6, 7], metal-oxide-semiconductor field-effect transistors (FET)[8], and high dielectric oxide materials for FET devices[9, 10]. Various growth techniques, such as molecular beam epitaxy (MBE)[11, 12], pulsed laser deposition (PLD)[6, 10, 13], sputtering[14, 15], chemical vapor deposition[16], sol–gel method[4], and hydride vapor phase epitaxy[17] have been explored to obtain β-Ga_2O_3 films. Among these methods, PLD shows several advantages due to completely compositional consistency from a target to the deposited film and it is suitable for low temperature growth of thin films.

We have systematically investigated the substrate temperature effect on the structural and optical properties of the β-Ga_2O_3 films on a (0001) sapphire substrate grown by PLD and revealed that $(\bar{2}01)$ oriented β-Ga_2O_3 can be obtained at a substrate temperature of 500 °C[13]. We have also investigated the carrier density of Si doped β-Ga_2O_3 films on the sapphire substrate by PLD using the targets with different Si contents and found that the carried density of the films can be varied between 10^{15} and 10^{20} cm^{-3} by changing Si contents in the target[18]. While PLD is advantageous for depositing monoclinic β-Ga_2O_3 film, the growth rate of the β-Ga_2O_3 film using PLD on a non-reactive O_2 background is quite slow. Using a reactive oxygen ambient in the PLD β-Ga_2O_3 film growth process could be a promising solution to increase the growth rate because PLD growth of some oxide films have shown an increased growth rate or favorable properties changes by switching from non-reactive background to reactive background[19–24]. Matsubara *et al.*[19] reported a room-temperature deposited Al-doped ZnO film by PLD in oxygen radical background and found growth rate and crystal quality changes related to RF power. Kakehi *et al.*[20] found that Li concentration of an epitaxial $LiNbO_3$ film fabricated by PLD method is largely influenced by oxygen radical. Another report showed significant increase of crystal quality, surface morphology, and density of Ga-doped ZnO films grown at a low temperature by plasma-assisted PLD method[21]. He *et al.*[22] compared tantalum oxide deposited on quartz glass substrates using PLD in non-reactive O_2 background and ionized plasma-assisted PLD. Film with favorable refractive index and optical band gap was obtained when ionized oxygen plasma is at optimal condition. Madi *et al.*[23] reported growth of chromium oxide (Cr_2O_3) by remote plasma-assisted PLD on Si substrate. Predominance of higher oxidation state of chromium was observed in Cr_2O_3 film deposited by PLD with remote plasma. Wakabayashi *et al.*[24] showed that homoepitaxial growth rate of β-Ga_2O_3 increases in reactive oxygen background at 800 °C and RF power of 300 W compared to nonreactive oxygen background. However, the effect of RF power change on heteroepitaxial growth rate of β-Ga_2O_3 on sapphire substrate was not discussed. Sapphire substrate is a popular choice for β-Ga_2O_3 film deposition and in this study, heteroepitaxial growth of β-Ga_2O_3 film in reactive oxygen background was investigated. Effect of RF power of plasma source on film growth rate was systematically studied at a substrate temperature of 500 °C and by changing RF power of plasma source from 0 to 300 W. It was shown that β-Ga_2O_3 film growth increased 2.7 times in reactive oxygen compared to a nonreactive oxygen background and the surface of film is smoother when RF power increases.

