Letter

Structure and photoluminescence properties of strong blue-emitting alumina film developed from a liquid sol at low temperature

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ABSTRACT

Strong blue photoluminescence emission at 450 nm from alumina films prepared from an alumina precursor was observed. Photoluminescence measurements indicate that the peak intensity of the blue emission changes with the pH value of the peptizing solution, the annealing temperature and the atmosphere. The blue emission appears at a low temperature of 50 °C and reaches a maximum strength at 400 °C in an oxygen atmosphere and 600 °C in a nitrogen atmosphere. HRTEM images show that the alumina films are composed of nanoparticles with a diameter of $\leqq 10$ nm. It is believed that the observed strong photoluminescence is associated with inherent defect centers in the material, where these are related to the structure transition and transformation from the boehmite phase to the γ-alumina phase and bond cleavage.

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1. Introduction

Alumina materials have attracted much attention due to their excellent properties and associated applications [1–3]. Recently, the structural and optical properties for different alumina materials have been investigated [4–11]. Yoldas et al. reported the structural transition from boehmite to γ-alumina, where five coordinated aluminum atoms are created, and showed that the photoluminescence (PL) of the resultant γ-alumina film has a strong relationship with these five coordinated aluminum atoms [12]. Additionally, Suga and co-workers observed that the oxygen deficiency in the aluminum hydroxide used to fabricate alumina films is closely related to the formation of the five coordinated aluminum atoms [13]. Therefore, the structural transition and inner defects of alumina materials are usually important factors for photoluminescence emission. Many processes are used to fabricate alumina materials, such as the solid-state decomposition process, sol–gel and precipitation. Most of the investigations have focused on the electrical properties or electronic applications. In contrast, up to now, no systematical photoluminescence properties on alumina films developed from wet-chemical process have been studied.

During the wet process, the pH value in aqueous solution is very important because it affects the solution reaction and structural transformation [14,15]. Domingos and Vollet reported that as the pH of the aqueous solution is varied, the powder composition and phase structure of the synthesized boehmite also changes. When the pH is adjusted to 4, pure boehmite is formed. When the pH value rises to 7, the powder is composed of boehmite and gibbsite phases. At a higher pH, i.e. higher than 9, phases of both boehmite and bayerite are detected [15]. However, there has not yet been a complete investigation of blue light-emitting alumina nanoparticles and films, including the associated phase transformations and fluorescent mechanisms. In addition, it was believed that the photoluminescence and characterization behaviors of the PL band for alumina nanoparticles were strongly dependent on the structural transition and inherent defect centers in the material.

In this work, a simple method combining the aqueous solution process with a thermal treatment is proposed to develop Al_2O_3 films with strong blue emission. The effects of the thermal treatment and pH value on the structural development and optical properties of alumina films on Si wafers will be investigated. This easy and convenient route to synthesize alumina films demonstrates a new way to develop nanostructures for optoelectronic applications.

2. Experimental

Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) was dissolved in deionized water. The hydroxide was co-precipitated in NH_4OH solution at pH = 10 and then washed several times with deionized water to remove unreacted ammonia and nitrate. The precipitate was then peptized to form a precursor solution with the pH value adjusted between 2 and 6. Subsequently, the precursor was deposited on a Si wafer

by dipping to fabricate alumina thin film and then dried at 50 °C. The samples were then rapidly annealed at different temperatures in air, oxygen and nitrogen atmospheres for 20 min.

The crystalline phases were determined by X-ray diffractometry (M18XHF, MAC Science, Tokyo, Japan) measurements using the Cu $K\alpha$ radiation and a scanning rate of 10° (2θ) per min over a 2θ range of 10–70 °C. The morphology of the alumina film was obtained by transmission electron microscopy (TEM) with a JEOL 2010 instrument, operated at 200 keV. Fourier-transform infrared (FTIR) spectroscopy was performed on a PerkinElmer 100 spectrometer. The optical properties of the alumina thin films were characterized by photoluminescence (PL) at room temperature with a He–Cd light source using an excitation wavelength of 325 nm.

