

Tris-(8-hydroxyquinoline) aluminum nanoparticles prepared by vapor condensation

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Tris-(8-hydroxyquinoline) aluminum (AlQ₃) spherical nanoparticles of the average size varying from 50 to 500 nm were synthesized by vapor condensation. The surface of the nanoparticles is quite sleek and smooth like that of pearls. The x-ray diffraction patterns reveal that the nanoparticles have an amorphous structure. The chemical bonding of AlQ₃ is preserved in the nanoparticles even after evaporation at 410 °C. The photoluminescence spectra of the nanoparticles show a broadened peak varying from 4500 to 7000 Å, with the maximum intensity at about 5380 Å. The maximum intensity increases as the particle size decreases, owing to the large specific surface area. © 2003 American Institute of Physics. [DOI: 10.1063/1.1591249]

In the past decades, the trend of technological development in electronics has been to make the device smaller and more powerful. This requires that each of the constituent materials be operated more efficiently and cost effectively. Since the discovery of the buckyball¹ and carbon nanotubes,² a great number of nanostructures such as nanoparticles, nanowires, and nanorods have been produced. The prescribed size, composition, and homogeneity should be well controlled to explore new applications such as field emission sources,³ single electron transistors,⁴ chemical and biological sensors,⁵ quantum dot lasers,⁶ and other optoelectronic devices.⁷ Though the nanoparticles for light emitting devices have been investigated for many years, they are all made of inorganic materials. Inorganic nanoparticles can be prepared by various methods such as chemical vapor deposition⁸ or molecular beam epitaxy,⁹ by which the nanoparticles are fabricated at high temperatures and controlled by the lattice mismatch.¹⁰ Since the first efficient electroluminescence of organic light emitting diode (OLED) with a low driving voltage was reported by Tang and VanSlyke in 1987,¹¹ tris-(8-hydroxyquinoline) aluminum (AlQ₃) has become one of the most important emitting materials for the OLED devices. It is then of great interest to prepare organic nanostructures due to many properties that may offer applications in nano-optoelectronic devices.^{12,13} In this work, the AlQ₃ nanoparticles were first synthesized by vapor condensation. The surfaces of the nanoparticles are found quite sleek and smooth like those of pearls. The photoluminescence (PL) spectra of AlQ₃ nanoparticles with different sizes are also measured for comparison.

The experimental setup for the vapor phase condensation of AlQ₃ is shown in Fig. 1. The AlQ₃ powder (TCI Ltd., T1527) was placed in a graphite boat, and the silicon substrate was placed under a liquid nitrogen-cooled trap. The

distance between the graphite boat and the substrate d was adjustable. An argon flow of pressure P_{Ar} was then launched into the chamber. The temperature of the boat T was regulated by a power supply and a K-type thermocouple. AlQ₃ nanoparticles were grown directly on the silicon substrate. The particle size was found to depend on P_{Ar} , T , and d .

Figure 2 shows the field emission gun scanning electron microscopy (FEGSEM) images of AlQ₃ nanoparticles. For instance, the size of AlQ₃ nanoparticles fabricated at $P_{Ar} = 133$ Pa, $T = 410$ °C, and $d = 10$ cm is about 50–100 nm, as shown in Fig. 2(a). As can be seen from the figure, the spherical particles tend to cluster together as reticular networks. At a higher pressure $P_{Ar} = 4$ kPa but with the same T and d , the size of AlQ₃ nanoparticle is increased to about 100–300 nm, as displayed in Fig. 2(b). When the pressure is increased even higher, e.g., $P_{Ar} = 13.3$ kPa and the distance is increased to $d = 20$ cm, most nanoparticles become isolated and have an average size of about 500 nm. The surface is quite sleek and smooth like that of pearls, as shown in Fig. 2(c). Moreover, the AlQ₃ nanoparticles remain stable in the FEGSEM for more than 3 h without any change of the surface morphology, indicating an excellent thermal stability.

The experimental results shown in Figs. 2(a)–2(c) indicate that the size and configuration of the particles are dependent on the argon pressure P_{Ar} , the distance d , and the

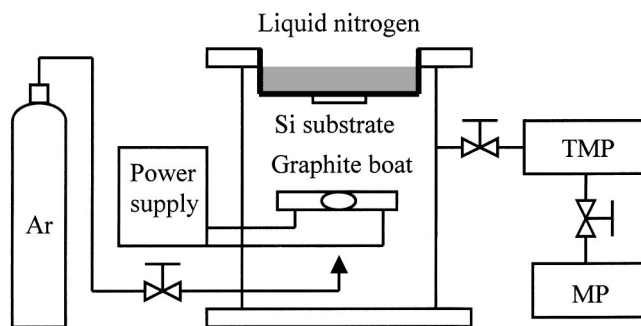
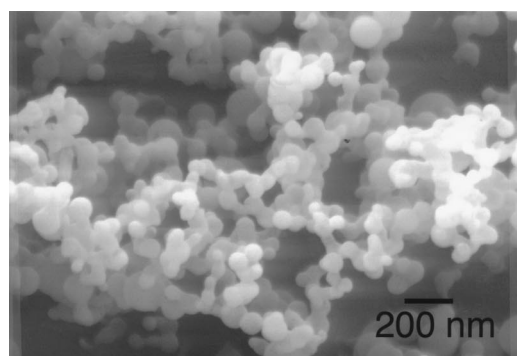