2. Experiment

Gallium oxide films were grown on a (0001) sapphire substrate with a homemade oxygen plasma-assisted PLD system

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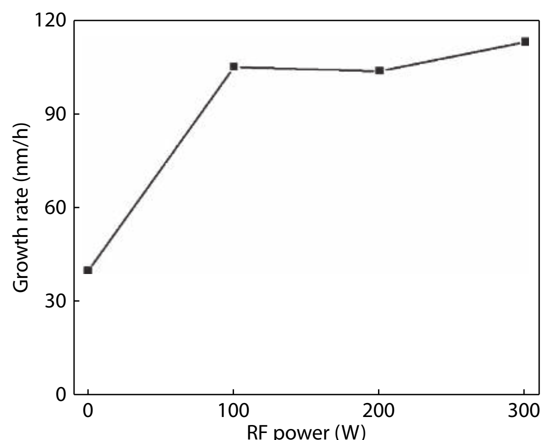

Fig. 1. Dependence of growth rate of film on plasma RF power ranged from 0 to 300 W at substrate temperature of 500 °C.

which has a growth chamber, an oxygen plasma source and a KrF excimer laser (λ = 248 nm) with a frequency of 2 Hz and energy of 225 mJ/cm^2. The oxygen plasma cell was surrounded by a helical RF (13.56 MHz) coil. The sapphire substrate was ultrasonically cleaned in methanol for 20 min and again in acetone for 20 min. Then, the substrate was etched in a hot acidic solution $H_3PO_4 : H_2SO_4$ (1 : 3) for 5 min to remove residual oxides on the surface. Finally, it was rinsed with deionized water and followed by N_2 blow drying before the substrate was introduced into the growth chamber. Facing the substrate, a 99.99% pure Ga_2O_3 ceramic disk was set as the target. Prior to deposition, the growth chamber was evacuated to pressure below 5 × 10^{-6} Pa with a turbo molecular pump. High purity oxygen gas (99.999%) was then introduced into the oxygen plasma cell through a mass flow controller. The oxygen pressure used in this work was kept at 0.01 Pa and substrate temperature was kept at 500 °C while applied RF power was varied from 0 to 300 W. The growth time was 180 min for all samples.

After growth, the thickness of the films were determined by a step profile analyzer. The structural properties of the films were characterized by X-ray diffraction (XRD) (Cu anode, Kα line, λ = 1.54 Å). Raman measurements were performed on a Horiba Jobin Yvon LabRAM HR 800 system with an Ar laser operating at a wavelength of 488 nm as the excitation source at room temperature. Optical transmittance spectra were measured by a UV-vis spectrophotometer. Surface morphology and roughness of the films were determined by an atomic force microscope (AFM).

3. Results and discussion

Fig. 1 shows the dependence of film growth rate for β-Ga_2O_3 on RF power at 500 °C. Film grown in plasma generated oxygen radical background shows significant increase in growth rate compared to film grown in non-reactive O_2 ambient. The growth rate of film in oxygen radical background was 2.7 times faster than film grown in non-reactive oxygen ambient (at 0.01 Pa). The 100 and 200 W samples had similar growth rate of 105 and 104 nm/h, respectively and the 300 W sample grew only slightly faster at 113 nm/h. In other words, increasing RF power of the plasma source made a small increase to film growth rate.

XRD patterns of θ–2θ scan for the samples fabricated

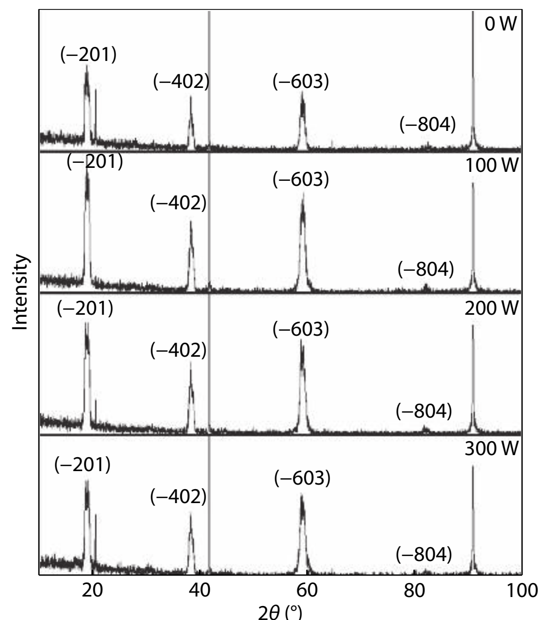

Fig. 2. XRD 2θ/θ scan for films fabricated at 500 °C and RF power ranged from 0 to 300 W.

