Extended Abstracts of the 2003 International Conference on Solid State Devices and Materials, Tokyo, 2003, pp. 568-569

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Blue Luminescence of Porous Alumina Membranes Prepared by Anodic Oxidation

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1. Introduction

Porous alumina membranes prepared by anodic oxidation have attracted much attention for the use to molds to fabricate nano-wires of several materials [1-3], dots [4, 5], or nano-particles of wide gap semiconductors ZnO [6], GaN [7], because the membranes have numerous holes with several tens of nano meter scale in diameter. Self – properties of the porous alumina with ordered pore array were reported by Y. Du [8]. They investigated luminescence property of two kinds of porous alumina anodized in oxalic and sulfuric acid solutions and pointed out that the samples prepared by oxalic acid had more intensive blue luminescence than prepared by sulfuric acid. The ordered pore array was formed by means of two-step anodic oxidation method which consisted of three processes; the first time anodic oxidation, elimination of alumina film formed in the first step, and the second time oxidation. For the practical application or the industrial use, shortening of the fabrication processes is very important. Therefore, in this letter, we have investigated luminescence property of the porous alumina which is prepared by single anodic oxidation process.

2. Experimental

For the preparation of porous alumina, aluminum sheets (99.5%) were used as the starting material. Before anodization the aluminum sheet was degreased with acetone and then planarized by electrolytic polishing in a perchloric acid/ethanol (1:4) solution at a constant current density of 160 mA / cm^2. The aluminum sheet was anodized for 1 – 50 hours in 0.5M oxalic acid solution with 40 V anodization voltage. The temperature of electrolyte was kept constant 3 $^{\circ}$C. The morphology observation of prepared samples was carried out using an atomic force microscope (AFM) and the cross-section of samples was observed using scanning electron microscope (SEM) to determine the film thickness. Photoluminescence (PL) spectra excited by 325 nm line of He-Cd laser were measured using a visible – ultraviolet spectrophotometer at room temperature. The stoichiometric ratio of Aluminum and oxygen is confirmed by energy dispersive analysis of X-ray (EDX).

3. Results and Discussion

The ratio of Al and O in the prepared samples measured by EDX is two to three. No impurity elements can be observed. Figure 1 shows AFM image of porous alumina membrane anodized for 30 hours. Many holes of about 30 nm in diameter can be seen in the surface. These holes are located randomly and are not ordered in one time anodization. The film thickness obtained from cross-section SEM observation depends on the anodic time and increase linearly with the ratio of 5.0 μm / hour as shown in figure 2. The thickness tends to saturate for the long anodic time. Figure 3 shows PL spectra of porous alumina anodized for two hours and commercial alumina substrate. The alumina substrate has one sharp peak at 679 nm and a broad emission peak at 754 nm in the orange – red region. In the ultraviolet – green range, few structures are observed. Visually regular alumina substrate appears to be pale orange color. On the other hand, porous alumina has a strong broad peak centered at 435 nm with full width at half maximum (FWHM) 110 nm. The large FWHM indicate that the luminescence center is located in the band gap of alumina. Y. Du *et. al* mentioned that the origin of blue luminescence seems to be singly ionized oxygen vacancies (F^+ center) from the result of electron paramagnetic resonance measurement [8]. The anodic time dependences of PL spectra are depicted in figure 4. The PL intensity depends on the anodic time strongly and its peak position slightly changes. The oscillatory behavior is observed in the one hour anodic alumina. The oscillation for wavelength seems to be due to the interference effect of the reflected light at the surface and the interface between alumina and residual aluminum. Figure 5 indicates the anodic time dependence of the PL intensity normalized with respect to the sample anodized for one hour and the peak position. The intensity increases rapidly up to ten hours and then increases with gently-sloping. This result indicates that the anodic time enhances the PL intensity easily. The peak position also depends on the anodic time slightly and shifts from 425 to 442 nm for 1 and 50 hours, respectively. The redshift of PL peak position is considered to be caused by an increase of oxygen vacancies in the porous alumina at anodic oxidation processes.

4. Conclusion

We have found that the anodic porous alumina membrane prepared by single anodic oxidation process has a blue emission which is different from the commercial alumina substrate. The PL intensity and its peak position depend on the anodic time. We propose the anodic porous alumina as a new blue emission material for electroluminescence device.

