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Photoluminescent properties of anodic aluminum oxide films formed in a mixture of malonic and sulfuric acid

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ABSTRACT

Anodic aluminum oxide (AAO) films with ordered nanopore arrays were fabricated electrochemically in the mixture electrolytes of malonic and sulfuric acids. Their photoluminescent (PL) properties have been investigated. There is no obvious PL band for the AAO films prepared in pure sulfuric acid, however, with the increase of the concentration of malonic acid in the mixture electrolytes, a PL band in the range from 300 to 500 nm appears, and its intensity is enhanced gradually. Obviously, the PL band is mainly attributed to the malonic impurities incorporated into AAO films, which corresponds to the excitation center at about 270 nm. Meantime, the increase of the sulfuric acid concentration results in a blueshift of the PL band. Further, the effect of annealing process on the PL properties is also investigated. As annealing temperature increases, the malonic impurities incorporated into AAO films are gradually decomposed, the PL intensity corresponding to excitation center at about 270 nm gradually becomes weak. But interestingly, with the decomposition of malonic impurities, the defects in AAO films mainly caused by a lattice mismatch and the difference in the coefficients of thermal expansion between alumina and incorporated malonic impurities are gradually produced, which form a new excitation center at about 250 nm, and its PL is firstly enhanced to

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maximum at 400 °C and then decreases with the further increase of annealing temperature.

1. Introduction

Anodic aluminum oxide (AAO) film with ordered nanopore array has been widely used to the self-assemble of various nanodevices [1–6], and exhibits perfect properties. It is worthy of noting that the nanopore array structure has great effects on the physical properties, especially optical properties. For example, the AAO films prepared in different electrolyte have obvious changes in photoluminescent (PL) property.

Over the past years, many efforts have been done to investigate the PL properties of AAO films formed in various electrolytes, such as oxalic acid [7–10], sulfuric acid [11], phosphoric acid [12], and the mixture electrolytes of oxalic acid and sulfuric acid [13,14]. However, the origin of blue luminescence remains unclear. Yamamoto et al. [15] and Gao et al. [9] attributed the PL of AAO films prepared in an oxalic acid to oxalic impurities incorporated into the film during the film formation. But Du et al. [7] and Li et al. [16] attributed the blue emission band of oxalic acid AAO film to the presence of singly ionized oxygen vacancies (F+ centers). Also, Xu et al. [17] assigned the blue emission band of oxalic acid AAO film to the coactions of the singly ionized oxygen vacancies (F+ centers) and the luminescent centers transformed from oxalic impurities. Similarly, in our group, Wang et al. [13] found that the PL emission of the mixture films originates from the oxalic ions and the sulfuric ions can tuned the PL properties. But Li et al. [14] found that the 290 and 325 nm emissions arise from the luminescent centres transformed from sulfuric and oxalic impurities in AAO membranes, respectively, and nonradiative energy transfer occurs between these two kinds of PL centres. Obviously, up to date, the mechanism behind the light emission of the AAO membranes remains very ambiguous and controversial. Hence, more in-depth studies on the luminescence characteristics of the AAOs are essential to reveal the origin of the PL emission characteristics.

Malonic acid as well as oxalic acid belongs to dicarboxylic acids with the only difference in the methylene group. Therefore, for the sake of further making clear the origin of PL of AAO film and comparing the luminescent behavior of the malonic acid AAO films with that of the films formed in oxalic acid, the PL properties of AAO films formed in mixture electrolytes of malonic acid and sulfuric acid were investigated. The results direct reveal that malonic impurities incorporated into the as-prepared AAO films are mainly converted into luminescent centres, and the sulfuric ions affect on the PL properties. The annealing process removes these malonic impurities and produces the structure defects in AAO films to form new PL centers. This work enhanced the understanding of the PL mechanism in the AAO films.

2. Experimental

High purity aluminum (99.999%, 25 mm × 15 mm × 0.25 mm) samples were used as the starting material. Before anodization the aluminum was degreased in acetone by using an ultrasonic cleaner. The surface of aluminum samples was electropolished in a mixed solution of perchloric acid and ethanol (1:4 in volume) under a constant voltage of 12 V for about 60–90 s to achieve a smooth surface, then a thorough rinsed in deionized water and transferred to a nitrogen environment to reserve for anodization. The two series of electrolyte was prepared by using double distilled, deionized water and PA grade $C_3H_4O_4$ and H_2SO_4. One is the mixture of malonic acid ($C_3H_4O_4$, 0.5 M) and sulfuric acids with different concentrations of 0.1, 0.2, 0.3, 0.4, 0.5 M, respectively, and another is that of sulfuric acid (H_2SO_4, 0.5 M) and malonic acid with different concentrations of 0.1, 0.2, 0.3, 0.4, 0.5 M, respectively. Anodic oxidation of aluminum was conducted under a constant cell potential condition of 20 V for 1 h at room temperature. A graphite electrode was used as the cathode. Annealing treatment of AAO films