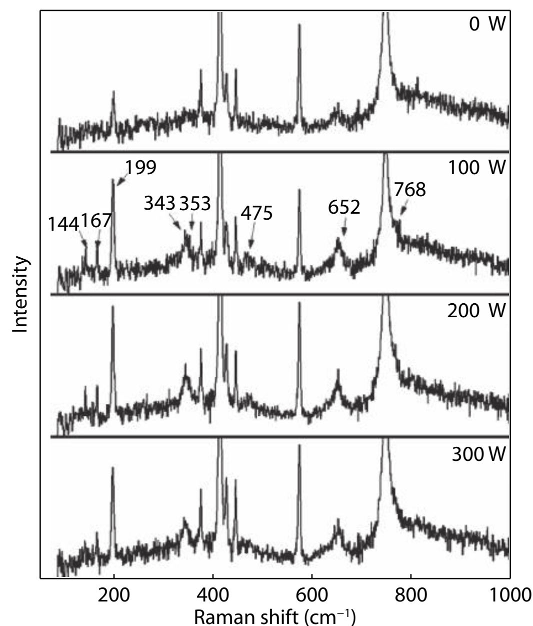

Fig. 3. Raman scattering spectra of samples prepared at substrate temperature of 500 °C and power ranged from 0 to 300 W.

with different RF power are shown in Fig. 2. All samples showed diffraction peaks at 18.9°, 38.2°, 58.9°, and 82.0° and by comparing these peaks to data in the International Center for Diffraction Data catalog, these peaks correspond to ($\bar{2}01$), ($\bar{4}02$), ($\bar{6}03$), and ($\bar{8}04$) planes of monoclinic β-Ga_2O_3, respectively.

Raman spectra, shown in Fig. 3, are obtained at room temperature for β-Ga_2O_3 films fabricated at different RF power to confirm the crystal structure. Raman spectroscopy identifies vibrational mode in a crystal structure. Raman shift peaks were identified for all samples ranging from 100 to 1000 cm^{-1}. For the 100 W sample, peaks were observed at 144, 167, 198.5, 350.4, 470, 652.6, and 767.8 cm^{-1} and assigned to phonon mode of $B_g^{(2)}$, $A_g^{(2)}$, $A_g^{(3)}$, $A_g^{(5)}/B_g^{(3)}$, $A_g^{(7)}/B_g^{(4)}$, $A_g^{(9)}/B_g^{(5)}$, and $A_g^{(10)}$, respectively by comparing these peaks to the data of

Table 1. Phonon modes for different samples compared with bulk β-Ga_2O_3.

Peak location (cm^{-1})					Phonon mode
0 W	100 W	200 W	300 W	Bulk	
–	144	143.4	142.1	147	$B_g^{(2)}$
–	167	167	166.4	169	$A_g^{(2)}$
198.5	198.5	198.5	198.5	199	$A_g^{(3)}$
–	348.3	345.2	344.6	346/353	$A_g^{(5)}/B_g^{(3)}$
–	470.7	–	–	475/475	$A_g^{(7)}/B_g^{(4)}$
652.6	652.6	652.6	652.6	651/657	$B_g^{(5)}/A_g^{(9)}$
–	767.8	768.4	763	763	$A_g^{(10)}$

