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Growth of β-Ga_2O_3 nanoparticles by pulsed laser ablation technique

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ABSTRACT This work investigates pulsed laser ablation for Ga_2O_3 nanoparticles. Nanoparticles with diameters of 10 to 500 nm were deposited on silicon substrates in large quantities, by KrF excimer laser ablation of a GaN (99.99% purity) target in high purity nitrogen (99.9995%) background gas at room temperature, without a catalyst. The particle size and phase structure of the as-deposited nanoparticles are examined by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), and selected-area electron diffraction (SAD). FE-SEM images show that the nanoparticles aggregate to form micron-size nanoclusters at chamber pressures of 1 and 5 Torr. On the other hand, nanoparticles aggregate with chain-like nanostructures, are synthesized at high chamber pressures (≥ 10 Torr). TEM images further reveal that chain-like nanostructures are formed by the aggregation of individual spherical and ellipsoidal nanoparticles. Photoluminescence measurement shows stable and broad blue emission at 445 nm.

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1 Introduction

The synthesis of nanoparticles is of great importance because interesting and unique physical and chemical properties are exhibited when the size of nanoparticles are of the order of the Bohr exciton, due to the quantum confinement effect. New potential applications in nanodevices such as light emitting diodes, resonant tunnelling devices, lasers, catalysis, and gas sensors, etc. are therefore under intense research. Considerable efforts have been made to synthesize many nano-material systems such as carbon, oxides, nitrides, carbides, and semiconductors. Among them, Ga_2O_3 can be used for a variety of applications including transparent conducting oxide [1, 2], an optical emitter for UV light [3], and high temperature gas sensors [4]. Monoclinic gallium oxide (β-Ga_2O_3) is a wide bandgap semiconductor material ($E_g \approx 4.9$ eV) [5] and it exhibits conduction [6, 7] and luminescence properties [3]. β-Ga_2O_3 is stable at high temperatures and exhibits n-type semiconductor properties when synthesized under reducing conditions [8]. Various techniques have been employed to synthesize 1D Ga_2O_3 nanowires and nanotubes, such as thermal oxidation [8], arc-discharge [9], laser ablation [10], and carbothermal reduction [11]. Recently, the laser ablation technique has been successful in synthesizing semiconductor nanoparticles and nanowires including silicon [12], germanium [13], II-VI [14] and III-V [15] compounds which require the assistance of either a template or catalyst and most often occur at high temperatures. However, no literature has reported the synthesis of Ga_2O_3 nanoparticles by laser ablation at room temperature. In this study, we report reactive laser ablation of a GaN target in a purified N_2 atmosphere for the synthesis of Ga_2O_3 nanoparticles in bulk quantity at room temperature. This method provides a simple and low temperature synthesis of Ga_2O_3 nanoparticles, which requires neither a metal catalyst nor the effect of nanometer-sized confinement. The experimental results highlight that by varying the chamber pressures, the size, shape, and degree of aggregation of the nanoparticles can be significantly altered by pulsed laser ablation techniques at room temperature.

2 Experimental

A pressed GaN powder target (purity 99.99%) and N_2 gas (purity 99.9995%) were used for the synthesis of the Ga_2O_3 nanoparticles. Figure 1 depicts schematics of the laser and chamber setup used in the experiment. A KrF excimer laser (Lextra 50, LAMBDA PHYSIK) operating at a wavelength of 248 nm, pulse duration of 23 ns, and with pulsed energies ranging from 100 to 200 mJ per pulse was used to ablate the GaN target. The beam area on the target is $0.04\ \text{cm}^2$. The target is rotated about its axis to ensure uniform ablation of the target. Target to substrate distance can be varied between 1 to 3 cm to operate in different pressure regions. A P-type silicon substrate with (100) orientation was cleaned with acetone and IPA and placed in a high vacuum chamber. The chamber was pumped down to a base pressure of 3.8×10^{-5} Torr and purified N_2 gas was released into the chamber to maintain 1 to 100 Torr chamber pressures during laser ablation. The collected nanoparticles on the silicon substrate were characterized by, an X-ray diffractometer (XRD, Rigaku) with Cu K_α radiation, transmission electron microscopy (TEM, JEM 2010), field emission scanning elec-

