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Influence of annealing treatment on the luminescent properties of Ta:β-Ga_2O_3 single crystal*

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Ta^{5+} doped β-Ga_2O_3 single crystals were grown by using the optical floating zone method, and then annealed in the air and nitrogen gas at 1400 °C for 20 hours. The transmittance spectra, photoluminescence (PL), x-ray irradiation spectra, and PL decay profiles of the samples were measured at room temperature. The relevant results show that the optical transmittance of the samples annealed in the air or nitrogen gas was improved. By drawing the $(ahv)^2$–hv graph, it can be seen that the band gap decreased after being annealed in the air, but increased in nitrogen gas. The PL spectra and x-ray irradiation spectra show that the luminescent intensity of the sample annealed in the air increased substantially, while decreased for the sample annealed in nitrogen. The PL decay time of the Ta:β-Ga_2O_3 annealed in the air increased significantly compared with that of the Ta:β-Ga_2O_3 sample without annealing, but the tendency after annealing in nitrogen gas was opposite.

Keywords: Ta:β-Ga_2O_3, floating zone method, transmittance spectra, annealing

PACS: 78.40.Fy, 78.55.–m **DOI:** 10.1088/1674-1056/28/7/077801

1. Introduction

As a semiconductor material with a wide band gap, gallium oxide has five structures (α, β, γ, δ, ε). β phase is the only stable phase at high temperature environment. Compared with GaN and SiC, β-Ga_2O_3 can be grown by melt methods such as edge-defined film fed growth (EFG),[1] Czochralski method (CZ),[2] and optical floating zone method.[3] At present, the research on bulk single crystals mainly focuses on monoclinic system β-Ga_2O_3. With the band gap of 4.8–4.9 eV, β-Ga_2O_3 has a wide application prospect in the field of high power electronic devices.[4] It is also an excellent material for the solar-blind ultraviolet detector.[5] In addition, β-Ga_2O_3, which has high light yield and fast decay time,[6] can be used in scintillation detection and high-energy physics applications.

The main luminescent peaks of β-Ga_2O_3 are ultraviolet light, blue light and green light.[7] Ultraviolet light is regarded as an intrinsic phenomenon due to the recombination of exciton. Blue light is related to the combination of donor and acceptor (DAP). Green light occurs only when certain elements are introduced in β-Ga_2O_3. Excited by high-energy radiation, β-Ga_2O_3 mainly emits ultraviolet light owing to the recombination of a free electron and a self-trapped hole.[8] Yuki Usui reported the luminescent properties by different doping.[8] However, there were few further reports on its luminescent performance by annealing. Therefore, it is meaningful to study the luminescent properties of Ta:β-Ga_2O_3 through reasonable annealing process.

In this paper, we describe how β-Ga_2O_3 single crystals doped with 0.01 mol% Ta were successfully grown through floating zone method. N-type β-Ga_2O_3 single crystal was formed by introducing Ta as a shallow donor.[9] After annealing the samples in the air and nitrogen respectively, we studied the luminescent properties of Ta:β-Ga_2O_3 and analyzed the relevant mechanism.

2. Experimental procedure

2.1. Crystal and sample preparation

6 N Ga_2O_3 and 4 N Ta_2O_5 powder were used as the starting material. Crystal was grown in an optical floating zone furnace with halogen lamps as the heating source. The growth atmosphere was flowing air and the growth speed was 5 mm/h. A high-quality single crystal with a length of about 60 mm and a diameter of 8 mm was obtained.

The (100) surface samples with the size of 8 mm × 10 mm × 1 mm were divided into three groups. The samples in the first group were not annealed, and the samples in the other two groups were annealed at 1400 °C for 20 hours in the air and nitrogen atmosphere, respectively. After annealing, the wafers were polished to ensure the same thickness and surface

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polishing degree.

2.2. Characterization

The carrier concentration of the samples was measured by HL5500 Hall Effect Measuring Instrument. V-570 UV/VIS/NIR spectrometer was used to measure the transmission spectra of the samples, and the measurement range was 200–800 nm. FP-6500/6600 fluorescence spectrometer was employed to measure PL spectra and PL decay curve profiles. x-ray irradiation luminescent spectra was measured by x-ray excitation luminescent spectrometer assembled by Shanghai Institute of Ceramics, Chinese Academy of Sciences. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Hall measurement

Table 1 shows the carrier concentration data of all the samples after Hall measurement. Compared with pure β-Ga_2O_3, the carrier concentration of Ta:β-Ga_2O_3 is higher.[10] It can be found that the carrier concentration of the sample without annealing is about 10^{18}/cm^{-3}. In contrast, the carrier concentration decreases to about 10^{16}/cm^{-3} after annealing in air and increases by about four times after annealing in nitrogen. The change of carrier concentration is related to the oxygen vacancy. After annealing the crystal in nitrogen, the oxygen vacancies increase to form more defects leading to the increase of carrier concentration.[11] In contrast, oxygen vacancies decrease after annealing in the air, and the number of defects is reduced resulting in reduction of carrier concentration.