3. Results and discussion

3.1. Structural development of alumina films with annealing temperature

Fig. 1 shows the XRD patterns of the alumina precipitates prepared from a pH = 10 precursor and annealed in the range of 50–1000 °C. When the alumina precipitate was peptized with pH = 2 solution, Fig. 1(a) shows that only pseudo-boehmite (JCPDS No. 21-1302) was detected at 50 °C and then transformed into γ-alumina at 400 °C. In contrast, for the precipitate peptized with pH = 6 solution, the phase structure of the resultant nanoparticles was identified as pseudo-boehmite and bayerite after drying at 50 °C, as shown in Fig. 1(b). When the samples were annealed above 200 °C for 1 h, the peaks corresponding to the bayerite phase in the XRD patterns disappeared, and only peaks corresponding to pseudo-boehmite remained. When the samples were annealed
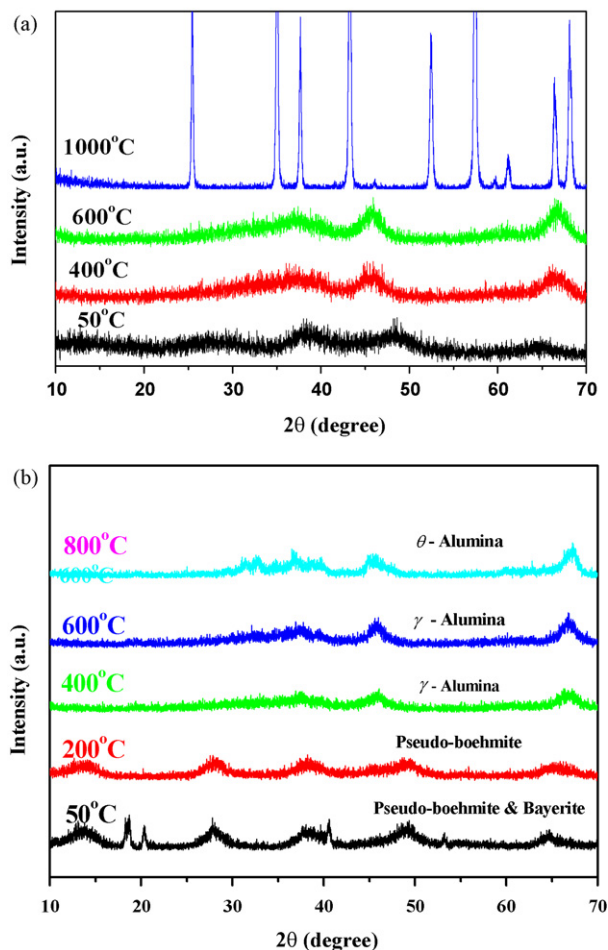

Fig. 1. XRD spectra of alumina nanoparticles peptized with a solution at (a) pH = 2 and (b) pH = 6. The samples were annealed in the range of 50–1000 °C.
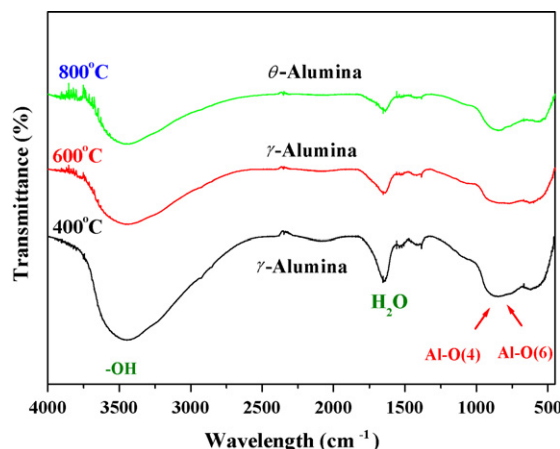

Fig. 2. FTIR spectra of alumina nanoparticles peptized with a solution at pH = 2 and annealed in the range of 400–800 °C.

at 400 °C for 1 h, γ-alumina started to develop from the alumina nanoparticles [13]. As the annealing temperature was raised above 400 °C, the phase of the alumina nanoparticles gradually transformed from γ-alumina to θ-alumina.

Fig. 2 shows the FTIR spectra of the alumina nanoparticles annealed from 400 to 800 °C for 1 h. It can be observed that the broad peak at 3300–3600 cm^{-1} significantly decreases at higher annealing temperatures. This decreased broad peak corresponds to a decreasing concentration of hydroxyl bonds as the annealing temperature is increased, which is due to the phase transformation from pseudo-boehmite to γ-alumina, and then later to α-alumina. A sufficiently high annealing temperature provides sufficient energy for the hydroxyl bond to break. The broad peak at 1650 cm^{-1} corresponds to the concentration of water molecules in the alumina nanoparticles. Similarly, this peak decreases as the annealing temperature is increased. The broad peak in the 500–1000 cm^{-1} range corresponds to different coordinates of the Al–O bonding. The nearby peaks at 800–1000 cm^{-1} are attributed to the four coordinates of Al–O. The broad peak near 600 cm^{-1} is due to the six coordinates of Al–O. In general, the γ-alumina is composed of four and six coordinated atoms, but the boehmite structure may be six coordinated aluminum atoms. From Fig. 2, the phase transition of the alumina nanoparticles from boehmite to γ-aluminum is clearly described by the transition of peaks corresponding to six coordinates to peaks corresponding to four coordinates. Fig. 3 shows the TEM image of the alumina films prepared from a precursor with pH = 2 annealed at 200 °C. The TEM micrograph in Fig. 3(a) shows that the film displayed plate-like morphology. A high-resolution TEM image in Fig. 3(b) further reveals that the alumina films are composed of pseudo-boehmite alumina nanoparticles with a particle size less than 10 nm.