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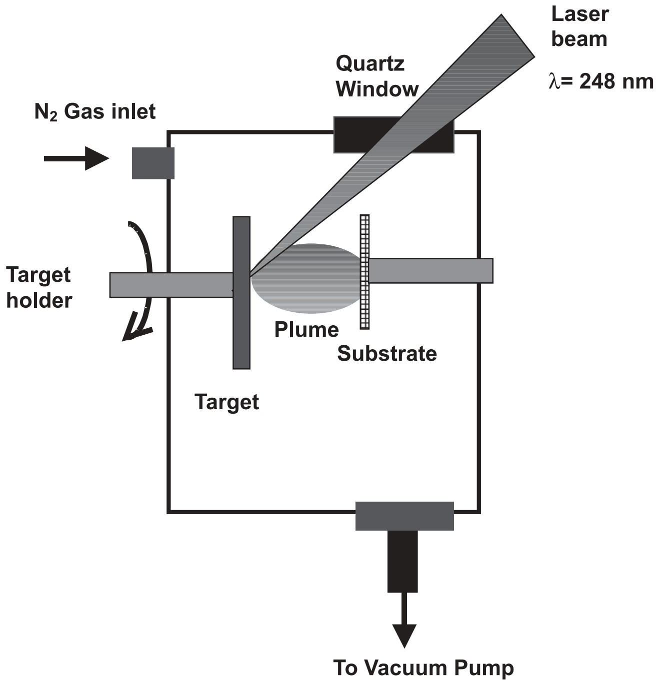

FIGURE 1 Schematic diagram of the experimental setup for the synthesis of Ga_2O_3 nanoparticles

tron microscopy (FE-SEM, JOEL JSM 6340F), and room temperature photoluminescence spectroscopy.

3 Results and discussion

During laser ablation of the GaN target, only the chamber pressure is varied, other parameters such as laser fluence, repetition rate, and deposition time were kept as constants. Figure 2 shows a typical X-ray diffraction pattern of the as-deposited nanoparticles synthesized at a 10 Torr chamber pressure and at a laser fluence of 4.25 J/cm^2. The diffraction peaks can be indexed as a monoclinic phase Ga_2O_3 (JCPDS Card 11-0370). The lattice constants calculated from the pattern are $a_0 = 5.80$ Å, $b_0 = 3.04$ Å, $c_0 = 12.23$ Å, and $\beta = 103.42°$ for Ga_2O_3. These values are in good agreement with published values [16]. However, the relative intensity is different, for which the strongest peaks of bulk Ga_2O_3 powder are (004), $(10\bar{4})$, (200), (111), and $(12\bar{2})$, whereas for β-Ga_2O_3 nanoparticles, the strongest peak is only $(11\bar{3})$.

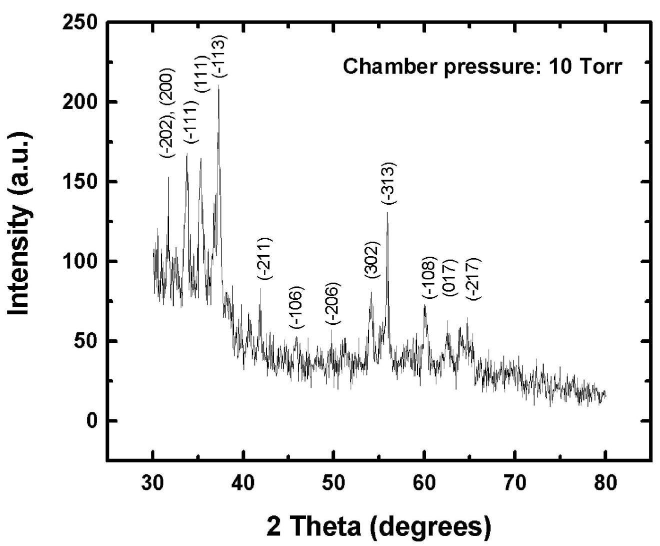

FIGURE 2 XRD pattern recorded on the as-deposited Ga_2O_3 nanoparticles at 10 Torr chamber pressure

