Influence of Post-Annealing on Properties of α-Ga2O3 Epilayer Grown by Halide Vapor Phase Epitaxy

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Effect of annealing to realize high-quality α-Ga2O3 epilayers grown by halide vapor phase epitaxy has been studied. The structural and optical properties of α-Ga2O3 changed with changing annealing duration. In particular, for an annealing duration of 3 min, the crystal quality improved from 51 and 2575 arcsec to 28 and 1539 arcsec for (0006) and (10–14) FWHM, respectively. X-ray photoelectron spectroscopy results confirmed that the oxygen gas during annealing reacted to compensate the oxygen vacancies in the α-Ga2O3 epilayers. These results show that the optimized thermal annealing improved the crystal quality of α-Ga2O3 epilayers.

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Interest in energy efficiency is increasing with the demand for electricity. Power semiconductors are essential for improving energy efficiency because they have wide band gaps and can help reduce power consumption.1,2 Recently, gallium oxide (Ga2O3), an ultra-wide bandgap (UWBG) semiconductor, has been actively studied to replace GaN and SiC. Ga2O3 primarily features in high-power and high-voltage electronic applications.3–5 It has an UWBG of 4.9–5.3 eV, a high breakdown electric field of 9 MV cm−1, and its measured Baliga figure of merit is >3000.6 Therefore, Ga2O3 has also been studied for optic devices, sensors, and transparent conducting oxides.7–9

Ga2O3 are grown in five phases (α, β, γ, ε, and δ) depending on growth parameters such as the growth temperature and pressure.10–12 Among them, the α-phase has a bigger bandgap (5.3 eV) than those of the other phases and is meta-stable at high temperatures (>600 °C). It has a similar crystal structure to that of sapphire. Since the sapphire substrate is widely used as a starting substrate for general heteroepitaxial growth, α-Ga2O3 is advantageous because the difference in the lattice constant is small: 3.3% (c-axis) and 4.5% (a-axis).13 Moreover, through alloying, it is possible to engineer the bandgap from indium oxide to aluminum oxide.14

However, α-Ga2O3 is still not fabricated in bulk and is prepared by only hetero-epitaxial growth. As is well known, the obstacles to high-quality epitaxial growth are the difference in the lattice constant and thermal expansion coefficient between the grown film and the starting substrate.15 These create a residual strain that results in the formation of defects. Since the temperature of the device fabricating process is higher than the growth temperature of α-Ga2O3, all thin film in the device should be the high stability at a high temperature (>500 °C). In a previous report,16 the full-width half maximum (FWHM) of α-Ga2O3 was measured to be about 50 arcsec on a symmetric plane and about 2000 arcsec on an asymmetric plane. In terms of the growth temperature, the growth temperature of the α-Ga2O3 epilayer was optimized by the HVPE method to 470 °C, which is lower than 500 °C for stable device processing. However, the dislocation density in the asymmetric plane is still very high, and this reduces the device performance.

To overcome these difficulties, thermal annealing of the grown film is considered appropriate. The thermal annealing process has been widely used as a method for improving the crystal quality in other oxide semiconductors. In particular, the annealing process at a suitable temperature relaxes the residual strain in ZnO thick films.17 Further, the crystal quality is improved by increasing the particle size and compensating the oxygen vacancies.18,19

In this study, we investigated the effect of thermal annealing on the crystal quality of α-Ga2O3 epilayers grown by HVPE. The crystal quality of α-Ga2O3 epilayers was quantified based on structural and optical properties.

Experimental

Before annealing, α-Ga2O3 epilayers were grown on sapphire substrates with a 2-inch diameter and with a single side polished by the horizontal HVPE method. The HVPE set up consists of two parts: the source zone and the growth zone. In addition, a resister heater in the horizontal hot wall was suitable for the α-Ga2O3 template. Nitrogen was used as the carrier gas. The source zone was loaded with 6N gallium (Ga) metal, which was used as a group III precursor. GaCl and GaCl3 were formed by the reaction of hydrochloric acid (HCl) gas with the Ga metal. The two reactions differ in the gas fraction depending on the temperature of the source zone. When the source zone temperature was above 600 °C, GaCl was mainly generated, and below 600 °C, GaCl3 was predominantly produced. In the growth zone, a sapphire substrate was loaded, and the reactions of GaCl and GaCl3 with flowing oxygen led to the growth of as-formed Ga2O3 on the sapphire substrate. The growth temperature and thickness were maintained at 600 °C and 1.6 μm, respectively. The growth rate of the α-Ga2O3 epilayer was 9.6 μm/h.

