Spectroscopic ellipsometry studies of GaN films deposited by reactive rf sputtering of GaAs target

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(Received 16 November 2007; accepted 29 January 2008; published online 25 April 2008)

GaN films have been deposited by reactive rf sputtering of GaAs target in 100% nitrogen ambient on quartz substrates at different substrate temperatures ranging from room temperature to 700 °C. A series of films, from arsenic-rich amorphous to nearly arsenic-free polycrystalline hexagonal GaN, has been obtained. The films have been characterized by phase modulated spectroscopic ellipsometry to obtain the optical parameters, viz., fundamental band gap, refractive index, and extinction coefficient, and to understand their dependence on composition and microstructure. A generalized optical dispersion model has been used to carry out the ellipsometric analysis for amorphous and polycrystalline GaN films and the variation of the optical parameters of the films has been studied as a function of substrate temperature. The refractive index values of polycrystalline films with preferred orientation of crystallites are slightly higher (2.2) compared to those for amorphous and randomly oriented films. The dominantly amorphous GaN film shows a band gap of 3.47 eV, which decreases to 3.37 eV for the strongly c-axis oriented polycrystalline film due to the reduction in amorphous phase content with increase in substrate temperature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2903443]

I. INTRODUCTION

The fabrication of GaN based light emitting diodes (LEDs) and laser diodes has been followed by a variety of short wavelength optoelectronic devices, such as solar blind photodiodes, UV LEDs, and detectors.¹–⁴ GaN has also received enormous attention due to its applications in white light sources,⁵ high frequency power transistors,⁶ high electron mobility transistors,⁶ and spintronic devices.⁷ Device quality epitaxial GaN films have usually been grown using metal organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE) techniques.¹,⁸ However, owing to their enormous application potential, there has recently been increasing interest in polycrystalline GaN films grown by MBE,⁹–¹⁴ MOCVD,¹⁵–¹⁸ and sputtering.¹⁹–³⁶ Polycrystalline,¹⁹ nanocrystalline,²⁰ and amorphous³⁷ GaN have also shown good luminescence characteristics. Applications of polycrystalline GaN films have been demonstrated in LEDs,³⁸,³⁹ white lighting,³⁹ UV photodetectors,⁴⁰ solar cells,⁴¹,⁴² thin film transistors,⁴³,⁴⁴ and field electron emitters,⁴⁵,⁴⁶ and suitability of GaN films for application in large area flat panel displays has also been explored.⁴⁶ The potential of GaN films for these applications has thus driven the search for low cost and low temperature deposition processes on low cost substrates.

The inherent ability of sputtering to deposit large area thin films on a variety of substrates at relatively lower temperature opens up enormous opportunities for GaN. There have been several early reports on the growth of GaN films by reactive sputtering of Ga target with nitrogen or nitrogen-argon mixture,²¹–²³ though problems of reproducibility arising out of the low melting temperature of gallium have been reported.²⁴ During the past few years, polycrystalline GaN films have been deposited by sputtering using Ga₂⁵–²⁸ or GaAs (Ref. 35) targets. Using the approach of reactive sputtering of a GaAs target with 100% nitrogen, the composition and structure of GaN films grown on amorphous quartz substrates have been recently studied.³⁶ It has been shown that the substrate temperature plays the most crucial role in controlling the composition and microstructure of these films. In the present communication, a comprehensive optical characterization of GaN films deposited on quartz substrates by this approach has been carried out by using spectroscopic ellipsometry (SE). By varying the substrate temperature, a series of films has been deposited, with a systematic variation in crystallinity from arsenic-rich amorphous phase to practically arsenic-free, c-axis oriented polycrystalline hexagonal GaN. These films have been characterized by SE by using a generalized model of optical dispersion for amorphous GaN (a-GaN) and crystalline GaN (c-GaN).

SE is presently being used not only for the determination of optical constants but also for a complete nondestructive depth profiling of thin films and is being applied in wide areas of material science and solid state physics.⁴⁷,⁴⁸ Conventional ellipsometry suffers from the drawback of slow data acquisition process and limited spectral range. However, the
phase modulated SE technique employed in this study, offers fast and precise data acquisition over a large wavelength range.