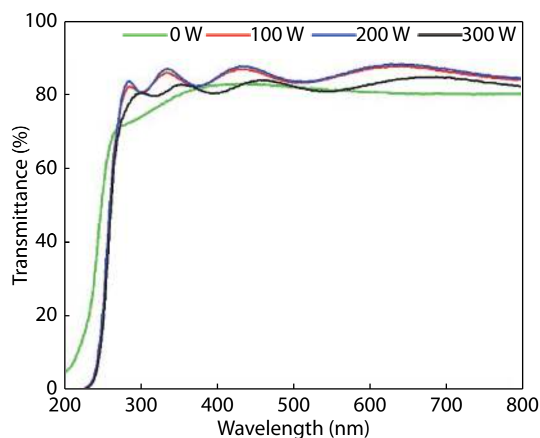

Fig. 4. (Color online) Transmittance of films fabricated at fixed substrate temperature of 500 °C but RF power ranged from 0 to 300 W.

bulk monoclinic β-Ga_2O_3[25]. Similarly, peaks of all samples and their respective phonon modes are summarized in Table 1. The results in Table 1 were consistent with the XRD analysis that all samples discussed above were monoclinic β-Ga_2O_3. It is noted that several peaks are not observed in the 0 W sample. This is probably because the intensity of peak observed for 0 W sample was much weaker than intensity of other samples and weak peaks cannot differentiate itself from the noise. This could be a result of insufficient thickness or deterioration in crystal quality.

The transmittances of the films, shown in Fig. 4, were above 80% in the visible and UV regions and sharp absorption edges were observed around wavelength of 250 nm for all the films grown in ambient oxygen radical. In addition, absorption edge of the samples with plasma treatment are steeper than the adsorption edge of the sample without plasma treatment but this is because the thickness of the films are not the same.

Fig. 5 shows morphology of samples by AFM. The surface morphology of sample without plasma treatment showed column shaped crystallites. This is a sign of typical island growth. Samples with plasma treatment also showed column shaped crystallites. The columns in AFM image of samples with plasma treatment are finer, denser, and trenches in between columns are shallower as applied RF power increases. it is also shown in Fig. 6 that the root mean squared (RMS) roughness of samples with higher RF power treatment is much lower than the samples with lower RF power plasma treatment or no treatment. In addition, the RMS roughness for samples with plasma treatment appears to decrease linearly with respect to the RF power applied.

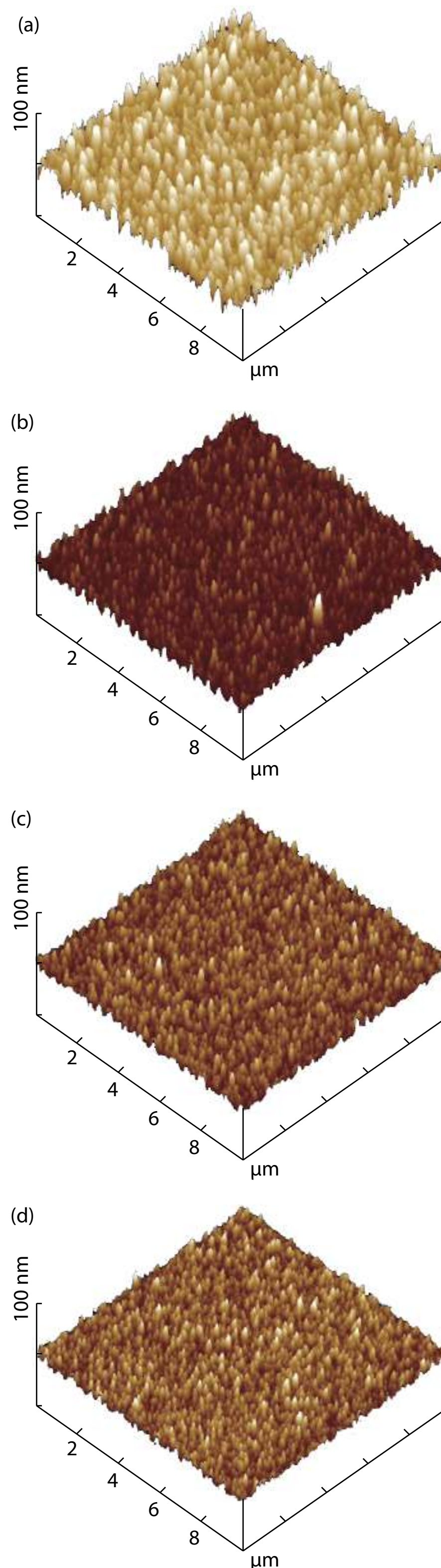

Fig. 5. (Color online) Surface morphology of Ga_2O_3 film at 0.01 Pa and at (a) 500 °C, 0 W; (b) 500 °C, 100 W; (c) 500 °C, 200 W; (d) 500 °C, 300 W on a 10×10 μm^2 area.