Table 1. Hall measurement results of 0.01 mol% Ta:β-Ga_2O_3 before and after annealing.

Samples	Carrier type	Carrier concentration/cm^{-3}
Without annealing	n	1.44×10^{18}
Annealing in air	n	5.41×10^{16}
Annealing in nitrogen	n	5.80×10^{18}

3.2. Transmission spectra

Figure 1 shows the transmission spectra of Ta:β-Ga_2O_3. The transmittance and band gap of Ta:β-Ga_2O_3 is lower than pure β-Ga_2O_3 single crystal.[10] After annealing in the air or nitrogen, the transmittance of Ta:β-Ga_2O_3 at 300–800 nm is improved slightly. Figure 2 shows the band gap obtained by drawing the $(ahv)^2$–hv graph. The band gap increases after annealing in nitrogen because more carriers are activated[12] to enter the bottom of the conduction band. Therefore, when the electron is excited from the valence band to the conduction band, it will enter into the higher position of the conduction band, thereby widening the band gap. The band gap decreases after annealing in air because of the decrease of carrier concentration.[13] As a result, the electron is more easily excited from valence band to the lower conduction band, which makes the band gap smaller. This conclusion is consistent with the change rule of band gap of Si:β-Ga_2O_3 annealed in air.[14]

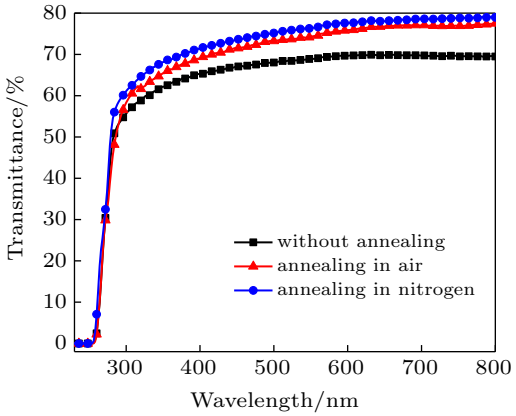


Fig. 1. Transmittance spectra of 0.01 mol% Ta:β-Ga_2O_3 before and after annealing.

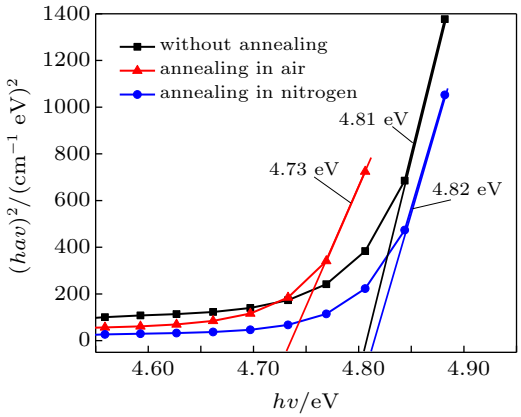


Fig. 2. Plot of $(\alpha hv)^2$ versus hv for 0.01 mol% Ta:β-Ga_2O_3 before and after annealing.

3.3. PL spectra

The main PL peak of pure β-Ga_2O_3 single crystal is about 370 nm.[15] Figure 3 presents the emission spectra of pure β-Ga_2O_3 and Ta:β-Ga_2O_3 under the excitation of 256 nm. It can be seen that Ta:β-Ga_2O_3 samples have the same blue emission peaks. Compared with the ultraviolet emission peak of pure β-Ga_2O_3, the changes of luminescent intensity and peak result from the introduction of donor impurities. As shown in Fig. 4, after Gauss fitting of 0.01 mol% Ta:β-Ga_2O_3 annealed in the air, there are two blue emissions with the peaks at 410 nm and 470 nm, but the ultraviolet emission cannot be distinguished from the spectrum. Under the excitation of high energy x-ray, ultraviolet emission is obvious because of the dominance of exciton recombination. On the contrary, the energy of 256 nm is low, donor–acceptor pair recombination is dominant, leading to the increase of blue emission.[16] Hence, ultraviolet emission is almost invisible but exists. After annealing in air, the luminescent intensity of Ta:β-Ga_2O_3 single crystal increases significantly, while that of the sample annealed in nitrogen decreases. According to the Hall measurement results shown in Table 1, the carrier concentration of the

sample annealed in air decreases, which means that most electrons from the donor are localized, instead of being excited to conduction bands. These electrons can participate in the combination of DAP, resulting in higher luminescent intensity. Annealing in nitrogen can activate carriers, and more electrons enter into the conduction band, which reduces the number of electrons involved in the combination of DAP and decreases the luminescent intensity of Ta:β-Ga_2O_3. Different annealing atmosphere is the key factor causing this change. Although annealing causes the change of luminescent intensity, it does not affect the position of the peak of Ta:β-Ga_2O_3.