For the annealing process, the prepared Ga2O3 epilayer was placed in a quartz tube in a resistively heated furnace under an O2 atmosphere. The annealing temperature and O2 flow rate were 600 °C and 200 sccm, respectively, and annealing was performed for 1, 3, and 5 min, respectively.

The surface morphologies of the Ga2O3 epilayers were observed using an atomic force microscope (AFM). The crystal structure and crystal quality were characterized by X-ray diffraction (XRD) θ/2θ scan and high-resolution XRD ω scan using a Cu Kα X-ray source. The transmittance and optical band gaps were analyzed using an ultraviolet-visible spectrophotometer. The atomic composition of the annealed Ga2O3 epilayer was determined by X-ray photoelectron spectroscopy (XPS).

Results and Discussion

The OM and AFM images of the as-grown and annealed samples are presented in Fig. 1, respectively. The surface of the as-grown sample is smooth and crack-free although small hilllocks and some pits can be observed. For an annealing duration of 3 min, no change in the surface morphology was observed. Moreover, the surface roughness gradually decreased from 9.2 to 7.1 nm, implying that the surface roughness of the sample annealed for 3 min was more stable. However, in the sample annealed for 5 min, surface cracks can be observed in
some areas, and the surface roughness slightly increased to 8.1 nm. It assumed that phase transition occurred at the surface because of the thermal decomposition or atomic migration of the α-Ga2O3 epilayers due to the longer exposure time at high temperatures that reached the growth temperature.

The XRD θ/2θ scan spectra of the samples before and after annealing are shown in Fig 2. The (0006) diffraction peak in the profile of the strain-free α-Ga2O3 epilayer is located at 40.26° (JCPDS no. 06-0503). The lattice constants of the α-Ga2O3 epilayer were $a = 4.982$ Å and $c = 13.433$ Å, and those of the α-Al2O3 substrate were $a = 4.765$ Å and $c = 13.001$ Å. The appearance of each (0006) peak at 40.24° indicates that all the samples have almost no residual strain. The (0006) peak of all samples was gradually shifted to 40.26° with increasing annealing duration. In a previous report, it was hypothesized that the optimized growth temperature of the α-Ga2O3 epilayer is in the range 450 to 650° C. At a temperature above 650° C, the phase transition occurs from the α- to β-phase. The as-grown α-Ga2O3 epilayer before annealing was grown at 600° C, and no phase transition occurred. There was little residual strain. This is because the crystal structures of α-Al2O3 used as the substrate and the α-Ga2O3 epilayer are the same, that is, the corundum structure; thus, the difference in the lattice constant is relatively small. The lattice constant of the c-axis in the as-grown α-Ga2O3 epilayer was calculated to be 13.436 Å, which was slightly higher than that of the strain-free α-Ga2O3 epilayer. However, in the sample annealed for 5 min, a peak corresponding to the β-phase was observed, which indicated phase transition. This sample predominantly consisted of the α-phase with a small amount of β-phase. The intensity of the (0006) diffraction peak increased with the annealing duration until 3 min, and then decreased with a further increase in the annealing duration. This suggested that the α-Ga2O3 epilayer is stable when annealed at 600° C for 3 min and the transformation from α-Ga2O3 to β-Ga2O3 gradually occurred at 600° C when annealed for 5 min.

The transmittance spectra of the α-Ga2O3 epilayers with different annealing durations are shown in Fig. 3. The transmittance was slightly lower than that of the as-grown sample for an annealing time of 1 min. The sample annealed for 3 min exhibited multiple reflections that generated a strong interference effect and had a transmittance of 80% in the UV region. However, the transmittance of the sample annealed for 5 min was significantly different. The decrease in the transmittance and the dissolution of multiple reflections indicate a very rough surface produced from not only the etch pits formed by thermal decomposition shown Fig 1, but also atomic migration to allow thermal stabilization.

