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Anti-reflective and hydrophobic surface of self-organized GaN nano-flowers

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ABSTRACT

GaN nano flowers were grown on various commercial substrates by a simple catalyst free chemical vapor deposition (CVD) technique. The size and shape of the nanostructures were characterized by scanning electron microscopy (SEM). The influence of the substrate, growth temperature, and ammonia flow rate on the size and shape of the nano-flowers were investigated along with their anti-reflective and hydrophobic properties. The normal incident reflectivity measurements carried out on the nano structures showed very low (5%) reflectivity. The wettability of the surface investigated by the static contact angle of water droplet revealed their hydrophobic nature with a large contact angle of about 145°. These results on catalysis-free nanostructures would be useful for anti-reflective surfaces/coatings in solar cell applications.

1. Introduction

Wurtzite GaN with wide and direct bandgap is suitable for various opto-electronic applications such as, laser diodes (LDs) and light emitting diodes (LEDs) [1,2]. Semiconductor nano structures without catalyst have been widely grown by molecular beam epitaxy (MBE) [3,4] as against the catalytic growth using chemical vapor deposition (CVD). In the presence of a catalytic particle the growth mechanics is explained by the celebrated vapor–liquid–solid process [5,6]. Atoms of the catalyst particle incorporated in to the nanostructures act as impurities hence there is lot of interest for non-catalytic growth [7]. III-Nitride compound semiconductors with high quantum efficiency [8] have attracted a lot of research interest in nitride based anti-reflective coatings in solar cells [9,10]. Low aspect ratio GaN nanorods have been reported to have graded refractive index with reduced reflection losses [11,12]. Wettability of surfaces is another important property which can affect the nucleation sites leading to unpredicted density and morphology of nanostructures [13]. Hydrophobic property of GaN surfaces helps in sensing polar liquids and gases depending on how much hydrophilic or hydrophobic the surface is. Nanostructures with large surface area can increase the sensing ability and depending on the amount of surface oxidation the wettability is also tunnable [14]. In the present work, an attempt has been made to grow self-organized GaN nano-flowers with anti-reflective and hydrophobic properties. The influence of growth parameters on the morphology has been investigated. The normal incidence reflectance studies have been carried out to demonstrate their use in anti-reflective surfaces. As demonstrated GaN nanostructures grown without catalysis by a simple thermal CVD reactor can be used for anti-reflective surfaces in solar cell applications.

2. Experimental

GaN nanostructures were grown on three different commercial substrates without any catalysis. The substrates include (0 0 1) oriented silicon, Ga-face terminated epitaxial p-GaN film on *c*-plane sapphire (about 5 μm in thickness) and Al-face terminated epitaxial AlN film on *c*-plane sapphire (about 1 μm in thickness). High purity Ga-metal and ammonia (NH_3) gas were used as source and the growth temperature was 1273 and 1323 K while the ammonia flow rate was 25 and 50 standard cubic centimeters per minute (SCCM). The substrates were placed to cover distances up to 25 mm from the gallium source. Before the start of the growth process, flow of ammonia at a rate of 500 SCCM was maintained for 1 h continuously to remove residual oxygen. The flow rate is then slowly reduced to desired rate and the temperature was increased to the growth temperature at a rate of 30 K/min. The growth was carried out for 3 h and then the reactor was cooled to room temperature while maintaining the ammonia flow. The nanostructures were characterized by field emission scanning electron microscopy (FESEM) and energy dispersive analysis of X-rays (EDAX) operated at 10 keV (Carl Zeiss, NTS GmbH SUPRA 40VP, USA). The normal incident reflectance studies were carried out from 400 to 850 nm range of wavelength through a 100× objective of Olympus BX51 microscope coupled to a high resolution spectrometer (HR2000, Ocean Optics,

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USA). A goniometer (Rame-hart Inc.) equipped with a microscope coupled to a CCD camera was utilized for contact angle measurements. The measurements were made in atmospheric conditions at room temperature. The water droplets were either 1.0 or 1.5 μL which was manually dropped on the substrate using a syringe.

3. Results and discussion

Fig. 1(a) shows the scanning electron microscopy (SEM) image of self-organized GaN nano-flowers on silicon substrate at 1323 K and 25 SCCM of ammonia flow. The 3-D nanostructure seems to have hierarchy in the morphology, (i) the triangular base of about 2 μm in size and (ii) the hexagonal facet at the top, less than 1 μm in size. Fig. 1(b) shows a similar nanostructure grown on silicon at 1323 K and 50 SCCM of ammonia flow. The size of the nanostructure is much smaller (about 200 nm) hence the hierarchy in the structure is not clearly visible. Fig. 1(c) and (d) also shows SEM images of nanostructures grown on GaN and AlN substrates respectively at 1323 K and 25 SCCM of ammonia flow. The nanostructures are similar to the ones grown on silicon substrate with slight variation in size, which could be due to differences in Ga-diffusion on different surfaces. Fig. 2(a) and (b) shows the nanostructures grown on GaN substrate at 1323 K and 25 SCCM but on substrates placed at a distance of 4 mm and 8 mm from the Ga-source. The nanostructure formation is complete on substrate placed at 4 mm distance but on the other substrate the nanostructure formation is incomplete. Fig. 2(c) shows the micrograph of nanostructure grown on GaN substrate at 1273 K and 25 SCCM at 4 mm distance, which clearly is smaller in size in comparison with Fig. 2(a). Fig. 2(d) shows an EDAX spectrum of the nanostructure with Ga:N ratio almost 1.15:1, which is slightly Ga-rich. This gives rise to interesting optical properties as investigated by luminescence studies [15], and not discussed further in this report. It is to be noted that there were no nanostructures observed on all the three substrates without catalysis below 1273 K for ammonia flow-rate between 25 and 100 SCCM and on substrates placed at distances between 2 and 25 mm from the Ga-source.

