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Structural, optical and dispersion characteristics of nanocrystalline GaN films prepared by MOVPE

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ABSTRACT

In this work, nanocrystalline GaN film was grown on a *c*-plane sapphire substrate by metal-organic vapor phase epitaxy (MOVPE). The structural and optical properties of the nanocrystalline GaN thin film were studied. The morphological and structural properties of GaN film were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. According to the X-ray diffraction spectrum, a GaN film was formed with a wurtzite structure, which is the stable phase. The optical parameters were determined using spectrophotometric measurements of transmittance and reflectance in the wavelength range 200–2500 nm. The analysis of the spectral behavior of the absorption coefficient in the intrinsic absorption region reveals a direct allowed transition with a band gap of 3.34 eV. The dispersion of the refractive index is discussed in terms of the single oscillator Wemple–Didomenico (WD) model. The single oscillator energy (E_o), the dispersion energy (E_d), the high frequency dielectric constant (ε_∞), the lattice dielectric constant (ε_L) and the free charge carrier concentration (N) were estimated. From the optical dielectric analysis, the optical conductivity, volume and surface energy loss functions were calculated. Moreover, the third-order nonlinear optical susceptibility $\chi^{(3)}$ was also considered.

1. Introduction

GaN in thin film form has a tremendous potential for applications in high power and high frequency electronic devices and optoelectronic devices having tailored band gaps with energies from visible to the deep ultra violet (UV) region. Large number of reports on synthesis and characterization of GaN had been published, which have been included in some recent reviews [1–7].

Semiconductor nanostructures with diverse shapes and morphologies have received extensive research interest in the past years due to their intriguing properties and technologically important applications in electronic fields [8–10]. Gallium nitride (GaN), with a wide direct band gap of 3.4 eV at room temperature, is an important III–V group semiconductor material and is of special interest and importance for its promising applications in high power laser, light-emitting diodes (LED) and detectors due to its excellent physical and chemical properties [11,12]. In particular, the nanostructured GaN materials with smaller size and huge surface area are ideal candidates for establishing building blocks for a variety of functional nanodevices such as nano-LED, nano-laser, nano-electron emitters and so on [13–15]. Because of its technological importance, extensive efforts have been devoted to the growth of various GaN nanostructures with controllable size, morphology and crystallinity [13,14]. Among all GaN nanostructures, highly symmetrical pyramid-like GaN nanostructures are of great importance and have attracted special research interest due to their potential applications in geometry-dependent lasers, as well as their enhanced quantum efficiency [3,16]. However, according to our experience, it is more difficult to obtain upright and well-ordered GaN nanorods directly by MOVPE but a relatively uniform nanostructured thin film could be obtained in the present study.

Moreover, the electrical, optical, and structural properties of epitaxial GaN are strongly influenced by the growth initiation [17]. Due to intrinsic obstacles to heteroepitaxy, such as lattice mismatch between epitaxial layers and substrates, a GaN nucleation layer (buffer layer) is usually introduced at low temperature prior to the growth of epitaxial GaN at high temperature. However, it has been demonstrated that the cubic and the hexagonal GaN phases coexist in the same growth process [18,19].

Up to now, the GaN material has often been epitaxially grown on foreign substrates such as sapphire [20–22], SiC [23,24] and Si [7,25] because of the lack of a large native substrate.

In recent times, synthesis of GaN in nanocrystalline or nanowire forms [26–28] has attracted the attention of the scientists globally and new exotic properties of GaN in nanocrystalline form are observed. Survey of literature indicates that there are not very many studies reported so far on GaN in nanocrystalline form. Thus, there is

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a need for more meaningful studies on this important material in nanocrystalline form so that the optical processes in the above material could be understood more faithfully.

Several techniques are used nowadays for epitaxial growth of semiconductors: liquid-phase epitaxy, chloride vapor-phase epitaxy, hydride vapor-phase epitaxy, molecular beam epitaxy and metal-organic vapor phase epitaxy (MOVPE). Each technique has its advantages and disadvantages [29,30]. The MOVPE technique is usually considered as one of the most progressive techniques for the growth of compound semiconductors containing the Group 13 elements, such as Al, Ga and In, due to intensified researches aimed at producing ultrapure precursors to grow epitaxial layers. Consequently, requirements for high purity organometallic compounds of MR3 (M=Al, Ga, In) type have become much tighter, because they can be widely used in production of semiconductor devices. A commercial use of alkyl derivatives of the above metals in MOVPE makes it possible to grow two-component (GaN, GaAs), three-component (AlGaAs, InGaAs, InGaP) and four-component (AlGaInP, AlGaInAs) epitaxial structures. These structures are used in production of broadband light-emitting diodes, solid-statelasers, solar cells, optical sensors, microwave devices, optical fiber and other devices. However, due to difficulties in production of high purity Al, Ga and In trialkyl compounds their use in MOVPE processes is restricted by high production cost and low availability of those organometallic precursors [29].