The optical bandgap of the α-Ga2O3 epilayers can be evaluated from the absorption edge. The optical bandgap of the as-grown sample was approximately 4.90 eV. As the annealing time increased up to 3 min, the bandgap was increased from 4.90 to 5.05 eV, which means that it is close to the theoretical value (5.2 eV). This implies that the crystal quality of α-Ga2O3 epilayers was enhanced through rearrangement and the compensation of oxygen vacancies during annealing in the O2 atmosphere. However, the transmittance of the sample annealed for 5 min decreased, which is possibly because of the effect of a mixed environment.
structure with the α-phase and β-phase. These optical bandgap results are consistent with those of the XRD measurements.

To evaluate the crystal quality of the as-grown and annealed samples, the FWHM rocking curve of (0006) and (10−14) were measured. Fig. 4 shows the FWHM profiles for the all samples, which were as-grown and annealed at different times. The profiles of (0006) and (10−14) show the same tendency. The (0006) and (10−14) FWHM values of the as-grown sample were 51 arcsec and 2757 arcsec, respectively. The FWHM values decreased with increasing annealing duration up to 3 min, with the lowest (0006) and (10−14) FWHM values being 28 arcsec and 1539 arcsec, respectively. The FWHM values of the as-grown sample were 51 arcsec and 2757 arcsec, respectively. The FWHM rocking curve of (0006) and (10−14) were measured. In addition, it is well known that the FWHM value of (0006) and (10−14) correspond to screw dislocation and edge dislocation, which can be calculated as follows:

\[
D = \frac{F^2}{9b^2}
\]

where D is the threading dislocation density (TDD), F is the FWHM value of the rocking curve, and b is the Burger vector. The screw and edge TDD of the as-grown α-Ga2O3 epilayer at the optimized growth temperature of 470 °C were less than 50 and 2000 arcsec, respectively. The crystal quality of the as-grown sample at 600 °C, which was the increased growth temperature, was not significantly different from the (0006) FWHM value of α-Ga2O3 grown at 470 °C, but the (10−14) FWHM value was lower by about 40%. However, the crystal quality was greatly improved by annealing for 3 min. It is supposed that the crystal quality was lowered when the α-Ga2O3 epilayer was grown at a relatively high temperature, but the crystal quality can be sufficiently improved by the annealing process. In addition, it is well known that the FWHM value of (0006) and (10−14) correspond to screw dislocation and edge dislocation, which can be calculated as follows:

\[
D = \frac{F^2}{9b^2}
\]

The (0006) FWHM (arcsec) transmittance of as-grown and annealed samples at 600 °C. Tauc plot for optical bandgap. In a previous report, the (0006) and (10−14) FWHM values of the α-Ga2O3 epilayer at the optimized growth temperature of 470 °C were less than 50 and 2000 arcsec, respectively. The crystal quality of the as-grown sample at 600 °C, which was the increased growth temperature, was not significantly different from the (0006) FWHM value of α-Ga2O3 grown at 470 °C, but the (10−14) FWHM value was lower by about 40%. However, the crystal quality was greatly improved by annealing for 3 min. It is supposed that the crystal quality was lowered when the α-Ga2O3 epilayer was grown at a relatively high temperature, but the crystal quality can be sufficiently improved by the annealing process. In addition, it is well known that the FWHM value of (0006) and (10−14) correspond to screw dislocation and edge dislocation, which can be calculated as follows:

\[
D = \frac{F^2}{9b^2}
\]

where D is the threading dislocation density (TDD), F is the FWHM value of the rocking curve, and b is the Burger vector. The screw and edge TDD of the as-grown α-Ga2O3 epilayer was calculated to be 7.8 × 10^5 cm^{-2} and 1.7 × 10^10 cm^{-2}, respectively. Also, the screw and edge TDD of the α-Ga2O3 epilayer with 3 min annealing was 2.3 × 10^5 cm^{-2} and 5.2 × 10^9 cm^{-2}, respectively. This implies that the annealing process greatly influenced the symmetric and asymmetric planes. The improvement in the crystal quality achieved by annealing could be attributed to recrystallization. However, for 5 min of annealing, the crystal quality of the α-Ga2O3 epilayer deteriorated by the generation of crystalline texture. This suggested that an appropriate annealing time improves the crystal quality of the α-Ga2O3 epilayer.