Reference

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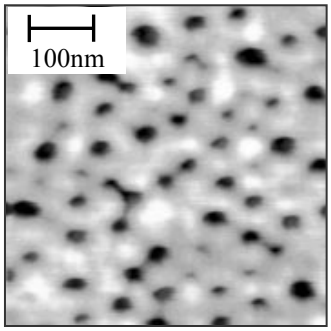

Fig. 1. AFM image of porous alumina membrane anodized for 30 hours.

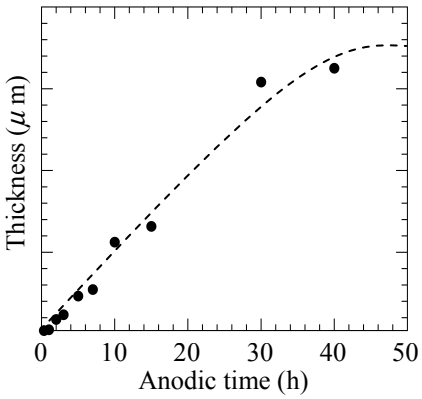

Fig. 2. Anodic time dependence of the film thickness of porous alumina.

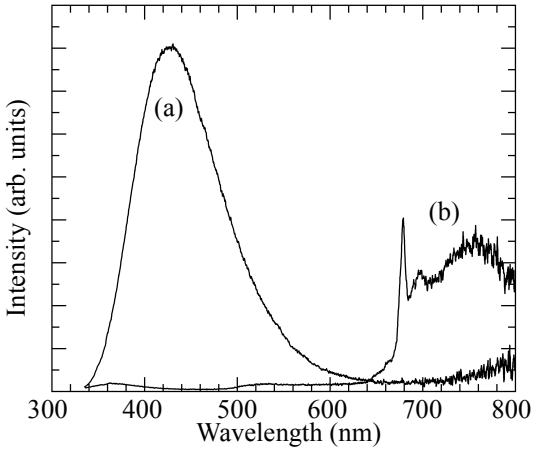

Fig. 3. PL spectra of porous alumina anodized for 2 hours (a) and commercial alumina substrate (b).

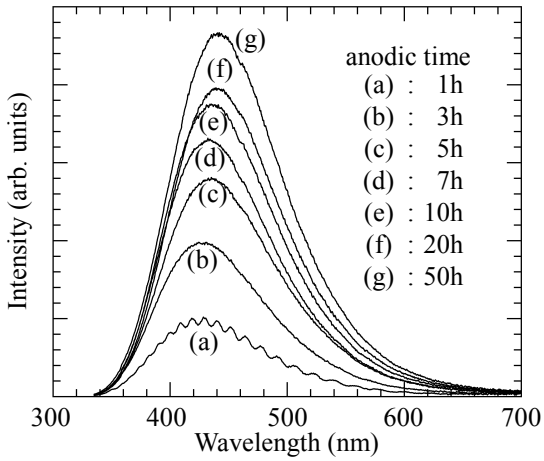

Fig. 4. Anodic time dependence of PL spectra at room temperature.

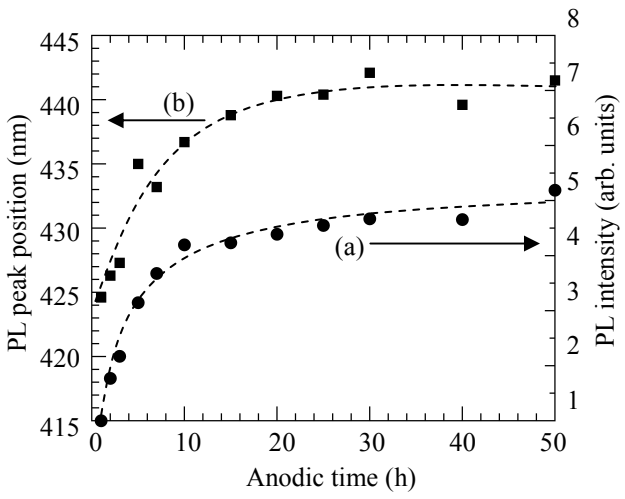

Fig. 5. Anodic time dependence of the PL intensity normalized by the one hour anodized sample (a) and peak positions (b).