Although several results of SE measurements have so far been reported on epitaxial or highly oriented GaN films grown by MBE or MOCVD techniques, sputtered GaN films have mostly been studied by optical absorption measurements, with only few reports available on SE measurements.

II. EXPERIMENTAL DETAILS

The films were deposited by rf magnetron reactive sputtering of a 3 in. GaAs target with 100% nitrogen as sputtering cum reactive gas. A Hartley-oscillator-type rf power supply (13.56 MHz) was used and the anode current was used to monitor the rf power. A rf shielded heater was used to control the substrate temperature from room temperature to 700 (± 10) °C. Film deposition was preceded by evacuating the chamber to a base pressure of 1 × 10−6 mbar, which was followed by presputtering with nitrogen at 8 × 10−3 mbar for 5 min. The films were deposited at a nitrogen pressure of 8 × 10−3 mbar and flow rate of 25 SCCM (SCCM denotes cubic centimeter per minute at STP). Atomic force microscopy (AFM) studies were carried out on the films in contact mode, with silicon nitride probes using Digital Instruments Nanoscope IV multimode Scanning Probe Microscope (SPM).

Ellipsometric data for GaN films were measured in a spectroscopic phase modulated ellipsometer (model UVISEL™ 460, ISA JOBIN-YVON SPEX) in the wavelength range of 300–1200 nm. In ellipsometry, the variation in the amplitude and the phase difference between the parallel (p) and perpendicular (s) components of the reflected light polarized with respect to the plane of incidence are measured. In general, reflection causes a change in the relative phase of p and s waves and in the ratio of their amplitudes. The effect of reflection is measured by the two quantities, viz., ψ (which measures the amplitude ratio) and Δ (which measures the relative phase change). These are given by

\[ \rho = \frac{r_p}{r_s} = \tan \psi \exp(i \Delta), \]

where \( r_p \) and \( r_s \) are the reflection coefficients for the p and s components of the waves, respectively. GaN films described in this communication have been characterized by phase modulated SE technique, in which the reflected light is modulated by a photoelastic modulator at a frequency of 50 kHz. The modulator is actually a fused silica bar, which is subjected to periodical stress induced by a piezoelectric transducer. Due to its photoelastic property, the modulator induces a phase shift \( \delta(t) \) between the two eigenmodes. The modulated intensity signal is detected and Fourier analyzed to generate the parameters of interest, viz., ψ and Δ. The above technique provides fast and accurate measurement of ψ and Δ over a large wavelength range. Taking into account the uncertainty in angular orientation of the optical components (±0.1°) of the SE, error in the calibration of the photoelastic modulator, nonlinearity of the photomultiplier detector, and error in the calibration of the frequency response of the detection system, the expected overall accuracy of the measured ψ and Δ values is better than 0.5°.

The measured ellipsometry spectra are then fitted with an appropriate theoretical model generated by assuming a realistic two-layer sample structure with a bulklike dense layer on the substrate and a top surface roughness layer. The surface roughness layer is modeled as a homogeneous mixture of 50% material and 50% void which is a usual practice in ellipsometric analysis of thin films. The effective dielectric constant of the surface roughness layer containing voids is obtained using the Bruggeman effective medium approximation (EMA). The optical constants of the quartz substrates have been obtained from standard references and appropriate dispersion relations for the optical constants of GaN have been used for the layers. By assuming the above sample structure, with trial thicknesses of the two layers and parameters of dispersion relation for the different layers as fitting parameters, the measured ellipsometric spectra are fitted by minimizing the squared difference (\( \chi^2 \)) between the measured and calculated values of the ellipsometric parameters (ψ and Δ) given by

\[ \chi^2 = \frac{1}{2N-P} \sum_{i=1}^{N} \left[ (\Psi_i^{\text{exp}} - \Psi_i^{\text{calc}})^2 + (\Delta_i^{\text{exp}} - \Delta_i^{\text{calc}})^2 \right], \]

where \( N \) is the number of data points and \( P \) is the number of model parameters. The maximum number of iteration allowed is 100 and the criterion for convergence used is \( \delta \chi^2 = 0.000 \ 001 \).