3.2. Effects of annealing atmosphere

Fig. 4 shows the XRD patterns of pH = 2 alumina films subjected to rapid thermal annealing (RTA) treatment at 400 °C for 20 min under different annealing atmospheres of air, oxygen, nitrogen and 5% H_2–95% N_2. No obvious change in phase was detected for alumina films annealed in different atmospheres. In Fig. 4(a), peak A corresponds to the (4 0 0) plane of γ-alumina, while peak B corresponds to the (0 5 1) plane of pseudo-boehmite. It was assumed that the relative intensity between the pseudo-boehmite and γ-aluminum films would be affected by different annealing atmospheres. It is shown in Fig. 4(b) that the A/B ratio increases when annealed in oxygen, indicating that oxygen promotes the phase transformation to γ-alumina. Furthermore, with increasing
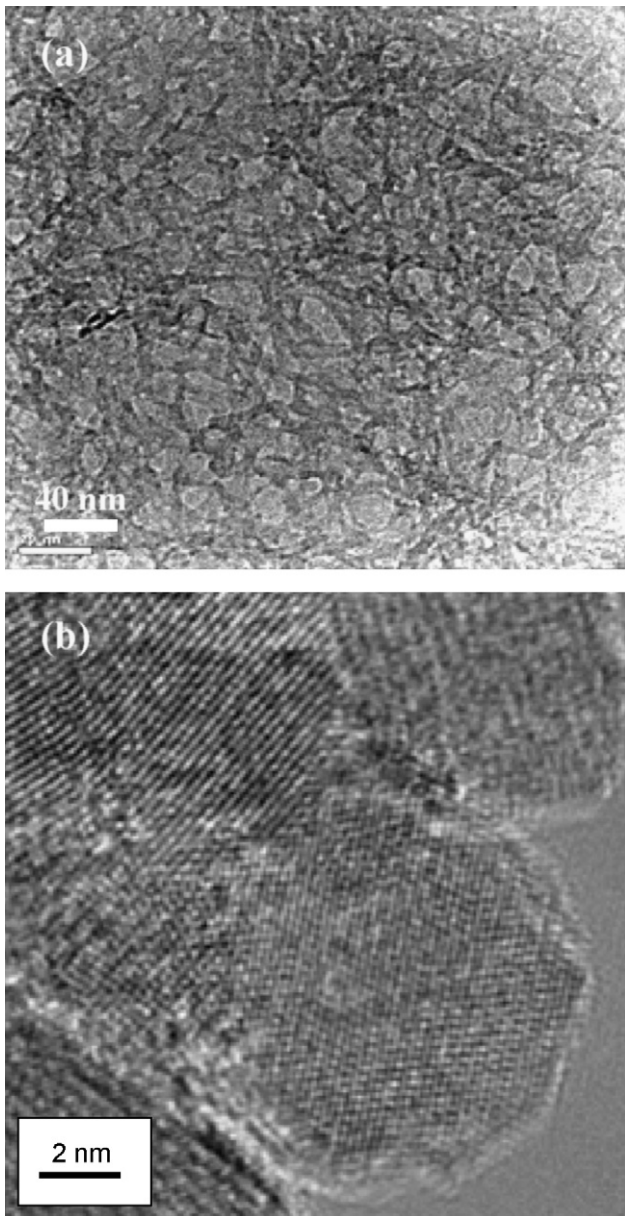
Fig. 3. (a) TEM micrograph and (b) HRTEM image of an alumina film deposited from a pH = 2 precursor solution and annealed at 200 °C.

annealing temperature, the OH band in the pseudo-boehmite structure tends to break, and the boehmite phase (an octahedrally coordinated structure) is thus transformed into γ-phase aluminum oxide (a tetrahedrally coordinated structure). During the phase transformation, pentahedrally coordinated aluminum is favored, along with the occurrence of singly ionized oxygen vacancies, which are regarded as the F$^+$ center.