The growth mechanism may be understood on the basis of the control parameters such as the temperature, ammonia flow rate, substrate and the distance between the substrate and Ga-source. At high temperatures the vapor pressure of gallium is high (2.25×10^{-3} Torr at 1323 K) and the ammonia (NH_3) decomposition to nitrogen and hydrogen is also 100% beyond 1200 K [16]. Hence at high temperatures combined with low ammonia flow rate will lead reduced diffusion length of gallium due to rapid reaction with the nitrogen to form GaN. The Ga-diffusion depends on the polarity of the surface, so the anisotropic diffusion rate can lead to 3-D growth with clear facets. Increasing the ammonia flow rate or decreasing the temperature would reduce the reaction rate and formation of GaN. This can lead to reduced growth rates hence the size of the nanostructure decreases. The distance dependence may be thought of similar to the temperature effect, near the source gallium vapor pressure would be more and far from the source the vapor pressure would be less.

The interesting result is the similar shape of the nanostructure irrespective of the substrate with variation in the size. It may be noted that the size of the nanostructure is large on silicon and smallest on GaN substrates. Shape of the nanostructure and the facets observed in SEM images can be used to identify the polarity. The hierarchal structure observed in our SEM images suggests that the triangular base with *m*-axis growth and the top hexagonal facet with *c*-axis growth. The triangular base is then non-polar but the sharp tip of the hexagonal facet indicates nitrogen polarity [17].

Fig. 3 shows the reflectance spectra measured at normal incidence for the nanostructures grown on different substrates and for GaN planar film for comparison. The GaN film shows high reflectance of about 25% between 400 and 850 nm. The nanostructures grown on GaN substrate shows less than 10% and on AlN substrate less than 5%. The reduced reflectance is attributed to the graded refractive index due to the presence of 3-D nanostructures. The reflectance measurements indicate that the nanostructures

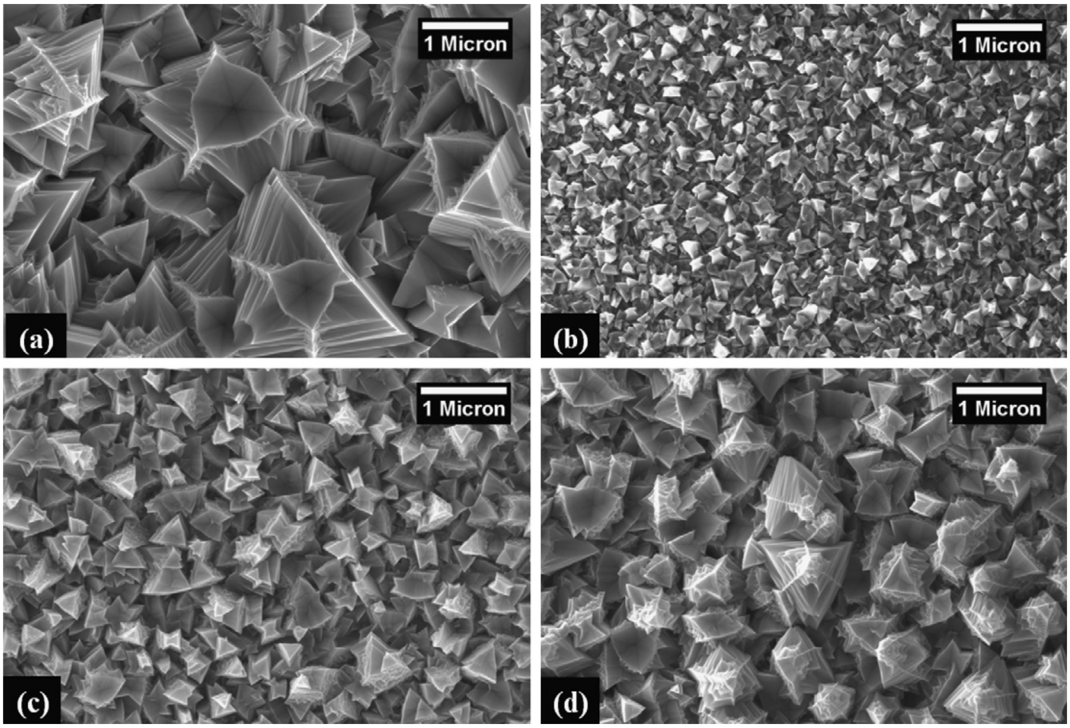

Fig. 1. SEM image of GaN nanostructures (a) and (b) grown on silicon substrate at 1323 K/25 SCCM and 1323 K/50 SCCM (c) and (d) on GaN and AlN substrates respectively grown with 1323 K/25SCCM.