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Citation: *Appl. Phys. Lett.* **89**, 051911 (2006); doi: 10.1063/1.2266665

View online: <http://dx.doi.org/10.1063/1.2266665>

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# Ultraviolet irradiation-induced photoluminescence degradation in $\gamma$ -alumina nanoparticles

Sufeng Liu, Ligong Zhang,<sup>a)</sup> Yi Fan, and Jinsong Luo

Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130032, China

Peiping Zhang

Department of Material Science and Engineering, Jilin University, Changchun 130023, China

Linan An<sup>a),b)</sup>

Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida 32816

(Received 11 April 2006; accepted 14 June 2006; published online 2 August 2006)

The photoluminescence (PL) behavior of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanopowder is studied. Two emission peaks at 343 and 378 nm and a broadband ranging between 400 and 600 nm are observed. The peaks are attributed to  $F^+$  center, while the broadband is attributed to impurities. It is found that irradiating the sample with intense ultraviolet (UV) light can cause significant decrease in the intensity of the two peaks, but has no effect on the broadband. A simple model is proposed to explain the kinetics of UV irradiation-induced PL degradation. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2266665]

The optical properties of alumina have attracted extensive interest because not only are they important for applications but also they can assist in the understanding of the defect and electronic structures and properties of the material. Earlier work primarily focused on thermally stable  $\alpha$ -alumina. Light-emission studies revealed that pure  $\alpha$ -alumina or irradiated sapphire exhibited major luminescence bands at 3.8 and 3.0 eV, among others.<sup>1–7</sup> The emission at 3.8 eV was attributed to the  $1B \rightarrow 1A$  transition of an  $F^+$  center (an oxygen-ion vacancy occupied by one electron), which has optical absorption bands at 4.8 and 5.4 eV.<sup>4,6</sup> The origin of the 3.0 eV emission was attributed to an  $F$  center (an oxygen-ion vacancy occupied by two electrons) with an intense absorption at 6.1 eV.<sup>4</sup> Recently the research focus has been switched to amorphous porous alumina membranes, driven by their important applications. It was revealed that the materials exhibited a broad blue photoluminescence band ranging between 400 and 600 nm. However, the origin of the emission is still not clear. Du *et al.*<sup>8</sup> attributed the emission to an  $F^+$  center based on electron paramagnetic resonance (EPR) results. Huang *et al.*<sup>9</sup> split the emission into two bands centered at 405 and 455 nm, respectively. They demonstrated by photoluminescence (PL) excitation (PLE) measurements that the two bands result from different emission centers, and attributed them to  $F^+$  and  $F$  centers, respectively. Xu *et al.*<sup>10</sup> also considered the emission to be from two centers, but attributed them to an  $F^+$  center (emission peak at 400 nm) and an oxalic impurity (emission peak at 470 nm). Wu *et al.*<sup>11</sup> observed PL peaks at 295, 340, and 395 nm under 240 nm excitation from Si-based anodic porous alumina and attributed them all to  $F^+$  centers since they had the same PLE peaks.

In contrast, less attention has been paid to  $\gamma$ -alumina, which is a metastable (also known as transition) phase and has a porous structure at nanometer scale with higher specific surface area and lower specific gravity as compared to

$\alpha$ -alumina, thus making it useful for applications such as catalyst/catalyst support and fluorescence matrices. Wrzyszc *et al.*<sup>12</sup> reported a broad PL band ranging from 350 to 650 nm in pure  $\gamma$ -alumina and attributed it to defects. A similar emission has also been observed by Xu *et al.*<sup>10</sup> from  $\gamma$ -alumina obtained by annealing amorphous porous alumina membranes at 800–950 °C. They attributed the emission to an  $F^+$  center (peak at 400 nm) and a carboxylic impurity (peak at 470 nm).