As shown from the above results, plasma treated samples show a significant increase of heteroepitaxial growth without losing crystallinity compared to a film without plasma treatment. One possible explanation is that crystallization growth of β-Ga_2O_3 follows the metal-insulator transition mechanism as proposed by Nagarajan *et al.*[26]. During crystallization, nucleation site starts to form. As the nucleation site expands, it uses more oxygen and leaves gallium atoms in high-

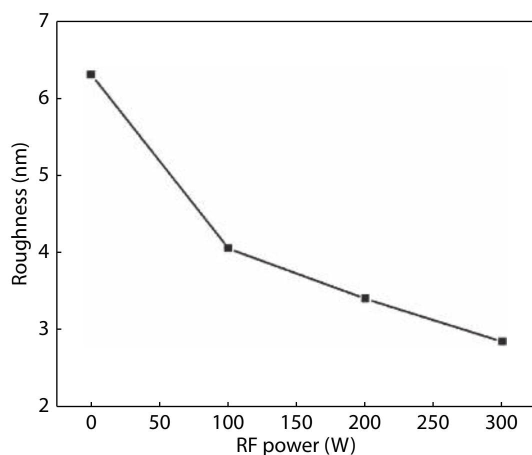

Fig. 6. Dependence of root-mean-squared surface roughness of Ga_2O_3 film on RF power ranged from 0 to 300 W at fixed substrate temperature of 500 °C.

er concentration in the amorphous region. In other word, the process of β-Ga_2O_3 crystallization "pushes" the gallium atom concentration higher in the amorphous region.

When plasma treatment was not applied, the deficiency of oxygen atom near the surface makes it much more likely to form the gaseous, volatile gallium suboxide, such as Ga_2O. This process was repeatedly reported in several studies of Ga_2O_3 growth in MBE process[27, 28]. When plasma treatment was applied, oxygen radicals migrated deep into the film and mitigated the formation of gallium concentration near the film surface. Zhen *et al.*[29] used an oxygen isotopic tracer to show that the concentration of background monoatomic oxygen in SnO_2 film deposited by plasma-assisted PLD method was at least 50%, whereas concentration of background diatomic oxygen in SnO_2 film deposited in non-reactive background was only 1%–4%. Ambient oxygen atom migrated much deeper into the film in reactive case than it was in non-reactive case. The same group found similar result for ZnO using PLD[30]. In addition, it is speculated that the growth rate of the plasma treated film did not increase as the applied RF power increased because the oxygen partial pressure and the amount of available monatomic oxygen remains the same as RF power increases. Since the plasma source cannot maintain capacitive discharge at 0.01 Pa if RF power dropped below 100 W, therefore is impossible to see if growth rate will gradually increase as RF power increase from 0 to 100 W.

The AFM images in Fig. 5 and roughness of surface relationship with applied RF power in Fig. 6 showed some insight of the effect of increased RF power. It is speculated that higher RF power results in more nucleation sites. As shown in Fig. 5, the crystallites are tall and big in the film grown without plasma treatment because the nucleation sites are scattered sparsely. Therefore, there is enough space for the crystallites to grow large and tall. However, as the RF power increase, the density of crystallites columns increases. This indicates that as RF power increases, more nucleation sites are available. The same amount of arriving species had to be shared by more nucleation sites. As a result, each crystallite is small and short and the roughness of sample at higher RF power showed smaller surface roughness.