3.3. Photoluminescence properties of alumina films

Fig. 5(a) shows the PL spectra of alumina films fabricated from the pH = 2 precursor sols and then annealed at 50–800 °C in an oxygen environment. As depicted by Fig. 5(a), a PL peak at a wavelength of 450 nm was detected for the as-deposited alumina films at 500 °C. By increasing the temperature to 400 °C, as the dehydration proceeds, the structure evolves through a series of disordered states during the phase transformation from pseudo-boehmite to the γ-phase, as demonstrated in Fig. 1. In this condition, it is believed
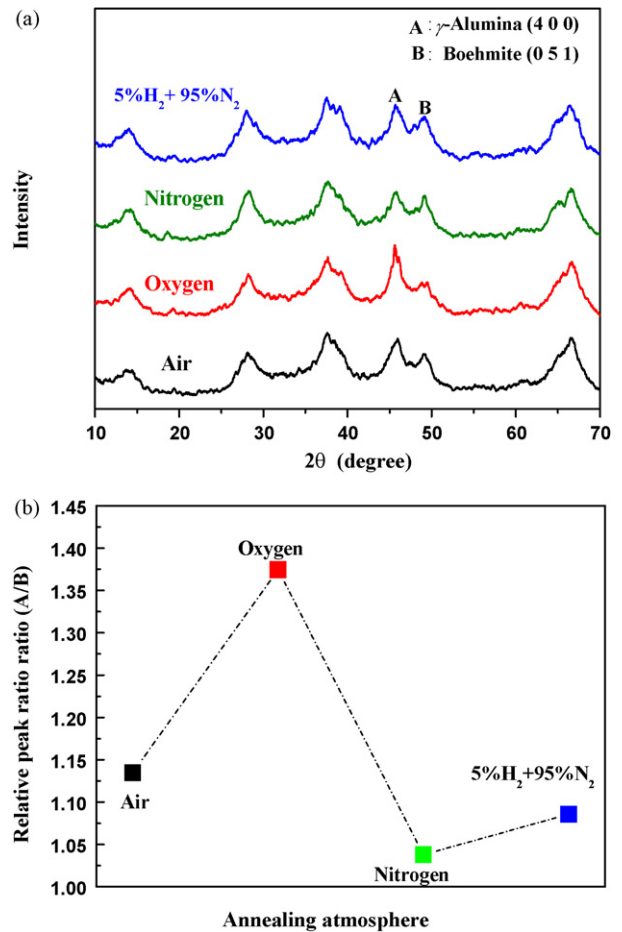

Fig. 4. (a) XRD spectra of alumina films annealed in different atmospheres and (b) the corresponding intensity ratio of the γ-alumina to boehmite phase.

that a certain transient phase exists between the six-coordinate pseudo-boehmite structure and the four-coordinate γ-phase structure, which causes five-coordinated aluminum sites and singly ionized oxygen vacancies (F$^+$ centers) to be generated. Therefore, an ultra-strong blue emission could be observed. At a higher temperature, i.e. 600 °C, although the position of the blue emission remains unchanged, it was found that the peak intensity weakened compared to that for the sample annealed at 400 °C. This indicates that the defect density of the main defects (F$^+$ centers) responsible for blue emission decreases with increasing annealing temperature up to 600 °C. This means that the F$^+$ centers are reduced due to compensation in an O$_2$ atmosphere. At a higher annealing temperature, above 600 °C, the compensation from the oxygen atmosphere is more apparent, and the phase transformation from γ to θ is induced, which not only leads to the reduction of the F$^+$ centers but also to the disappearance of the blue emission for the samples annealed above 800 °C. Furthermore, it was noted that the blue emission of the post-annealed alumina films is not only dominated by the annealing temperature but also the annealing atmosphere because the PL emission is very sensitive to defect type. As illustrated in Fig. 5(b), it was observed that the strongest blue emission of the alumina films appears at 600 °C instead of 400 °C when the alumina films were annealed in a N$_2$ atmosphere. This can be attributed to the fact that the singly charged oxygen vacancies (F$^+$ centers) are not compensated, and they can be further generated in the nitrogen atmosphere at 600 °C in a N$_2$ atmosphere where the γ-alumina remains.