In this letter, we report the PL and UV-induced PL degradation of high purity (99.99%)  $\gamma$ -alumina nanoparticles of 50 nm, synthesized by thermal decomposition of bohemite ( $\gamma$ -Al-OOH). According to the provider (Dalian Luming Inc., China), the powder contains impurities: Si < 30 ppm, Ti < 5 ppm, Fe < 2 ppm, and Cr < 2 ppm. The PL spectra of the powders were measured using an UV-lamb microzone spectroscopy in a backscattering geometry at room temperature. The 325 nm (3.8 eV) line of a HeCd laser was used as the excitation source. The laser beam of 40 mW was first focused on the sample through a microscope with a spot size of  $\sim 20 \mu\text{m}$  in diameter. Taking a loss in optical route into consideration, the light power density cast on the sample was more than  $10^3 \text{ W/cm}^2$ . To investigate the effect of UV exposure on the emission behavior of the  $\gamma$ -alumina, the powder without milling was exposed to the UV light for different times before measuring PL spectra.

Figure 1 compares the PL spectra of the  $\gamma$ -alumina powder measured at irradiation times  $t=0$  and  $t=3$  min. It can be seen that the PL spectrum of the as-received sample without irradiation exhibits two strong emission peaks centered at 343 nm (3.6 eV) and 378 nm (3.3 eV) and a broadband ranging between 400 and 600 nm centered at 497 nm. On the other hand, the PL spectrum measured from samples irradiated for 3 min shows that the intensities of signals at 3.3 and 3.6 eV are significantly decreased, while the intensity of the broadband between 400 and 600 nm remains almost the same. This result clearly demonstrates that the emissions at 3.3 and 3.6 eV can be degraded by UV irradiation, and the emission center for the PL signals below 400 nm is different

<sup>a)</sup> Authors to whom correspondence should be addressed.

<sup>b)</sup> Electronic mail: lan@mail.ucf.edu

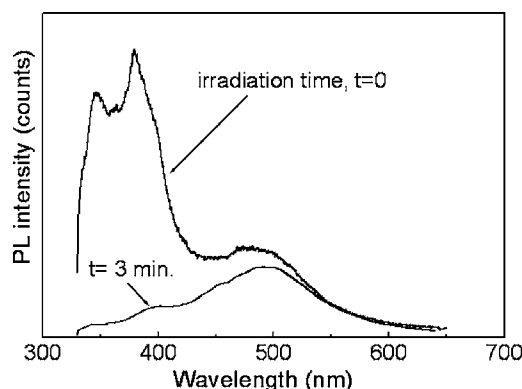


FIG. 1. Comparison of the PL spectra of  $\gamma$ -alumina powders irradiated for  $t=0$  and  $t=3$  min.

from that for the broadband between 400 and 600 nm. The strong PL emissions at 343 and 378 nm suggest that the as-received material contains a high density of the emission centers that respond to the emission.

From aforementioned experimental results and analysis on amorphous porous alumina membranes, we have learned that the blue emission centered at 497 nm could come from either an  $F$  center<sup>9</sup> or an impurity.<sup>10</sup> If the emission is from an  $F$  center, the intensity of the emission should decrease with UV irradiation because of the  $F \rightarrow F^+$  transition, similar to that observed in  $\alpha$ -alumina.<sup>5</sup> However, present results show that UV irradiation has no effect on the emission. Consequently, we tentatively attribute the emission to impurities. Considering that the  $\gamma$ -alumina powder was obtained by thermal decomposition of bohemite ( $\gamma$ -Al-OOH), the presence of oxygen-related impurities in the powder is very possible. Previous studies demonstrated that the impurities in alumina could act as luminescence centers. Yamamoto *et al.* have suggested that the oxalic impurities in porous alumina membranes can be transformed into luminescence centers, which showed a blue PL band around 470 nm.<sup>13</sup> Gao *et al.*<sup>14</sup> further proved that the blue PL band in porous alumina membranes came from oxalic impurities rather than the  $F^+/F$  centers through EPR and infrared transmission studies. Xu *et al.*<sup>10</sup> also proposed that oxalic impurities were responsible for a blue emission band in porous alumina membranes. At higher temperatures, the oxalic impurities were transformed to carbon dioxide, which responded to a blue emission band in  $\gamma$ -alumina.

