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Synthesis of Ga_2O_3: Co nanocrystals at normal temperature and atmospheric pressure

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abstract

Synthesis of Ga_2O_3: Co at normal temperature and atmospheric pressure was carried out. As the amount of Co added was increased, the shape of the fibrous nanocrystals became irregular and film-like structures appeared. By the X-ray diffraction evaluation, the nanocrystals were confirmed to be ε-type when the addition of Co was increased up to Ga: Co = 2: 1. However, it was suggested that the crystal changed to γ-Ga_2O_3 in Ga: Co = 1: 1 molar ratio. By the evaluation of energy band structure based on the optical absorption spectra, it was found that the band gap widened as the addition of Co was small. The band gap narrowed conversely when the addition was further increased to Ga: Co = 1: 1.

1. Introduction

Gallium oxide (Ga_2O_3) has been actively studied recently as a promising wide gap semiconductor, and it is expected to realize high efficiency and low loss power devices that take advantage of its material characteristics [1]. Ga_2O_3 crystal has five different crystal structures of α, β, γ, δ, and ε. The most stable structure is β-type and the others are metastable structures. The crystals are usually synthesized under high temperature or high pressure. There is a research report that Ga_2O_3 of fibrous nanocrystals were grown to produce p-type semiconductor [2]. There is also a research report that the energy band gap of Ga_2O_3 can be controlled by adding Co [3]. In this study, Ga_2O_3 nanocrystals containing Co were synthesized at normal temperature and atmospheric pressure. The basic properties of the nanocrystals produced were evaluated.

2. Experimental

Ga_2O_3 crystals were synthesized by the following procedure [4]. 2-butanol (5.9 ml) was added dropwise to $GaCl_3$ (2.64 mg) at the constant rate of 1.2 ml/min and stirred for 10 minutes. After confirming that $GaCl_3$ was sufficiently dissolved, 2-butanol (31.2 ml) was added dropwise at 1.0 ml/min and stirred for 1 hour. Deionized water (2.94 ml) was added dropwise at 0.2 ml/min and crystals were precipitated by hydrolysis. After heating at 70°C for 23 hours, the solution was left overnight to complete the reaction. A white precipitate of the solution was collected using centrifugation, ethanol washing was repeated, and then redispersed in ethanol. To grow Ga_2O_3: Co crystals, Co was added by dissolving $CoCl_2$ in 2-butanol in advance in the above process. The amount of $CoCl_2$ was controlled in the range of 9: 1 to 1: 1 (Ga: Co) molar ratio with respect to the amount of $GaCl_3$.

Crystal shape was evaluated by transmission electron microscopy (TEM) and crystal structure was evaluated by X-ray diffraction (XRD) measurement. The energy band structure was also evaluated by measuring the light absorption spectra using a UV / visible / near infrared spectrophotometer.

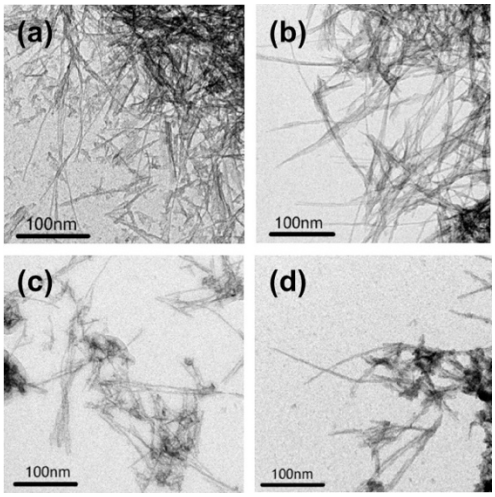

Fig. 1 TEM images of nanocrystals : (a) Ga_2O_3 , (b) Ga: Co = 9: 1, (c) Ga: Co = 2: 1, and (d) Ga: Co = 1: 1.

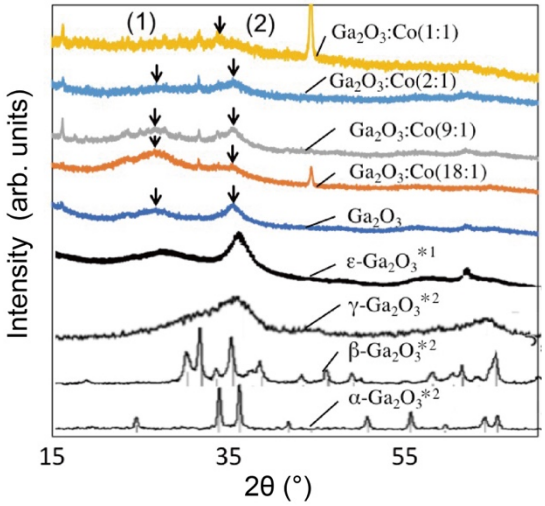

Fig. 2 XRD curves of Ga_2O_3 and Ga_2O_3:Co nanocrystals.