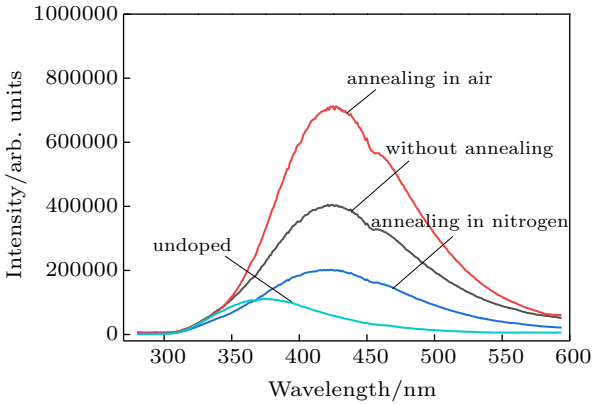


Fig. 3. PL spectra for pure β-Ga_2O_3 and 0.01 mol% Ta:β-Ga_2O_3 before and after annealing under the excitation of 256 nm.

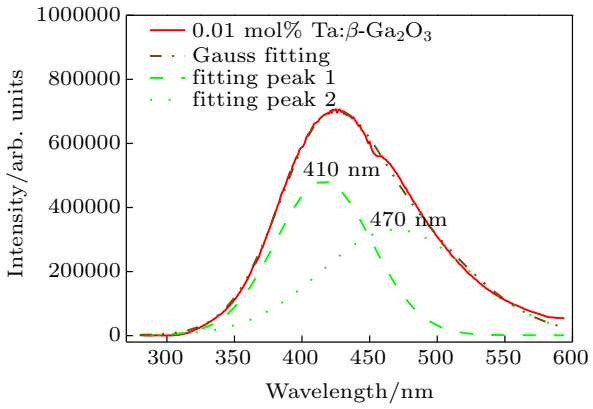


Fig. 4. PL spectra of 0.01 mol% Ta:β-Ga_2O_3 after annealing in air under the excitation of 256 nm. Green lines are Gaussian fitting results.

3.4. PL decay curve profiles

The decay curve profiles of pure β-Ga_2O_3 single crystal at 340 nm and 435 nm under the excitation of 262 nm have been reported.[17] The fast decay time constant of pure β-Ga_2O_3 is about 9 ns.[8] As shown in Fig. 5, the decay curve profiles of 0.01 mol% Ta:β-Ga_2O_3 were monitored under the excitation of 256 nm at 370 nm and 420 nm, respectively. By fitting with an exponential decay function,[6] the obtained PL decay time constants are summarized in Table 2. Compared with Ta:β-Ga_2O_3 without annealing, the fast decay time constant increases by several nanoseconds after annealing in the air. After annealing in air, more localized electrons are involved in the combination of exciton and DAP, resulting in longer PL decay time. In contrast, the fast PL decay time decreases slightly after annealing in nitrogen, which is the same as the band gap and carrier concentration, both of them change slightly. In parentheses of Table 2, the slow decay proportion of Ta:β-Ga_2O_3 is relatively higher than the data of pure β-Ga_2O_3[8] because of introducing Ta as donor impurity. This conclusion is consistent with Sn:β-Ga_2O_3.[6]