Identifying the origin for the peaks at 3.3 and 3.6 eV is more difficult since very few PL data are available for  $\gamma$ -alumina. Earlier studies on  $\gamma$ -alumina did not report the emissions at this energy range.<sup>10,12</sup> It is well documented that for  $\alpha$ -alumina the emission peak from  $F^+$  centers is at 3.8 eV,<sup>4,6</sup> while the peak moves to 3.1 eV for amorphous alumina.<sup>8-10</sup> The decrease in emission energy was attributed to the lower symmetry of amorphous alumina as compared to  $\alpha$ -alumina. Previous study on amorphous alumina also revealed an increase in the emission energy with increasing annealing temperatures, which leads to higher symmetry.<sup>11</sup> Considering that the symmetry of  $\gamma$ -alumina is higher than that of amorphous alumina but lower than that of  $\alpha$ -alumina, we attribute the peaks at 3.3 and 3.6 eV to  $1B \rightarrow 1A$  and  $2A \rightarrow 1A$  transitions, respectively, to  $F^+$  centers in the  $\gamma$ -alumina powder.<sup>11,15</sup> Most recently, Gorbunov *et al.* studied the cathodoluminescence (CL) of  $\text{Al}_2\text{O}_3$  nanoparticles

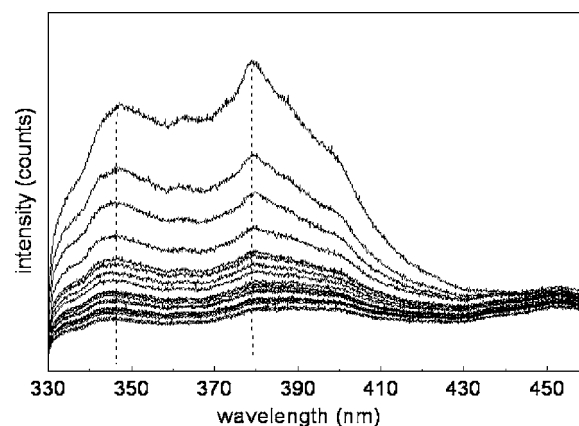


FIG. 2. PL spectra of  $\gamma$ -alumina powders irradiated for different times.

composed of both  $\gamma$  phase and  $\delta$  phase, and reported CL peaks at 2.4, 3.2, and 3.8 eV.<sup>16</sup> The authors attributed the origin of the CL peaks to surface  $F^+$  center. This conclusion is similar to what we proposed here.

We also studied the kinetics of PL degradation by measuring PL spectra of the  $\gamma$ -alumina powders irradiated at different times ranging from 0 to 50 s with an interval of 2.6 s (Fig. 2). It can be seen that the intensity of the PL peaks at 3.3 and 3.6 eV decreases gradually with irradiation times. Figure 3 shows intensity as a function of irradiation time for peaks at 343 and 347 nm in a linear-linear manner (a) and logarithmic-linear manner (b). It can be seen that for a short term ( $<10$  s) the intensity decreases linearly with irradiation time, while for long term ( $>10$  s) the  $\log(\text{intensity})$  is linearly related to irradiation time.