III. RESULTS AND DISCUSSION

The GaN films discussed in the present communication have been deposited at substrate temperatures ranging from room temperature to 700 °C. The composition and microstructure of these films were studied by x-ray fluorescence spectrometry, x-ray diffraction, transmission electron microscopy (TEM), and Raman spectroscopy. These results have been presented elsewhere and a summary of the important results is given below. Below the substrate temperature of 300 °C, the sputtered films were predominantly amorphous and contained a large quantity of arsenic. The As/Ga ratio decreased from ~0.9 to ~0.6 as the substrate temperature was changed from room temperature to 300 °C. The amorphous phase consisted of GaN or GaAsN and some elemental arsenic could also be present in these films. Above a substrate temperature of 300 °C, a drastic decrease in the arsenic content of the films takes place, along with a clear indication of the appearance of the polycrystalline phase of hexagonal GaN. The films deposited above 300 °C were dominantly polycrystalline GaN. The arsenic content of the films decreased to ~1 at. % at substrate temperatures ~500 °C. GaN crystallites exhibited a (101) preferred orientation in films deposited at 300–350 °C, which changed to (101) preferred orientation (closer to random) in films deposited in the range of 400–550 °C. The films deposited at
600 and 700 °C, however, showed a strong (0002) orientation of crystallites and contained negligible amount of arsenic (≤0.5 at. %).

In most of the SE analysis carried out so far on polycrystalline or amorphous films of GaN or other III-V compound semiconductors,\textsuperscript{55,61} simplified analytical expressions proposed by Jellison, Jr. and Modine\textsuperscript{52} (Tauc–Lorentz model) or Ferlauto \textit{et al.}\textsuperscript{63} (Cody–Lorentz model) have been used. Here, we have used a generalised optical dispersion model for crystalline and amorphous materials proposed by Adachi \textit{et al.}\textsuperscript{64} which is derived from the basic quantum mechanical principle of absorption of light inside a material.

For the derivation of the dispersion relations for complex dielectric functions of crystalline semiconductors, Ninomiya and Adachi\textsuperscript{65} had started with the following expression relating the energy band structure and imaginary part of the complex dielectric function (taking into consideration momentum conservation in crystalline semiconductors):

\[
\varepsilon_2(E) = \frac{4\varepsilon^2\hbar^2}{\pi\mu^2E^2} \int dk|P_{\text{so}}(k)|^2 \delta'[\varepsilon_s(k) - \varepsilon_{\text{so}}(k) - E],
\]\n
(3)

where \(\mu\) is the combined density of states mass, the Dirac \(\delta\) function represents the joint spectral density of states between the valence \(\varepsilon_s(k)\) and the conduction band \(\varepsilon_{\text{so}}(k)\) states differing by the energy \(E = \hbar\sigma\) of the incident light, \(P_{\text{so}}(k)\) is the momentum matrix element between the valence and the conduction band states, and the integration is performed over the first Brillouin zone.

By introducing the concept of joint density of states at the critical points (CPs) and using the analytical expressions for different CPs, expressions for the imaginary part of the dielectric constants \(\varepsilon_2\) at different CPs can be obtained from Eq. (3) and then using the Kramers–Kronig relation, an expression for the real part of the dielectric function \(\varepsilon_1\), and hence for the complete dielectric function \(\varepsilon\), can be generated over the whole spectral range.

According to the above formalism, the expression for the total dielectric function \(\varepsilon(E)\) corresponding to the \(E_0\) and \(E_0 + \Delta_0\) transitions is obtained as

\[
\varepsilon(E) = \varepsilon_\infty + \varepsilon_0(E) + \varepsilon_{\text{opt}}(E),
\]\n
(5)

where \(\varepsilon_\infty\) is the high frequency component of the dielectric constant and \(\varepsilon_0(E)\) is the contribution of \(E_0\) band gap to the complex frequency-dependent dielectric constant and is given by Eq. (4).

The term \(\varepsilon_{\text{opt}}(E)\) in Eq. (5) is the excitonic contribution at \(E_0\) and \(E_0 + \Delta_0\) CPs arising due to the Coulomb-like interaction between the electrons and holes and is given by

\[
\varepsilon_{\text{opt}}(E) = \sum_{n=1}^{\infty} \frac{A_n}{n^2} \left[ \frac{1}{E_0 - (G_0/n^2) - E - i\Gamma} \right] + \frac{1}{2} \left[ \frac{1}{E_0 + \Delta_0 - (G_0/n^2) - E - i\Gamma} \right],
\]\n
(6)

where \(A_n\) is the exciton strength parameter and \(G_0\) is the exciton binding energy.