3. Results and discussion

The results of TEM observation are shown in Fig. 1. It was confirmed that Ga_2O_3 without Co added was fibrous nanocrystals having a width of 3.5 to 4.3 nm and a length of 100 nm or more. Even when Co was added, Ga_2O_3 nanocrystals were fibrous. However, the width changed irregularly in the range of 3.4 to 6.0 nm. When the Ga: Co molar ratio was 2: 1 or more, filmy crystals were found in addition to the fibrous crystals. The more Co added, the more irregularly shaped nanocrystals were found.

Table I Peak angle and crystal structure by XRD analysis.

Ga: Co	peak (1)	peak (2)	crystal
1: 0	26.80°	35.54°	ε
18: 1	26.58°	35.27°	ε
9: 1	26.63°	35.27°	ε
2: 1	27.09°	35.31°	ε
1: 1	--	33.52°	γ

The results of XRD measurement are shown in Fig. 2. Diffraction curves of various gallium oxide crystals already reported are also shown in the figure [4, 5]. Since the diffraction curve, particularly the two peak positions, agreed well with the literature, it was confirmed that the crystal without Co was ε-Ga_2O_3. By adding Co, the diffraction curve slightly changed. Table I summarizes the change in peak position. It is shown that the two peaks slightly moved to the small angle side and then returned to the large angle side as the amount of Co added was increased. Also, in the case of Ga: Co = 1: 1, one of the peaks disappeared and a clear position shift toward the small angle side was observed for the remaining peak. Comparing the diffraction curve with the literature, the Ga: Co = 1: 1 crystal could be γ-Ga_2O_3.

Figure 3 shows the results of light absorption spectra evaluation using a spectrophotometer. Two absorption peaks were observed. The dependence of the peak wavelength on Co/ Ga ratio is shown in an inset. The second peak on the longer wavelength side should reflect the band gap energy, but the shift was slight and difficult to identify.

Therefore, the band gap of the nanocrystals was determined from the Tauc plot [6], which is derived by the equation:

$$(h\nu\alpha)^{1/n} = k(h\nu - Eg), \qquad (1)$$

where h is a Plank's constant, ν is a frequency, α is an absorption coefficient, k is a proportionality constant, and Eg is a band gap energy. Although n varies depending on the type of optical transition of semiconductor material, n = 1/2 in the case of direct allowed transition was used in the analysis. Figure 4 shows the Co/ Ga ratio dependence of the band gap energy obtained as a result of the analysis. Up to Co/ Ga = 0.5, the band gap widened as the amount of Co added increased, but it turned to narrow when increasing Co/ Ga ratio to 1. Specific change in the case of Ga: Co = 1: 1 is consistent with the change in crystal structure suggested by TEM and XRD evaluations.

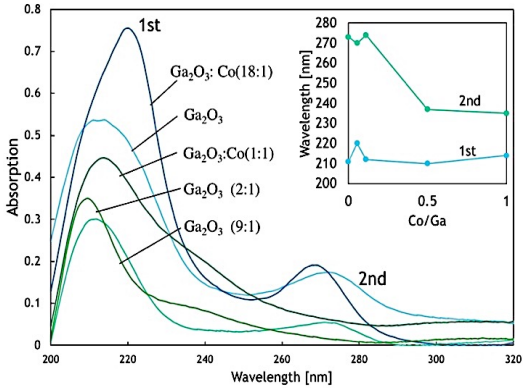

Fig. 3 Light absorption spectra of Ga_2O_3 and Ga_2O_3:Co nanocrystals. Inset shows the dependence of peak wavelength on Co/ Ga ratio.

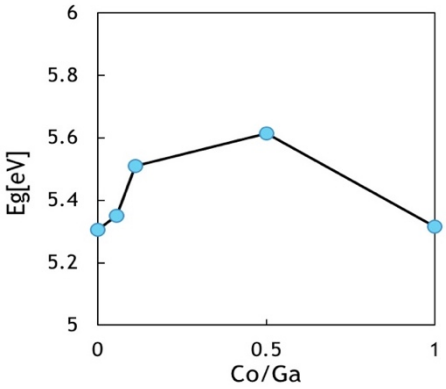

Fig. 4 Band gap energy as a function of Co/ Ga ratio.

4. Conclusions

Synthesis of Ga_2O_3: Co nanocrystals at normal temperature and atmospheric pressure was reported. As the amount of Co added was increased, shape of the fibrous nanocrystals became irregular, and film-like nanocrystals appeared. By the XRD evaluation, it was confirmed that the nanocrystals were ε-type in the cases where Co was added up to Ga: Co = 2: 1. At Ga: Co = 1: 1, it was suggested that the crystal could be γ-Ga_2O_3. In the evaluation of the energy band structure using spectrophotometer, band gap widening was confirmed as the amount of Co added increased up to Ga: Co = 2: 1. When Ga: Co was further increased to 1: 1, the band gap energy narrowed conversely. It was shown that the specific change of the band gap and the change of the crystal structure occurred under the conditions of Ga: Co = 1:1.

References

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