For comparison, Fig. 6 shows the relative peak intensity of the blue emission for the films developed from precursors with
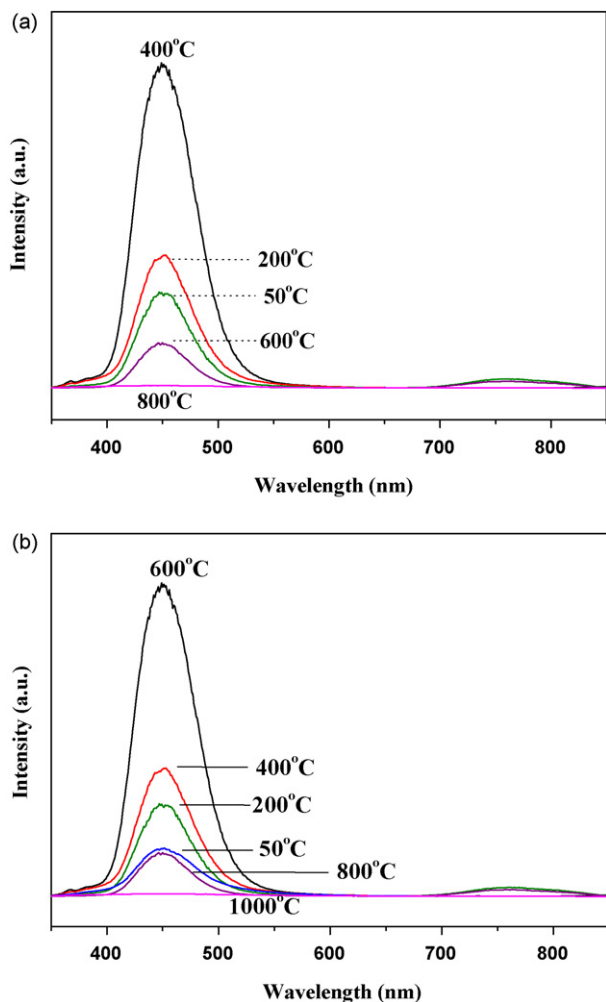
Fig. 5. PL spectra of alumina films fabricated from a pH = 2 precursor solution and annealed in the range of 50–800 °C in (a) oxygen and (b) nitrogen atmospheres.

Fig. 6. PL spectra comparison of alumina films deposited from solutions of pH = 2 and 6. Both films were annealed at 50 °C.

4. Conclusion

In summary, a low-temperature synthetic route was developed to form alumina thin films on Si wafers. A strong blue photoluminescence emission at 450 nm was observed from alumina films prepared from the alumina precursor. The peak intensity of the strong blue emission depends on atmosphere, annealing temperature and the pH value of the solution. Photoluminescence measurements indicated that the blue emission appears at a low temperature of 50 °C and reaches a maximum strength at 400 °C in an oxygen atmosphere and 600 °C in a nitrogen atmosphere.

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pH = 2 and 6 at 50 °C. The former film is composed of only pseudoboehmite, but in the latter (pH = 6), the XRD in Fig. 1(b) shows that the alumina nanoparticles consist of pseudo-boehmite and bayerite phases. The original source of the blue emission is mainly the debonding of the pseudo-boehmite phase and not the bayerite phase. Therefore, as illustrated in Fig. 6, at 50 °C, a weaker blue intensity was detected from the films prepared from the pH = 6 solution. However, with increasing annealing temperature, the PL spectra of both films present a similar trend. The maximum peak inten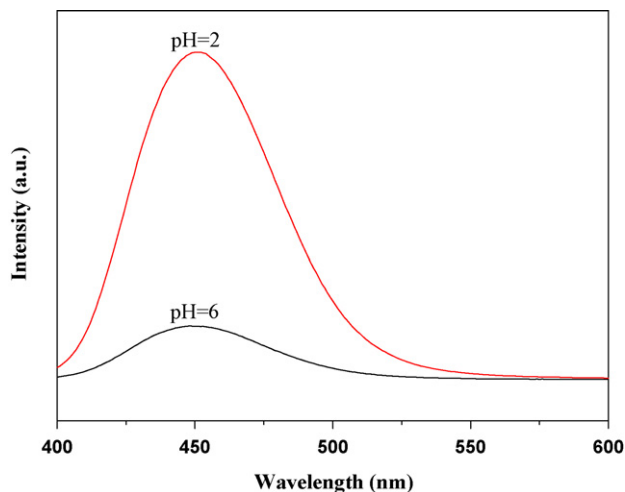sity occurs at 400 °C in an oxygen atmosphere.