Similar expressions can be derived for the variation of the dielectric functions near the other CPs also (i.e., at \(E_1, E_2\) gaps, etc.).

Adachi and co-workers have used their model over a large number of II-VI and III-V semiconductor compounds and binary alloys.\textsuperscript{66–68} According to Adachi \textit{et al.}\textsuperscript{64} the above expressions for the real and imaginary parts of the dielectric constants of a crystalline semiconductor can be used for its amorphous counterpart with different values for CP energies and broadening parameters. The dielectric function \(\varepsilon_2(E)\) of an amorphous material shows a relatively featureless spectrum with one broad peak centered near the \(E_1\) CP (two-dimensional \(M_0\)-type) peak of the corresponding crystalline material. According to Adachi \textit{et al.}\textsuperscript{64} since the short range coordination in the structures of amorphous materials is preserved, the local coordination of the structure and the values of the first-nearest-neighbor distance, coordination number, or binding energy remain more or less the same in the amorphous and crystalline phases though the sharp structure in the optical dispersion is absent in the amorphous phase because of the nonexistence of long range order. If the short range order in the amorphous state is similar to that in the corresponding crystal, one can expect the electronic and phonon density of states to show some similarity, and thus the density of states in the amorphous state would be a broadened version of that of the crystalline state. This idea was confirmed by fitting the experimentally measured \(\varepsilon(E)\) spectrum of amorphous Si to the model dielectric function (MDF) proposed by Adachi \textit{et al.}\textsuperscript{64} for crystalline Si with different CP and broadening parameters. Subsequently, the model was also used to describe the optical dispersion function of amorphous GaAs.\textsuperscript{69} Tripura Sundari\textsuperscript{70} has also followed the CP based approach to describe the common optical dispersion function of crystalline and amorphous Si, and thus the estimated amorphization of crystalline Si by ion irradiation. For GaN also, as has been observed by Budd et al.,\textsuperscript{71} by extended x-ray-absorption fine structure measurements with synchrotron radiation, the first-nearest-neighbor coordination is similar for \(a\) - and \(c\)-GaN, and thus the generalized MDF model of Adachi \textit{et al.}\textsuperscript{64} discussed above should be applicable.

Figures 1(a)–1(c) show the experimental spectra of \(\psi\) and \(\Delta\) for three representative GaN films deposited at substrate temperatures of 200, 400, and 700 °C, respectively, over the wavelength range of 300–1200 nm, along with the best-fit theoretical simulations. The theoretical simulations
have been carried out by using the dispersion model of Adachi et al., given by Eqs. (4) and (6) for the dispersion of the optical constants of GaN. Because of the limited range of measured data, in the present analysis, the contribution to $\varepsilon(E)$ from the fundamental transition at $E_0$ has only been assumed and the spin-orbit splitting factor ($\Delta_0$) has been assumed to be zero. As has been discussed earlier, the sample deposited at 200 °C is predominantly amorphous, the film deposited at 400 °C is polycrystalline film with small grains, while the film deposited at 700 °C has large grains with strong (0002) orientation. The quality of the ellipsometric fitting shown in Figs. 1(a)–1(c) shows the suitability of the model of Adachi et al. in describing the optical dispersion of both amorphous and crystalline samples.

As mentioned in the previous section, the best fits in all the above cases are obtained with a two-layer model assuming a bulklike dense layer on the substrate and a top surface roughness layer with 50% void. Miyazaki et al. have also found that a two-layer sample structure is required to fit the ellipsometric spectra of rf sputtered GaN films, where surface layers were found to contain up to 41% void. The thicknesses of the bulklike and surface layers of all the films deposited at different substrate temperatures, ranging from room temperature to 700 °C, including the above three samples are shown in Table I. Figure 2(a) shows the variation of the percentage fraction of surface layer thickness over the total thickness of the film as a function of substrate temperature, which shows that the fraction varies between 0% and 5%.