4. Conclusion

Monoclinic β-Ga_2O_3 films were fabricated by oxygen plasma-assisted PLD method. A film grown in oxygen radical ambient is 2.7 times thicker than films grown in non-reactive O_2 background. Increasing strength of RF power showed small increase on growth rate of monoclinic β-Ga_2O_3 film. XRD and Raman spectroscopy verified that β-Ga_2O_3 films grown in oxygen radical ambient at 500 °C. The film also showed typical island growth and film grown at higher RF power showed a smoother surface than film grown at lower RF power or no plasma. Transmittance of these films is at least 80% and shows sharp absorption edge at 250 nm. It is speculated that a higher film growth rate in the reactive case is because monoatomic oxygen can migrate deep into the as-deposited film to support Ga_2O_3 formation and ease the excess concentration of Ga atom near the surface so that Ga_2O formation is mitigated. Further research by manipulating oxygen pressure and laser pulse setting should change the crystalline quality and growth rate. In addition, using an oxygen isotopic tracer to study the concentration of background oxygen atom in Ga_2O_3 would help to reveal the the mechanisms of Ga_2O_3 heteroepitaxial growth.

Acknowledgements

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References

[1] Huang C Y, Horng R H, Wuu D S, et al. Thermal annealing effect on material characterizations of β-Ga_2O_3 epilayer grown by metal organic chemical vapor deposition. Appl Phys Lett, 2013, 102, 011119
[2] Roy R, Hill V G, Osborn E F. Polymorphism of Ga_2O_3 and the system Ga_2O_3–H_2O. J Am Chem Soc, 1952, 74(3), 719
[3] Binet L, Gourier D. Origin of the blue luminescence of β-Ga_2O_3. J Phys Chem Solids, 1998, 59(8), 1241
[4] Kokubun Y, Miura K, Endo F, et al. Sol-gel prepared β-Ga_2O_3 thin films for ultraviolet photodetectors. Appl Phys Lett, 2007, 90(3), 8
[5] Oshima T, Okuno T, Arai N, et al. Vertical solar-blind deep-ultraviolet schottky photodetectors based on β- Ga_2O_3substrates. Appl Phys Express, 2008, 1(1), 011202
[6] Orita M, Ohta H, Hirano M, et al. Deep-ultraviolet transparent conductive β-Ga_2O_3 thin films. Appl Phys Lett, 2000, 77(25), 4166
[7] Orita M, Hiramatsu H, Ohta H, et al. Preparation of highly conductive, deep ultraviolet transparent β-Ga_2O_3 thin film at low deposition temperatures. Thin Solid Films, 2002, 411(1), 134
[8] Higashiwaki M, Sasaki K, Kamimura T, et al. Depletion-mode Ga_2O_3 metal-oxide-semiconductor field-effect transistors on β-Ga_2O_3 (010) substrates and temperature dependence of their device characteristics. Appl Phys Lett, 2013, 103(12), 123511
[9] Lee S A, Hwang J Y, Kim J P, et al. Dielectric characterization of transparent epitaxial Ga_2O_3 thin film on n-GaN/Al_2O_3 prepared by pulsed laser deposition. Appl Phys Lett, 2006, 89(18), 182906
[10] Matsuzaki K, Yanagi H, Kamiya T, et al. Field-induced current modulation in epitaxial film of deep-ultraviolet transparent oxide semiconductor Ga_2O_3. Appl Phys Lett, 2006, 88(9), 092106
[11] Oshima T, Okuno T, Fujita S. Ga_2O_3 thin film growth on *c*-plane sapphire substrates by molecular beam epitaxy for deep-ultraviolet photodetectors. Jpn J Appl Phys, 2007, 46, 7217
[12] Oshima T, Arai N, Suzuki N, et al. Surface morphology of homoepitaxial β-Ga_2O_3 thin films grown by molecular beam epitaxy. Thin Solid Films, 2008, 516(17), 5768