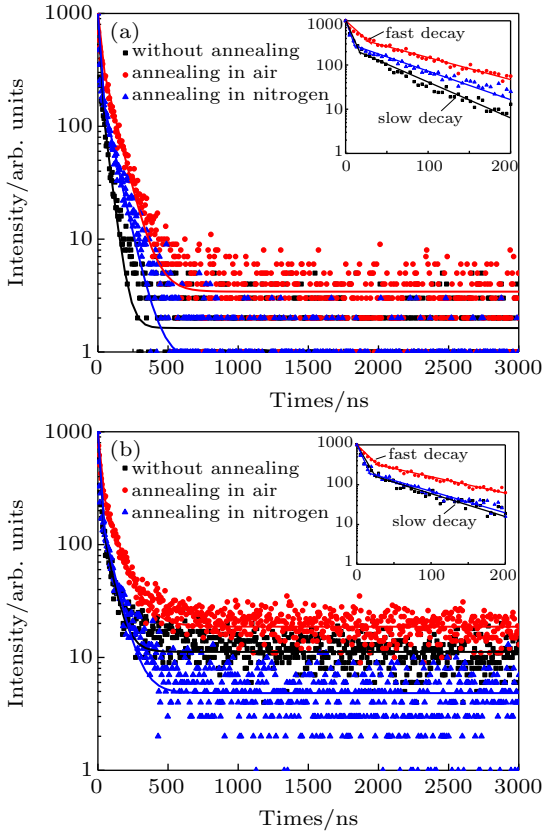


Fig. 5. PL decay profiles of 0.01 mol% Ta:β-Ga_2O_3 before and after annealing measured under excitation of 256 nm. The monitoring wavelengths are (a) 370 nm and (b) 420 nm. The lines indicate the fitting curves.

Table 2. PL decay time constants of 0.01 mol% Ta:β-Ga_2O_3 before and after annealing measured under excitation of 256 nm while monitoring the emissions at 370 nm and 420 nm. The percentage in parentheses shows the emission ratio.

Em.	370 nm		420 nm	
	l_1/ns	l_2/ns	l_1/ns	l_2/ns
Without annealing	4.7(68.1%)	42.7(31.9%)	6.1(76.3%)	61.1(23.7%)
Annealing in air	7.7(50.2%)	82.5(49.8%)	11.6(62.5%)	100.0(37.5%)
Annealing in nitrogen	4.4(72.4%)	76.7(27.6%)	5.4(76.1%)	76.1(23.9%)

3.5. X-ray irradiation spectra

Figure 6 shows the x-ray irradiation spectra for undoped and 0.01 mol% Ta:β-Ga_2O_3. Compared with PL spectra, the emission peak under x-ray irradiation mainly concentrates on the ultraviolet light around 365–390 nm owing to the dominant recombination of exciton.[8] The luminescent intensity of Ta:β-Ga_2O_3 is lower than pure β-Ga_2O_3, and it increases after annealing in the air but decreases after annealing in nitrogen. This change is caused by the change of exciton density. The carrier concentration of pure β-Ga_2O_3 is lower than Ta:β-Ga_2O_3, so electrons in the valence band are more easily excited to form exciton leading to higher exciton density. After annealing Ta:β-Ga_2O_3 in the air, the carrier concentration decreases, resulting in more bound exciton formed by trapping electrons and holes in defect and impurity centers. The bound exciton can participate in the combination of exciton, which increases the luminescent intensity. In contrast, annealing in nitrogen can activate carriers, and electron delocalization leads to lower exciton density and lower luminescent intensity of Ta:β-Ga_2O_3. The peak of Ta:β-Ga_2O_3 without annealing is about 375 nm. Annealing in different atmosphere results in slightly blue shift or red shift because of different exciton energy. After annealing in air, the decrease of exciton energy leads to red shift, while the increase of exciton energy leads to blue shift after annealing in nitrogen.

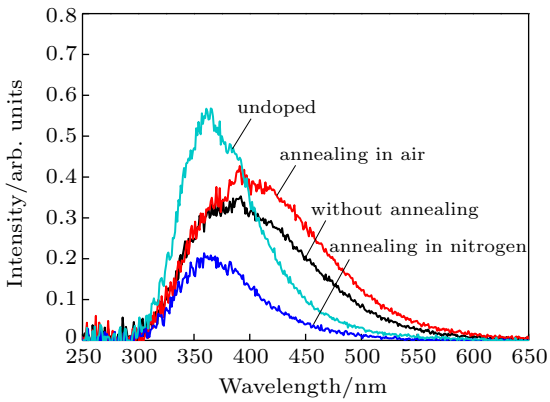


Fig. 6. The x-ray stimulated luminescence spectrum for pure β-Ga_2O_3 and 0.01 mol% Ta:β-Ga_2O_3 before and after annealing.

4. Conclusion and perspectives

In conclusion, annealing can be used as an effective method to improve the transmittance of Ta:β-Ga_2O_3. After annealing in nitrogen, the carrier concentration, PL decay time, and band gap of Ta:β-Ga_2O_3 change slightly and behave the opposite tendency compared with the sample annealing in the air, which demonstrates some correlation. In addition, after annealing in the air, both the blue and the ultraviolet luminescent intensity of Ta:β-Ga_2O_3 increase. The increase of ultraviolet luminescence intensity indicates that annealing in the air may improve the light yield of Ta:β-Ga_2O_3. However, due to the lack of experimental data, the scintillation performance of Ta:β-Ga_2O_3 should be further studied in the future.

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