XPS was carried out to investigate the effect of the annealing process on the chemical bonding state. Fig. 5 shows the O1s photoelectron peaks of the as-grown and 3-min-annealed samples. The O1s photoelectron peak was fitted by two components at 530.3 and 532.0 eV corresponding to the Ga-O bond (Peak I) and the oxygen or oxygen-related vacancies (Peak II), respectively. The oxygen O1s photoelectron peak was fitted by two components at 530.3 and 532.0 eV corresponding to the Ga-O bond (Peak I) and the oxygen or oxygen-related vacancies (Peak II), respectively. The peak area corresponding to the Ga-O bonding for annealing for 3 min was relatively increased by 60% as compared to that of as-grown sample. After annealing, the integrated intensity of the peaks increased, implying that the number of Ga-O bonds increased. In addition, the average Ga/O ratio in the α-Ga2O3 epilayer was estimated from the integrated peak area ratio of the deconvoluted XPS components calibrated using sensitivity factors. The Ga/O ratio was calculated as 0.62 for annealing for 3 min, which is similar to 0.67 for stoichiometric bulk Ga2O3. Thus, it was hypothesized that annealing decreased the oxygen or oxygen-related vacancies and other defect states.
Conclusions
In this study, we found that the crystal quality of $\alpha$-Ga$_2$O$_3$ epilayers grown by HVPE was improved by annealing. The growth and annealing temperatures were both maintained at 600°C. To determine the optimized annealing condition, the annealing duration was varied as 1, 3, and 5 min. The sample annealed for 3 min had a smooth and crack-free surface, which indicated that the $\alpha$-Ga$_2$O$_3$ epilayer is stable when annealed at 600°C for 3 min. Further, the lowest (0006) and (10–14) FWHM values were 28 arcsec and 1539 arcsec, respectively. Further, the XPS results revealed that the number of Ga-O bonds increased for the stoichiometric ratio compared to that of the as-grown sample. However, increasing the annealing time to 5 min resulted in surface cracks and phase transition to the $\beta$-phase because of thermal decomposition. Therefore, annealing for 3 min is effective for improving the crystal quality of the epilayers.