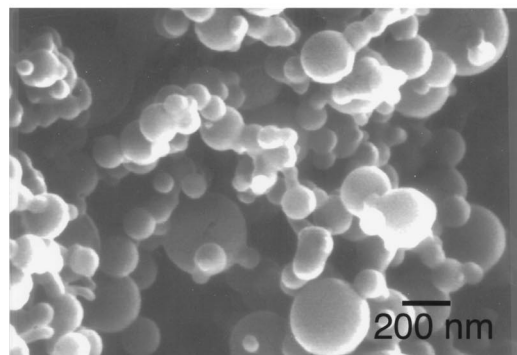
FIG. 1. Experimental setup of the vapor condensation system.

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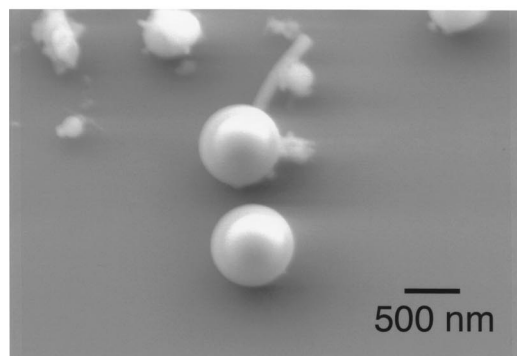
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(a)



(b)



(c)

FIG. 2. FEGSEM images of AlQ_3 nanoparticles prepared under different conditions. (a) $P_{\text{Ar}}=133$ Pa, $T=410$ °C, and $d=10$ cm, (b) $P_{\text{Ar}}=4$ kPa, $T=410$ °C, and $d=10$ cm, and (c) $P_{\text{Ar}}=13.3$ kPa, $T=400$ °C, and $d=20$ cm.

boat temperature T .^{14,15} For simplicity, the boat temperature T is set at 410 °C, and the dependences of particle size on P_{Ar} and d are considered separately. At fixed T and d , the average size of particles increases significantly and the range of size distribution becomes larger when P_{Ar} increases, as shown in Fig. 3(a). Similarly, at fixed T and P_{Ar} , the average size also increases when d increases, as shown in Fig. 3(b). In general, the boat temperature should be controlled at 400–410 °C in order to form the nanoparticles when P_{Ar} is higher than 133 Pa. When the pressure is lower than 133 Pa, the boat temperature must be carefully controlled. For example, when $P_{\text{Ar}}=13.3$ –133 Pa, nanoparticles can be obtained only at $T=405$ –410 °C.

Although the dependence of the particle size on P_{Ar} and d has been reported for inorganic nanoparticles,¹⁴ it is surprising that the AlQ_3 molecule with a molecular weight much larger than that of Ar atom also exhibits similar behav-

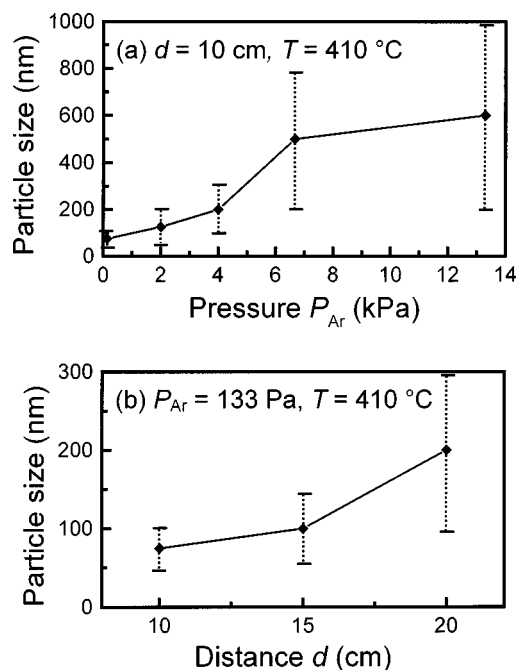


FIG. 3. (a) Relationship between the particle size and argon pressure P_{Ar} , and (b) relationship between the particle size and separation distance d .

ior. This can be understood by the collision mechanism during the evaporation. The AlQ_3 molecules collide with the Ar atoms and gradually lose their energy. Since the substrate is cooled down to -196 °C by liquid nitrogen, it is believed that this temperature is low enough to stop nanoparticles from coalescing on the substrate. The particle size is related to the energy loss, which can be realized by the ratio between the atomic weights of evaporated material and Ar.¹⁵ For those inorganic materials whose atomic weights are comparable to that of Ar, their kinetic energy can be reduced by colliding with the Ar atoms. For instance, the atomic masses of Si and Ar are 28 and 40, respectively. The ratio of the atomic masses is 0.7. The molecular weight of AlQ_3 is 459, and the ratio becomes about 11.5. This value is much greater than that for Si, and the particle size should be larger under the same condition.¹⁵ Previously, the sizes of Si nanoparticles prepared at $P_{\text{Ar}}=133$ Pa and $d=10$ cm are about 4–8 nm.¹⁶ The sizes of the AlQ_3 nanoparticles prepared in this study under the same condition are about 50–100 nm. These results agree with the prediction.