A complete description of the optical properties of nanocrystalline GaN film requires knowledge of a set of values at least two optical constants (n and k). In general, the optical and certain electronic properties are only specified if the optical constants are well known. Hence, GaN has been investigated as organic laser material; knowledge of the refractive index is essential in determining the population inversion density required for lasing. Also, information about the actual spectral absorption characteristic of nanocrystalline GaN film is required to analyze the action spectra for the solar cell applications.

Due to the increasing interest of nanocrystalline GaN films, the current investigation attempts to prepare high quality nanocrystalline GaN film by MOVPE technique suitable optoelectronic applications given to its structural and optical properties. Moreover, the spectral behavior, optical constants and dielectric characteristics as well as third-order $\chi^{(3)}$ were also studied.

2. Experimental procedures

2.1. Materials and preparation

Layer of GaN was grown on a c-plane sapphire substrate by metal-organic vapor phase epitaxy (MOVPE) in a 6 in. × 2 in. Thomas Swan Close Coupled Showerhead reactor. Trimethyl gallium (TMG), silane (50 ppm SiH_4 in H_2) and ammonia (NH_3) were used as precursors and hydrogen as carrier gas. A GaN nucleation layer was grown at 813 K, followed by a GaN epilayer with a nominal thickness of 4.5 μm grown at 1239 K, with the top 1.6 μm doped with Si to provide an electron density of 2.6×10^{18} cm^{-3} at 300 K.

2.2. Measurements

The structural characterization was investigated by using X-ray diffraction patterns (XRD). A Philips X-ray diffractometer (model X' pert) was used for the measurements with utilized monochromatic CuKα radiation operated at 40 kV and 25 mA. The diffraction patterns were recorded automatically with a scanning speed of 2° min^{-1}.

Scanning electron microscope (SEM) model JEOL-5940 was used to study the surface morphology of the GaN at accelerating voltage of 30 kV.

The measurements of the transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were carried out using a double beam spectrophotometer model (type JASCO, V-570, UV–vis-NIR, Japan) at normal incidence of light in the wavelength range 200–2500 nm. An uncertainty of 1% was given by the manufacturer for the measurements obtained by this spectrophotometer. All the measurements were carried out at room temperature (~300 K).

2.3. Methods of calculations

The spectral data (transmittance, T and reflectance, R) obtained directly from the spectrophotometer were transformed to absolute values after corrections of the absorbance and reflectance of the substrate.

The calculated values of reflectance $R(n,k)$ and transmittance $T(n,k)$ of an absorbing film of thickness d on a substrate at normal incidence are expressed by Murmann's exact equations [31]. In practice the equation giving $R(n,k)$ and $T(n,k)$ explicity in terms of the optical constants of the film and substrate are very complicated and have multiple solutions [32].

To calculate the refractive index, n, and absorption index, k, of films, our research group introduced a computer program comprising a modified search technique [33] based on minimizing $|\Delta T|^2$ and $|\Delta R|^2$ simultaneously where

$$|\Delta T|^2 = |T_{(n,k)} - T|^2 = \text{minimum} \tag{1a}$$

$$|\Delta R|^2 = |R_{(n,k)} - R|^2 = \text{minimum} \tag{1b}$$

By applying such a computer program technique [27], unique values of n and k are obtained with desired accuracy. An optimization step-length technique follows to speed up the convergence as well as to shorten the run time needed to improve associated accuracy. The experimental errors are taken into account as follows: ±0.1% for T and R calculations, ±3% for refractive index, ±2.5% for absorption index measurements and the experimental error in the film thickness is ±3–5%.

3. Results and discussion

3.1. Morphlogical and structural characterizations

Fig. 1 shows the surface morphology of the GaN film using scanning electron microscope (SEM). The fine features such as extremely small grain size and high dense as well as fine grain were obtained. There is no pinhole and no cracks were observed in the image under high magnification. The average particle size indicated that the prepared film has a nanostructure feature.

Crystallographic structure of the GaN film was analyzed by the X-ray diffraction (XRD). XRD profile of the GaN thin film at room temperature is shown in Fig. 2. As observed, the pattern indicates a single wide peak that appears at two theta values of 34.2–35.2°. This X-ray diffractogram represents the preferred (0 0 2) orientation, which confirms the epitaxial growth with wurtzite structure in agreement with that published by Metzger et al. [34]. The average crystallite size was calculated using the well-known Scherrer's equation as ~11 nm that indicates a nanostructure for GaN films. This result is in agreement with that obtained by SEM.