[13] Zhang F B, Saito K, Tanaka T, et al. Structural and optical properties of Ga_2O_3 films on sapphire substrates by pulsed laser deposition. J Cryst Growth, 2014, 387, 96
[14] Fleischer M, Hanrieder W, Meixner H. Stability of semiconducting gallium oxide thin films. Thin Solid Films, 1990, 190(1), 93
[15] Liu J J, Yan J L, Shi L, et al. Electrical and optical properties of deep ultraviolet transparent conductive Ga_2O_3/ITO films by magnetron sputtering. J Semicond, 2010, 31(10), 103001
[16] Shinohara D, Fujita S. Heteroepitaxy of corundum-structured α-Ga_2O_3 thin films on α-Al_2O_3 substrates by ultrasonic mist chemical vapor deposition. Jpn J Appl Phys, 2008, 47, 731
[17] Murakami H, Nomura K, Goto K, et al. Homoepitaxial growth of β-Ga_2O_3 layers by halide vapor phase epitaxy. Appl Phys Express, 2015, 8(1), 015503
[18] Zhang F, Arita M, Wang X, et al. Toward controlling the carrier density of Si doped Ga_2O_3 films by pulsed laser deposition. Appl Phys Lett, 2016, 109(10), 102105
[19] Matsubara K, Fons P, Iwata K, et al. Room-temperature deposition of Al-doped ZnO films by oxygen radical-assisted pulsed laser deposition. Thin Solid Films, 2002, 422(1/2), 176
[20] Kakehi Y, Okamoto A, Sakurai Y, et al. Epitaxial growth of $LiNbO_3$ thin films using pulsed laser deposition. Appl Surf Sci, 2001, 169/170(1/2), 560
[21] Oh M S, Hwang D K, Seong D J, et al. Improvement of characteristics of Ga-doped ZnO grown by pulsed laser deposition using plasma-enhanced oxygen radicals. J Electrochem Soc, 2008, 155(9), D599
[22] He X, Wu J, Zhao L, et al. Synthesis and optical properties of tantalum oxide films prepared by ionized plasma-assisted pulsed laser deposition. Solid State Commun, 2008, 147(3/4), 90
[23] Madi C, Tabbal M, Christidis T, et al. Microstructural characterization of chromium oxide thin films grown by remote plasma assisted pulsed laser deposition. J Phys Conf Ser, 2007, 59(1), 600
[24] Wakabayashi R, Oshima T, Hattori M, et al. Oxygen-radical-assisted pulsed-laser deposition of β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ films. J Cryst Growth, 2015, 424, 77
[25] Dohy D, Lucazeau G, Revcolevschi A. Raman spectra and valence force field of single-crystalline β Ga_2O_3. J Solid State Chem, 1982, 45(2), 180
[26] Nagarajan L, De Souza R A, Samuelis D, et al. A chemically driven insulator-metal transition in non-stoichiometric and amorphous gallium oxide. Nat Mater, 2008, 7(5), 391
[27] Vogt P, Bierwagen O. Reaction kinetics and growth window for plasma-assisted molecular beam epitaxy of Ga_2O_3: Incorporation of Ga vs. Ga_2O desorption. Appl Phys Lett, 2016, 108(7), 072101
[28] Vogt P, Bierwagen O. The competing oxide and sub-oxide formation in metal-oxide molecular beam epitaxy. Appl Phys Lett, 2015, 106(8), 081910
[29] Zhen Y, Ohsawa T, Adachi Y, et al. Investigations of growth kinetics of pulsed laser deposition of tin oxide films by isotope tracer technique. J Appl Phys, 2010, 108(10), 104901
[30] Matsumoto K, Adachi Y, Sakaguchi I, et al. Preparation and characterization of $Zn_{18}O/Zn_{16}O$ isotope heterostructure thin films. J Eur Ceram Soc, 2010, 30(2), 423