The surface morphologies of the laser-synthesized nanoparticles were characterized by field emission scanning electron microscope (FE-SEM). Figure 3 depicts the shapes and surface morphologies of the nanoparticles grown at different chamber pressures. SEM observation reveals an aggregate of nanocrystals. Large and irregular shaped nanoclusters were formed at 1 and 5 Torr chamber pressures (see Fig. 3a and b). With increasing chamber pressures, nanoparticles with chain-like nanostructures were formed randomly and abundantly on the substrate at 10 and 100 Torr as shown in Fig. 3c and d respectively. The shape and sizes of the nanoparticles were found to be affected by the chamber pressures during laser ablation of the target. At higher magnification, Fig. 3e and d further illustrate that individual spherical and ellipsoidal nanoparticles aggregated one-dimensionally at 10 and 100 Torr chamber pressures to form nanochains. It is understood from previous literature findings that the formation of the nanoparticles on the substrate at room temperature is attributed to the condensation of the species emitted from the target in the ablation plume. However, it is of considerable

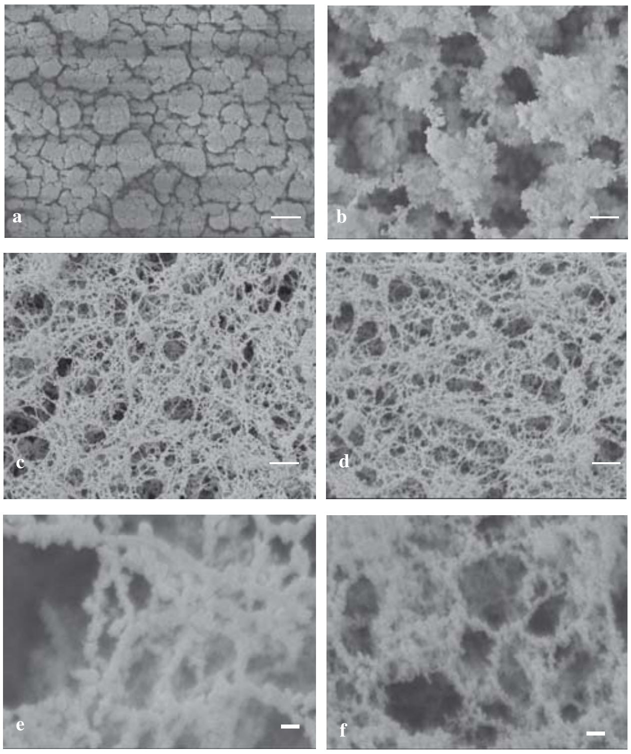

FIGURE 3 FE-SEM images of Ga_2O_3 nanoparticles grown at (**a**) 1 Torr, (**b**) 5 Torr, (**c**) 10 Torr, (**d**) 100 Torr, chamber pressures on silicon substrate. Scale bar is 1 μm. Higher magnification of FE-SEM images of Ga_2O_3 nanoparticles grown at (**d**) 10 Torr, (**e**) 100 Torr chamber pressures. Scale bar is 100 nm. A laser fluence of 4.25 J/cm^2, repetition rate of 10 Hz, and deposition time of 10 minutes were adopted

interest that the shape, size, and degree of aggregation of the individual nanoparticles were altered by laser ablation at different chamber pressures at room temperature. Furthermore, no in situ or post annealing treatment of the samples was performed to change the surface morphologies of the nanoparticles. This result can be attributed to the fact that low chamber pressures result in faster and bigger plume expansions due to the lower resistance of the ambient gas. Hence, less collisions take place between the ejected species from the target and nitrogen gas molecules in the chamber, and this results in growth and greater aggregation of the larger nanoclusters. On the other hand, due to the sufficiently long residence time of the ejected species in the gas phase, high background pressure, and higher collision probability between the ejected species and nitrogen gas molecules, it is proposed that the nanoparticles agglomerate to a lesser extent to form chain-like nanostructures.