AlQ_3 powder may exist in a variety of phases, such as α , β , and γ phases,^{17,18} and their x-ray diffraction (XRD) patterns are quite different after evaporation. From the XRD patterns illustrated in Fig. 4, the AlQ_3 powder has good crystallinity before evaporation, but the nanoparticles become amorphous after sublimation. To check if the AlQ_3 molecules are decomposed during evaporation, the chemical bondings of AlQ_3 in the nanoparticles, thin film, and original powder were examined by Fourier-transform infrared spectrum (FTIR). The FTIR test samples were prepared by growing AlQ_3 nanoparticles directly on a potassium bromide (KBr) pellet. A thin film of thickness 1200 Å was also deposited on another KBr pellet at a pressure of 1.33×10^{-3} Pa and a deposition rate of 3 to 5 Å/s controlled by a quartz monitor. Except for the peaks due to CO_2 and H_2O , all the other absorption peaks between 600 and 2000 cm^{-1}

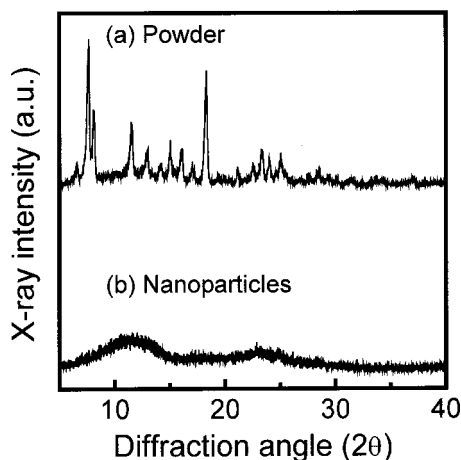


FIG. 4. XRD patterns of AlQ₃: (a) powder before evaporation and (b) nanoparticles of the size 50–100 nm.

are found in good agreement with the reported results.¹⁹ The absorption peaks of the nanoparticles and the thin film are consistent with those of the AlQ₃ powder, indicating that the bonding of the molecule is preserved even after evaporation at 410 °C.

The PL spectra were obtained by exciting with a He–Cd laser of a wavelength 325 nm and a power 50 mW. The He–Cd laser beam was focused on an area of about 1 mm² to ensure that all the samples had a similar irradiated area. The PL spectra of the AlQ₃ nanoparticles with diameters of 50–100 and 100–300 nm are shown in Figs. 5(a) and 5(b), respectively. In addition, that of an AlQ₃ thin film of a thickness 1200 Å is also displayed in Fig. 5(c) for reference. The PL peaks show the same maximum intensity at about 5380 Å and are broadened ranging from 4500 to 7000 Å. The

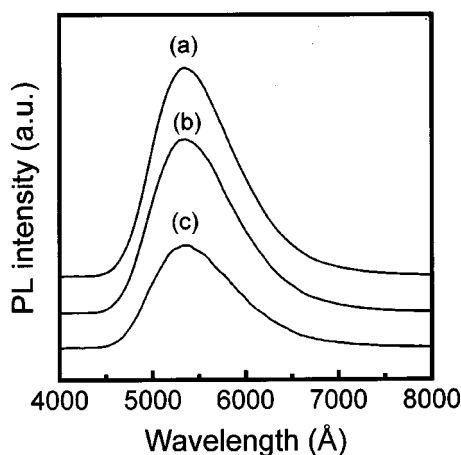


FIG. 5. PL spectra of AlQ₃: (a) nanoparticles of the size 50–100 nm, (b) nanoparticles of the size 100–300 nm, and (c) thin film of a thickness 1200 Å.

maximum PL intensities of the nanoparticle samples are higher than that of the thin film, and the maximum PL intensity increases as the particle size decreases. It is generally agreed that the specific surface area increases as the particle size decreases.^{14,15} For ultrafine particles, they have very large specific surface area and surface energy. The larger specific surface area of the smaller nanoparticles increases the optical absorption and further enhances the intensity of luminescence. It is noted that the chemical bonding and surface morphology of the AlQ₃ nanoparticles are preserved after aging in air at room temperature for more than one week, according to the FTIR spectra and FEGSEM images. However, degradation of the PL intensity occurs, and the degradation is more pronounced for the nanoparticles than for the thin film due to the larger specific surface area.

In summary, AlQ₃ nanoparticles of the average size varying from 50 to 500 nm were synthesized by vapor condensation. The nanoparticles are spherical and have an amorphous structure. The chemical bonding is preserved after evaporation. The larger specific surface area of smaller nanoparticles increases the optical absorption and further enhances the intensity of photoluminescence. Related work will be of great interest for future study.

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