Polarized Light from in-Plane Aligned Y_2WO_6:Gd Nanorod Films Prepared by Dip Coating Method

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Keywords: Y_2WO_6:Gd, nanorod film, dip coating method

ABSTRACT

In-plane aligned Y_2WO_6:Gd nanorod films were prepared by dip coating method. Weakly polarized emission band around 460 nm was observed from the films. The observed polarization was found to be explained by the theory of emission affected by the light confinement effect in nanorods.

1 INTRODUCTION

In recent years, nanorods, which are one-dimensional nanomaterials, are expected to be applied in the field of liquid crystal displays (LCDs) because they show linearly polarized light emission properties due to dielectric confinement of photoelectric fields derived from their shape anisotropy and quantum confinement of carriers [1]. To utilize the polarized light for devices such as LCD backlight panels, nanorods should be aligned along in-plane direction in films. Various nanorod alignment methods using magnetic or electric fields have been studied [2,3], but it is difficult to align over large areas using these methods. In order to overcome such problems, there is a demand to establish a nanorod alignment method which is simple and align over large area. In this study, we focused on the dip coating method, which is a simple method for aligning nanorods in macroscopic region. The polarization characteristics of the emission from alignment films obtained by this method were investigated, and we verified and considered using the theory of the light confinement effect in nanorods. As nanorods for in-plane orientation in this study, Y_2WO_6:Gd nanorods synthesized by the flux method previously reported by us were used [4,5].

2 EXPERIMENT

2.1 Preparation of Y_2WO_6:Gd nanorod by flux method

Y_2WO_6:Gd (2 %) nanorods were prepared by the flux method because synthesis and shape control of nanorods at low temperatures can be easily [4,5]. Gd ions do not act as emitting centers but additive dopant for improvement of nanorod crystallinity [5]. LiCl was used as a flux (solvent), and solutes (Y_2O_3, WO_3, Gd_2O_3) were stoichiometrically weighed together with LiCl and then mixed in an agate mortar for 1 hour. The mixed powder was filled in a 50 ml alumina crucible and melted in a programable electric furnace (As One, ROP-001H). The temperature of the electric furnace was first raised from room temperature to 700 °C with a rate of 50 °C/h and held for 10 hours. Thereafter, it was gradually cooled to 500 °C with a rate of 100 °C /h, and then allowed to cool to room temperature naturally. Next, the flux containing deposited nanorods was dissolved in warm water, and the precipitated nanorods were collected after centrifugation (Violamo, 444315-100) for 30 minutes at 8000 rpm. The washing and collection processes were performed 4 times. Finally, the nanorods were dried at 120 °C for 24 hours on a hot plate (As One, RSH-4DN) to remove moisture, and the final product of Y_2WO_6:Gd nanorods was obtained. The crystal phase of the obtained nanorods were characterized using an X-ray diffractometer (Shimadzh XRD-7000, 40 kV, Cu-K_α) and the shape was observed by FE-SEM (Hitachi S-4000, 15 kV,10 μA) .

2.2 Preparation of in-plane aligned nanorod film by dip coating method

A nanorod alignment film was prepared by a dip coating method because in-plane nanorod arrangement are expected with simple facilities. In this study, polyvinylpyrrolidone (PVP), which is commonly used for thin film formation by dip coating [6,7], was selected as the polymer. The solvent used in this study was 2-propanol and the solution for the dip coating prepared by suspending 15 wt.% nanorods and 15 wt.% polymer and stirred for 1 hour (Nanorods and polymer concentrations were changed in the range of 3-15 wt.% in advance, and 15 wt.% for each was found to be the optimum condition). Before dip coating, the nanorods are dispersed in the solution again for 15 minutes using an ultrasonic homogenizer (As One, ASU-3). Thereafter, the glass substrate washed with pure water and ethanol was immersed in the solution for several minutes, and the glass substrate was pulled up from the solution at a uniform speed of about 40 mm/s. The glass substrate pulled up was placed on a hot plate (As One, EHP-170N) and dried at 80 °C for 12 hours. The morphology of dip coated films and orientation of the nanorods was observed by the FE-SEM, and the polarization PL characteristics were measured using a He-Cd laser(Kimmon Koha, IK3252R-E, 30 mW, 325 nm) as an excitation light source, a spectrometer (Andor, Shamrock 163, *f* = 163 mm, slit 25 μm x 3 mm), a CCD detector (Andor, iDus DV420A-OE), a linear polarizer (Sigma

Koki, SPF-30C-32), and an auto-rotating polarizer holder (Suruga Seiki, FPW06360C).

3 RESULTS

3.1 Properties of Y_2WO_6:Gd nanorods

Fig. 1 shows the XRD pattern of Y_2WO_6:Gd (2 %) and ICDD data of Y_2WO_6. The obtained XRD pattern is almost corresponding to the ICDD data, showing that Y_2WO_6:Gd are obtained successfully and no other phase except Y_2WO_6 are found.