As mentioned above, the composition and microstructure of these films critically depend on the substrate temperature. Since the surface morphology of the films has direct relevance to the analysis of ellipsometric data, it has been independently investigated by AFM and typical AFM images are shown in Fig. 3. The films deposited up to a substrate temperature of 300 °C, which were dominantly amorphous, show smooth and uniform surface features of lateral size of 25 ± 5 nm and surface roughness of ~2 nm. Nearly similar features were seen for the films deposited up to a substrate temperature of 400 °C, but for higher substrate temperatures, the films exhibited a significantly different surface morphology. The film deposited at 500 °C shows an
increase in surface roughness as well as the size of surface features, which also tend to become asymmetric in shape. With increase in substrate temperature to 550 °C, a drastic change in the shape of surface features is clearly seen, which become elongated and needlelike. With further increase in substrate temperature up to 700 °C, the lateral size of the surface features continues to increase, but the asymmetry in shape remains to some extent. It must be mentioned here that the lateral surface features seen in Fig. 3 may not represent individual crystallites, since transmission electron microscopy (TEM) studies have shown that the films deposited below 300 °C were dominantly amorphous and those deposited above 300 °C were polycrystalline with crystallite size in the range of 8–16 nm. In contrast, the size of the lateral features seen from the AFM images varies from 30 nm to well above 100 nm, indicating that these surface features represent agglomerates of crystallites. However, the increase in overall size of surface features is possibly related to increase in crystallite size and thus correlates well with TEM studies. It is interesting to note that the drastic change in surface morphological features with substrate temperature, seen in the AFM images, is associated with the significant change in the growth rate of the films above 300 °C that takes place concurrently with the efficient removal of arsenic from the growing film and the onset of polycrystallinity. The correlation between the surface morphological features and the microstructure of the films, particularly crystallite orientation, is a noticeable and interesting feature but will not be discussed in detail here.

The values of surface roughness of the films deposited at different substrate temperatures have been obtained from the AFM images and are plotted in Fig. 2. The experimental error in the measurement of surface roughness was found to vary between 3% and 5%. The error was smaller for the films deposited below 300 °C. It can be seen that the correlation between the fractional thickness of the surface layer and the measured surface roughness of the films is extremely good over the entire range of substrate temperature studied. This justifies the two-layer model used for the analysis of ellipsometry data. It may be mentioned that Koh et al. have also shown by real time AFM and SE analysis of Plasma-enhanced Chemical Vapour Deposition (PECVD) grown $\alpha$-Si$_1-x$C$_x$:H films that the thickness of the surface roughness layer obtained from the ellipsometric analysis gives a realistic estimation of the surface roughness of the films. It is thus inferred from Figs. 2(a) and 2(b) that the steady increase in fractional thickness of the surface layer with substrate temperature manifests the increase in surface roughness of the films, as the structure of the films changes from amorphous to polycrystalline with oriented crystallites. However, the films deposited at high temperatures (600–700 °C) show a

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Thickness of bulk layer (Å)</th>
<th>Thickness of surface roughness layer (Å)</th>
<th>$e_x$</th>
<th>$E_0$ (eV)</th>
<th>$\Gamma_0$ (eV)</th>
<th>$A_0$ (eV$^{1/2}$)</th>
<th>$A_{0b}$ (eV)</th>
<th>$G_0$ (eV)</th>
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<tr>
<td>Room temperature</td>
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<td>38</td>
<td>1.13</td>
<td>3.34</td>
<td>0.359</td>
<td>48.83</td>
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<td>0.405</td>
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<tr>
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<td>7681</td>
<td>35</td>
<td>1.27</td>
<td>3.39</td>
<td>0.209</td>
<td>52.41</td>
<td>0.003</td>
<td>0.478</td>
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<tr>
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<td>0.011</td>
<td>0.313</td>
</tr>
<tr>
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<td>2.16</td>
<td>3.44</td>
<td>0.145</td>
<td>45.38</td>
<td>0.017</td>
<td>0.341</td>
</tr>
<tr>
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<td>44.62</td>
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<tr>
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<tr>
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<td>3.37</td>
<td>0.064</td>
<td>42.29</td>
<td>0.011</td>
<td>0.157</td>
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</table>

TABLE I. Best-fit sample structure and best-fit parameters of the dispersion relation as obtained from ellipsometric analysis of the GaN films deposited at different substrate temperatures.
small decrease in surface roughness, which is attributed to the increase in lateral size of surface features, as seen from the AFM images.