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References
1. K. Shenai, IEEE Trans. Electron. Devices., 62(2), 248 (2015).
2. Assessment of Ga$_2$O$_3$ technology, Defense Technical Information Center, http://www.dtic.mil/dtic/tr/fulltext/a2/1035362.pdf, 2016 (accessed 15, September 2016).
3. S. J. Pearton, J. Yang, P. H. Cary IV, F. Ren, J. H. Kim, M. J. Tadjer, and M. A. Mastro, Appl. Phys. Rev., 5(1), 011301 (2018).
4. J. Y. Taso, S. Chowdhury, M. A. Hollis, D. Jena, N. M. Johnson, K. A. Jones, R. J. Kaplan, S. Rajan, C. G. Van de walle, E. Bellotti, C. L. Chua, R. Collazo, M. E. Coltrin, J. A. Cooper, K. R. Evans, S. Graham, T. A. Grotjohn, E. R. Heller, M. Higashiwaki, M. S. Islam, P. W. Juodawlkis, M. A. Khan, A. D. Koehler, J. H. Leach, U. K. Mishra, R. J. Nernheim, R. C. N. Pilawa-Podgurski, J. B. Shealy, Z. Sitar, M. J. Tadjer, A. F. Witulski, M. Wraback, and J. A. Simmons, Adv. Electron Mater., 1600041, (1) (2017).
5. M. A. Mastro, A. Kuramata, J. Calkins, J. H. Kim, F. Ren, and S. J. Pearton, ECS J. Solid State Sci. Technol., 6(5), P536 (2017).
6. A. T. Neal, S. Mou, R. Lopez, J. V. Li, D. B. Thomson, K. D. Chabak, and G. H. Jensen, Sci. Rep., 7, 1312 (2017).
7. W. Y. Kong, G. A. Wu, K. Y. Wang, T. F. Zhang, Y. F. Zou, D. W. Wang, and L. B. Liao, Adv. Mater., 28(48), 10725 (2016).
8. L. Mazeina, Y. N. Picard, S. I. Maximenko, F. K. Perkins, E. R. Glaser, M. E. Twigg, J. A. Freitas, and S. M. Prokes, Cryst. Growth Des., 9, 4471 (2009).
9. L. Dong, R. Jia, B. Xin, B. Peng, and Y. Zhang, Sci. Rep., 7, 40160 (2017).
10. T. Oshima, T. Okuno, and S. Fujita, Jpn. J. Appl. Phys., 46(11), 7271 (2007).
11. D. Machon, P. F. McMillan, B. Xu, and J. Dong, Physical Review B, 73, 094125 (2006).
12. H. Sun, K. H. Li, C. G. T. Castanedo, S. Okur, G. S. Tompa, T. Salagaj, S. Lopatin, A. Genovese, and X. Li, Cryst. Growth Des., 18(4), 2370 (2018).
13. Y. Oshima, E. G. Villora, and K. Shimamura, Appl. Phys. Express., 8, 055501 (2015).
14. S. Fujita, M. Oda, K. Kaneko, and T. Hitora, Jpn. J. Appl. Phys., 55, 1202A3 (2016).
15. S. A. Kukushkin, A. V. Osipov, V. N. Bessolov, B. K. Medvedev, V. K. Nevolgin, and K. A. Tcirk, Rev. Adv. Mater. Sci., 17, 1 (2008).
16. H. K. Son and D. W. Jeon, J. Alloys. Compd., 773, 631 (2019).
17. S. Yang, B. H. Lin, W. R. Liu, J. H. Lin, C. S. Chang, C. H. Hsu, and W. F. Hsieh, Cryst. Growth Des., 9(12), 5184 (2009).
18. S. Yang, B. H. Lin, C. C. Kuo, H. C. Hsu, W. R. Liu, M. O. Eriksson, P. O. Holtz, C. S. Chang, C. H. Hsu, and W. F. Hsieh, Cryst. Growth Des., 12, 4745 (2012).
19. J. Fan, Y. Hau, C. Munuera, M. G. Hernandez, F. Guell, E. J. Johnson, G. Boschloo, A. Hagfeldt, and A. Cabot, J. Phys. Chem. C., 117(32), 16349 (2013).
20. H. K. Son, Y. H. Lee, J. H. Kim, J. Hwang, S. H. Wanga, and D. W. Jeon, Thin solid films, 626, 66 (2017).
21. X. Feng, Z. Li, W. Mi, and J. Ma, Vacuum, 124, 101 (2016).
22. Y. Chen, H. song, D. Li, X. Sun, H. Jiang, Z. Li, G. Miao, Z. Zhang, and Y. Zhou, Mater. Lett., 114, 26 (2014).
23. J. Bruncko, A. Vincze, M. Netrvalova, P. Sutta, D. Hasko, and M. Michalka, Thin solid films, 520(2), 866 (2011).
24. S. L. Ou, D. S. Wuu, Y. C. Fu, S. P. Liu, R. H. Horng, L. Liu, and Z. C. Feng, Mater. Chem. Phys., 133(2–3), 700 (2012).
25. Y. An, S. Wungm L. Duan, and J. Liu, Appl. Phys. Lett., 102, 212411 (2013).
26. A. Samariya, R. K. Singhal, S. Kumar, Y. T. Xing, S. C. Sharma, P. Kumari, D. C. Jain, S. N. Dolia, U. P. Deshpande, T. Shripathi, and E. Saitovitch, Appl. Surf. Sci., 257, 585 (2010).