Fig. 2(a) shows an SEM image of Y_2WO_6:Gd (2 %) prepared by the flux method, and Fig. 2(b) shows an enlarged view of Fig. 2(a). It can be confirmed that obtained Y_2WO_6:Gd (2 %) has a good nanorod shape. The rod diameter and rod length were measured by selecting 100 nanorods randomly from the several SEM images. It was found that the diameter of the nanorods is distributed in the range of about 70 to 240 nm (average is 130 nm) and the length is distributed in the range of about 500 to 4000 nm.

3.2 Properties of the in-plane aligned nanorod film

Fig. 3(a) shows the surface SEM image of the dip-coated film, and Fig. 3(b) shows the cross-section SEM image. From the surface image, nanorod orientation in the substrate pulling up direction is confirmed to a certain degree. The average deviation of the angle between the nanorods is estimated to be $s_{\theta 1}$=11.7 °, and the average deviation of the angle between the substrate and the nanorods is $s_{\theta 2}$=7.13 °. Therefore, linearly polarized light emission from this film is expected. However, there may be other effects to destroy the polarization such as light scattering caused by nanorods which are not along to the pulling up direction seen near the substrate and bad morphologies of the film surface. Therefore, the improvement of the film quality and the further orientation of the nanorods along with substrate is a future issue.

Fig. 4 shows the polarization PL characteristics of the dip-coated film. The solid line represents the polarization ratio, the black broken line represents the PL intensity where the electric field is parallel to the substrate pulling up direction, and the red broken line represents the PL intensity where the electric field is perpendicular to the substrate pulling up direction. From the solid line in Fig. 4, the PL has polarization has weak polarization perpendicular to the pulling up direction in the wavelength range of 370 to 520 nm and the maximum polarization ratio is about -0.02 (The sign indicates the polarization direction). On the other hand, the PL shows weak polarization parallel to the pulling up direction over 520 nm. This shows that the polarization ratio depends on the emission wavelength, and an inversion of the polarization direction was occurred. A small polarization ratio can be observed despite the existence of the effects destroying the polarization mentioned in the previous section. Therefore, in order to confirm whether the obtained polarization is due to the nanorod orientation or not, analysis using the theory of emission affected by the light confinement effect will be done in the next section.

4 DISCUSSION

The polarization property of a single nanorod is dominated by the effect of “dielectric confinement of the photoelectric field due to the difference in dielectric constant between the nanorod and the surrounding environment” in the case of a thick nanorod with the diameter exceeding tens of nanometers [1,2]. The Y_2WO_6:Gd (2 %) nanorods used in this study are considered to be linearly polarized due to the optical confinement effect because they are relatively thick with an average diameter of 130 nm. Therefore, we tried to verify and examine the obtained polarization characteristics of the in-plane nanorod aligned film using the theoretical formula describing the light confinement effect [9]. Since the dielectric constant of Y_2WO_6:Gd (2 %) used in this study is unknown, the dielectric constant of La_2WO_6, where the Y is substituted with the same group element of La, were used as alternative values [10]. ε = 7, 6.5, 6 and 5.5 (for wavelength of 310 nm, 413 nm, 496 nm and 620 nm, respectively). However, the dielectric constant of Y_2WO_6 may be a little smaller than the La_2WO_6, since the dielectric constant is determined by the number density of electrons generally. The dielectric constant of the environmental PVP was obtained from the refractive index and ε_0 = 2.357 (n = 1.593) was used.

Fig. 5 shows the wavelength dependence of the calculated polarization ratio of the nanorods with the diameters of 130 nm and 160 nm for various dielectric constants between 5.5 and 7. 130 nm is the average diameter of the nanorods obtained in this study and 160 nm is the best one which reproduce the measured polarization ratio in Fig. 4. For comparison, the measured polarization ratio is redrawn in Fig. 5. The calculation shows that the polarization ratio changes with wavelength and the polarization ratio can be inverted. From Fig. 5, the wavelength dependent of the measured polarization ratio seems to be consistent when the rod diameter is 160 nm not 130 nm which is the actual average diameter. This suggests that the effect to the polarization ratio by thicker nanorods is larger than that by the nanorods with average diameter. For the thicker nanorods, the light emission becomes stronger because of their smaller specific surface area. Therefore, the contribution of the thicker nanorods to the polarization characteristics is considered to become larger. Since the calculated polarization ratio reproduces the measured one mostly, the observed polarization characteristics of the in-plane aligned nanorod film in this study are due to the dielectric confinement effect of photoelectric fields.

Fig. 6 shows the nanorod diameter dependence of the calculated polarization ratio at emission wavelengths of 400 nm and 600 nm, and the actual number distribution of nanorods. It was found that the polarization ratio changed with the nanorod diameter, and the polarization ratio was canceled due to variations with the nanorod diameter. In addition, in the case of 130 nm, which is the average diameter of the nanorods used in this study, the polarization ratio was about -0.05 and 0.5 for 400 nm and 600 nm, respectively, and a high polarization ratio could not be expected. From these results, in order to obtain a higher polarization ratio, it is considered that further control of the nanorod diameter is necessary, such as further reducing the diameter of the nanorod and improving the distribution of nanorod diameter which causes the cancellation of the polarization ratio. In this study, bad morphologies of the dip coated film surface and non-orientated nanorods were also observed, so it is necessary to investigate and reduce these effects on the polarization ratio in the future.