A low magnification TEM image of the nanoparticles with chain-like nanostructures synthesized at a 100 Torr chamber pressure is presented in Fig. 4a. It is obvious that the growth of the nanochains proceeds non-uniformly with lengths up to tens of micrometers. The TEM image is also in good agreement with the FE-SEM image whereby it shows that the chain-like nanostructures are formed by the coalescence of individual nanoparticles, which are not perfectly spherical. The HRTEM image and SAD inset in Fig. 4b show the crystalline nature of the nanoparticles, surrounded by amorphous layers. The HRTEM image also illustrates that individual spherical nanoparticles are coalesced together to form the chain-like nanostructures with (100) atomic planes. The diffraction pattern analysis and lattice spacing of 0.55 nm revealed that the nanoparticles consist of Ga_2O_3, with a monoclinic structure. EDX analysis of the nanoparticles also indicates the presence of gallium and oxygen atoms. The growth of the gallium oxide nanoparticles may be attributed to the thermal decomposition of GaN upon laser irradiation of the GaN target with KrF excimer laser ($\lambda = 248$ nm). GaN decomposes thermally via the following possible reactions:

$$4\mathrm{GaN(s)} \rightarrow 4\mathrm{Ga(l)} + 2\mathrm{N_2(g)} \tag{1}$$

$$4\mathrm{Ga(s)} + 3\mathrm{O_2(g)} \rightarrow 2\mathrm{Ga_2O_3(s)} \tag{2}$$

Here, the decomposition of GaN proceeds via a photochemical laser ablation mechanism. The photon energy of the laser beam of about 4.9 eV is sufficient to break the chemical bonds between gallium and nitrogen. As a result, the Ga metal will react with oxygen present in the chamber to form Ga_2O_3. Due to the higher combinability of gallium with oxygen than with nitrogen, the formation of a Ga_2O_3 phase results. A possible source for oxygen may be the presence of residual oxygen in the N_2 flow. The adherence of the Ga_2O_3 nanoparticles with one dimensional chain-like nanostructures is not fully understood. Briefly, we propose that the unique morphology of the nanochains may be attributed to a vapor–solid (VS) process [17]. Further studies are required to fully understand the growth of the coalesced nanochains and some work on this is now in progress.

The photoluminescence (PL) spectra were excited with the 325 nm line of a 20 mW He-Cd laser. Figure 5 shows

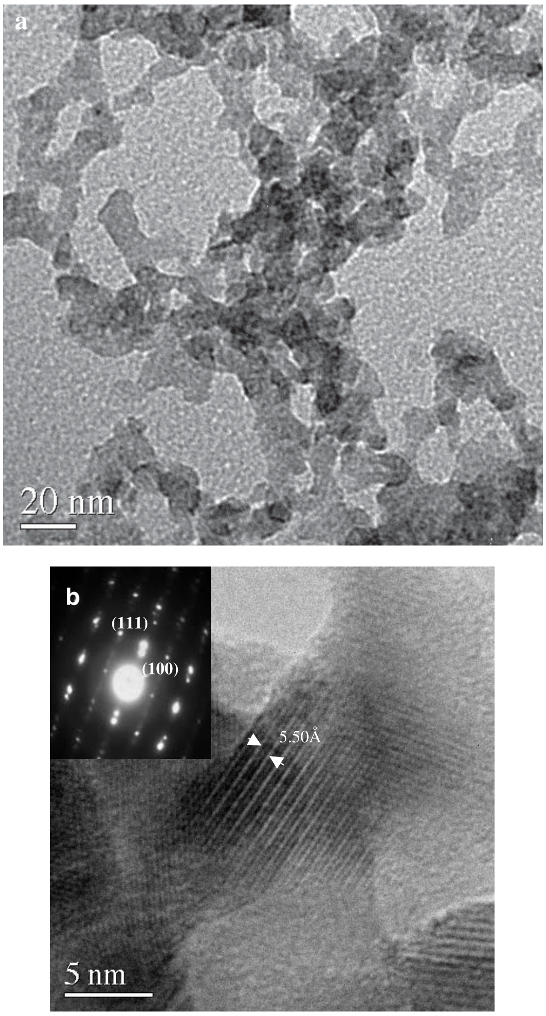

FIGURE 4 **a** Low magnification TEM image of Ga_2O_3 nanoparticles grown at a 100 Torr chamber pressure, at a repetition rate of 10 Hz, deposition time of 10 minutes, and laser fluence of 4.25 J/cm^2, and **b** HRTEM image of the Ga_2O_3 nanoparticles and corresponding selected area electron diffraction pattern (*inset*)