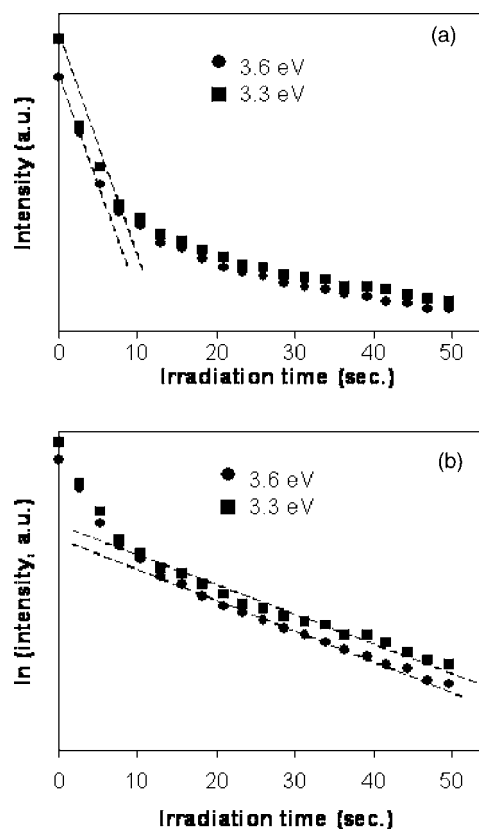


FIG. 3. PL intensities of the peaks at 3.3 and 3.6 eV as a function of irradiation time. The dots are experimental data, and the dash lines in (a) and (b) are plotted using Eqs. (3b) and (3d), respectively.

The irradiation-induced PL degradation can be explained in terms of decrease in  $F^+$  center concentration  $N$  as a function of irradiation time  $t$  via the following reaction:



where  $h\nu$  represents the UV phonons and  $O$  is reaction products, which could be nonradiative or high excitation energy centers. The reaction occurs through two steps: the phonons first reach  $F^+$  centers (referred as to step 1) and then react with  $F^+$  centers to form the product  $O$  (referred to as step 2). Since the power of the UV source is constant during the reaction, the reaction rate is independent of UV phonon numbers in the current study. Consequently, the rate of the decrease in  $N$  is controlled by reaction (1). The rate of step 1,  $R_1$ , is related to the concentration  $N$  and can be expressed as

$$R_1 = k_1 N, \quad (2a)$$

where  $k_1$  is the reaction rate constant of step 1. The rate of step 2 is constant and independent of  $N$ , and can be expressed as

$$R_2 = k_2, \quad (2b)$$

where  $k_2$  is the reaction constant of step 2. The overall reaction rate  $R$  can be related to the above two rates by

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} = \frac{R_1 + R_2}{R_1 R_2} = \frac{k_2 + k_1 N}{k_2 k_1 N}, \quad (2c)$$

$$R = \frac{k_2 k_1 N}{k_2 + k_1 N}.$$

At the beginning of irradiation,  $N$  is so high (strong emission) that the rate of step 1 is much larger than that of step 2; thus Eq. (2c) can be reduced to

$$-\frac{dN}{dt} = R = k_2, \quad (3a)$$

$$N = N_o - k_2 t, \quad (3b)$$

where  $N_o$  is the original concentration of the  $F^+$  center. When  $N$  is reduced to a relatively lower level after irradiation for certain times, the rate of step 1 becomes lower than that of step 2. Equation (2c) can then be reduced to

$$-\frac{dN}{dt} = R = k_1 N, \quad (3c)$$

$$N = N' \exp(-k_1 t), \quad (3d)$$

where  $N'$  is the numbers of  $F^+$  centers after a certain irradiation time when step 1 becomes the rate control step. By assuming that the PL intensity is linearly proportional to the concentration of the defect centers, the experimental results on intensity decreases can be compared to Eqs. (3b) and (3d). It can be seen from Fig. 3 that the experimental data fit the model very well.

In summary, we have investigated the PL behavior of  $\gamma$ -alumina nanopowder of 50 nm. Two relatively sharp and strong emission peaks at 3.3 and 3.6 eV and a broadband ranging between 400 and 600 nm were observed. The peaks at 3.3 and 3.6 eV were attributed to  $1B \rightarrow 1A$  and  $2A \rightarrow 1A$  transitions, respectively, to  $F^+$  centers, while the broadband was attributed to oxygen-related impurities. It was also observed that UV irradiation can remarkably decrease the intensity of the two sharp peaks, but had no effect on the broadband. The kinetics of irradiation-induced PL degradation was measured and explained by assuming that the interaction between the  $F^+$  centers and UV phonons follows a zero order reaction at the beginning and a first order reaction for the long term.

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