5 CONCLUSIONS

Polarized characteristics of emission from the in-plane nanorod aligned film prepared by the dip coating method were measured. A very weak polarization ratio (approximately 0.02) perpendicular to the long axis of the nanorods was observed around the emission wavelength of 460 nm. At the same time, the polarization ratio depended with the emission wavelength and the inversion of the polarization ratio was observed. The obtained polarization characteristics were verified and examined using the theoretical formula of the light confinement effect for nanorods. As a result, changes in the polarization ratio with the emission wavelength and inversion of the polarization ratio were also observed with the theoretical calculation. It has been found that further control of the nanorod diameter, the further orientation of the nanorods along with substrate and the improvement of the dip coated film quality are necessary to obtain higher polarization ratios.

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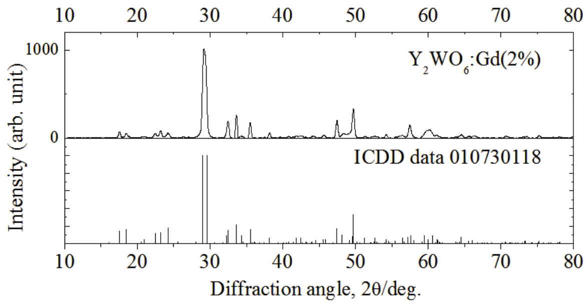

Fig. 1 XRD patterns of the Y_2WO_6:Gd (2 %) prepared by flux method.

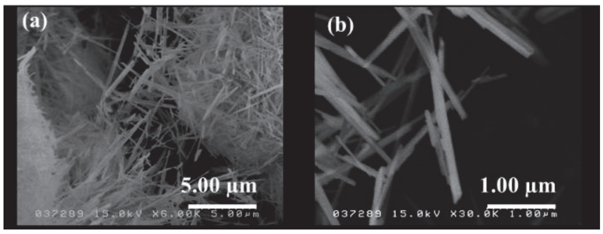

Fig. 2 SEM images of the Y_2WO_6:Gd (2 %) prepared by flux method.
(a) Overall view, (b)Enlarged view

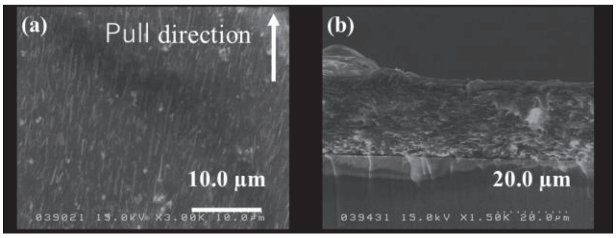

Fig. 3 SEM images of the Y_2WO_6:Gd nanorod films prepared by dip coating method. (a) surface, (b)cross section

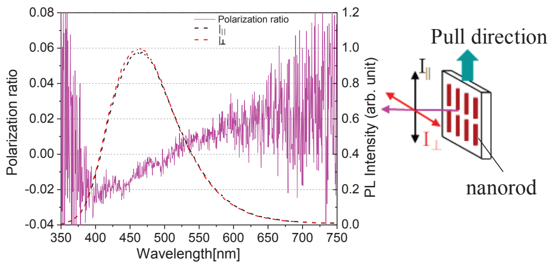

Fig. 4 The polarization PL characteristics of the prepared thin film (The solid line represents the polarization ratio, the black broken line represents the PL intensity where the electric field is parallel to the substrate pulling up direction, and the red broken line represents the PL intensity where the electric field is perpendicular to the substrate pulling up direction).

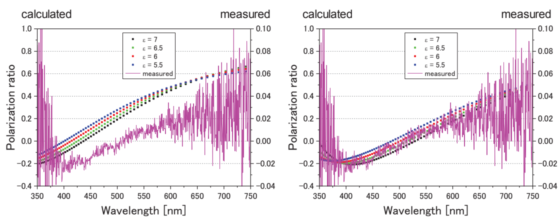

Fig. 5 The calculated wavelength dependence of the polarization ratio of the nanorods with diameters of 130 nm (left) and 160 nm (right).

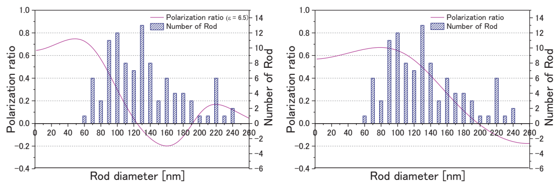

Fig. 6 The nanorod diameter dependence of the calculated polarization ratio at emission wavelengths of 400 nm (left) and 600 nm (right), and the actual number distribution of nanorods.