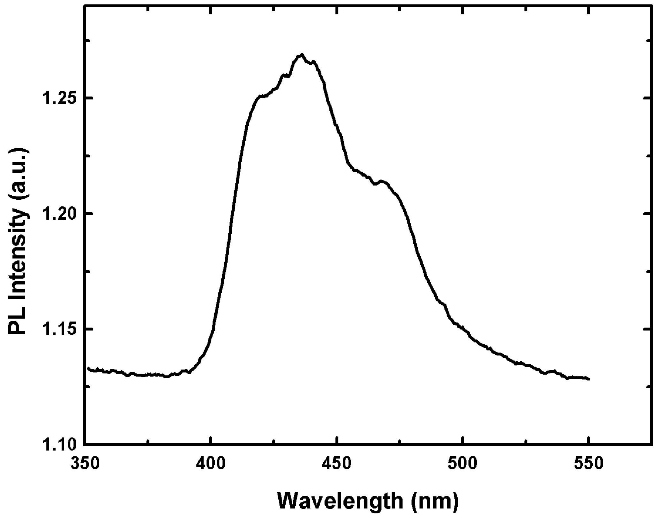

FIGURE 5 Room temperature PL spectra of Ga_2O_3 nanoparticles synthesized at 10 Torr chamber pressure, under 325 nm excitation

the PL spectra of bulk Ga_2O_3 nanoparticles. The emission at 445 nm indicates a blue shift of 30 nm compared with the PL feature peak 475 nm of Ga_2O_3 powder. The blue shifts of Ga_2O_3 nanoparticles can be ascribed to the quantum confinement effect. The mechanism of the blue emission of the Ga_2O_3 originates from the recombination of an electron on the donor by oxygen vacancies and a hole on the acceptor by gallium vacancies [7]. An electron in a donor band is captured by a hole on an acceptor to form a trapped exciton, which recombines radiatively and emits a blue photon. Oxygen vacancies have been recognized as being responsible for the donor band in Ga_2O_3, while the acceptors can be formed by gallium vacancies or gallium-oxygen vacancy pairs [7, 18, 19]. By this method, only 3000 laser pulses were employed to grow Ga_2O_3 nanoparticles for an area of 1 cm^2. If a laser with a high repetition rate of up to 1 kHz is chosen, ultra-pure Ga_2O_3 nanomaterials can be growth in a few seconds by laser ablation techniques. Laser ablation is proven to be an effective and simple technique for the high speed and high purity growth of nano-materials.

4 Conclusions

In summary, Ga_2O_3 nanoparticles with monoclinic structures were successfully synthesized at room temperature, by pulsed laser ablation of a GaN target in a high purity nitrogen gas ambient. Varying the chamber pressures can significantly control the size, shape, surface morphologies, and the degree of aggregation of the nanoparticles. The results clearly demonstrate that diameters of the nanoparticles decrease at higher chamber pressures, and also to a lesser extent, with aggregation. The aggregation of the nanoparticles also proceeds one dimensionally to form nanochains when the chamber pressure is increased. TEM results indicate that the spherical and ellipsoidal nanoparticles typically have diameters of 10 to 20 nm when grown at 100 Torr chamber pressures. The PL spectrum of the nanoparticles shows a strong emission peak at 445 nm which indicates a blue shift of 30 nm for Ga_2O_3 nanoparticles under excitation at 325 nm at room temperature. The fabrication and characterization of Ga_2O_3 nano-field effect transistors is also currently in progress.

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