The best-fit values of the parameters of the dispersion model for all the films are also shown in Table I. It is found that the parameters are of the same order of magnitude as those obtained by Kawashima et al. in their SE analysis of MOCVD grown hexagonal GaN films. It may be noted from Table I that the broadening parameter of the fundamental transition $\Gamma$ decreases continuously as the substrate temperature is increased for the GaN films manifesting the increase in crystallinity of the films with increase in substrate temperature. The variation in refractive index $n$ and extinction coefficient $k$ in the wavelength range of 300–1200 nm generated by the best-fit parameters of the dispersion model are shown in Fig. 4 for the films deposited at 200, 400, and 700 °C. Yan et al. and Kawashima et al. have showed a similar variation in refractive index for MOCVD and MBE grown epitaxial hexagonal GaN films measured by SE, though their values of refractive index at higher wavelengths were slightly larger than those of the rf sputtered polycrystalline GaN films discussed in the present work.

The refractive index $n$ values at 1200 nm for all the films are plotted in Fig. 5 as a function of the substrate temperature. The amorphous films with high arsenic content show a small increase in $n$ from 2.05 to 2.1 as the substrate temperature approaches 300 °C. With increase in substrate temperature to 350 °C, a jump is seen in the refractive index

FIG. 3. (Color online) AFM images of films deposited at different substrate temperatures (as indicated in the figure).
value to \( \sim 2.2 \), beyond which it again decreases to \( \sim 2.1 \) in the substrate temperature range of 450–550 °C. Finally, the films deposited at substrate temperatures of 600 and 700 °C again show stable refractive index values of 2.2. The fluctuation in refractive index with substrate temperature shows an interesting correspondence with the dependence of growth rate on substrate temperature, which has also been plotted against substrate temperature in the same figure. As mentioned above, the variations in growth rate with substrate temperature above 300 °C have been attributed to changes in the nature of crystallite orientation of polycrystalline GaN films. The films having strong (1010) preferred orientation (substrate temperature \( \sim 350 \) °C) or (0002) preferred orientation (substrate temperature \( > 550 \) °C) exhibit a slightly larger value of refractive index, \( \sim 2.2 \), which is close to the values of 2.25 and 2.3 reported for epitaxially grown GaN films. Miyazaki et al. have also found that the refractive index of the polycrystalline GaN films prepared by reactive sputtering of metallic Ga is slightly less than the corresponding value for epitaxial GaN film deposited by MOCVD. The lower values of refractive index in the present case for films deposited in the substrate temperature range of 400–550 °C, however, is due to variation in crystallite orientation or near random orientation of crystallites in the above films.

The variation of fundamental transition energy \( (E_g) \) or the band-gap value obtained from ellipsometric analysis is plotted as a function of substrate temperature in Fig. 6(a). It is found that the band gap initially increases with substrate temperature and exhibits the largest value (3.47 eV) for the film deposited at a substrate temperature of 300 °C. With further increase in substrate temperature, the band gap decreases in a systematic fashion and the band-gap value of 3.37 eV for the film deposited at a substrate temperature of 700 °C matches very well with the standard value for hexagonal GaN (3.38 eV).

As has been discussed above, the films deposited up to a substrate temperature \( \sim 300 \) °C are amorphous in nature and...
contain significant quantity of arsenic, which may be in one or more forms, such as $a$-GaN and elemental As and/or amorphous GaAsN. The smaller band gap of these films is attributed to the presence of arsenic, since amorphous GaAsN is known to have a smaller band gap than pure GaN.\(^7^5\) The increase in the measured band gap of the amorphous films with initial increase in substrate temperature is attributed to the reduction in their arsenic content. Large discrepancies exist in literature regarding the band-gap values of $a$-GaN films. Bittar et al.\(^7^6\) have reported a band gap of 3.1 eV for $a$-GaN films deposited by ion-assisted thermal evaporation of Ga under N\(_2\) ambient, while Kang and Ingram\(^7^7\) have reported a band gap of 2.5 eV for $a$-GaN films prepared by ion-assisted reactive evaporation. However, Khosman and Kordesch\(^5^5\) have reported a value of 3.44 eV for $a$-GaN films obtained by reactive rf sputtering of Ga target. Knox-Davies et al.\(^2^7\) and Miyazaki et al.\(^2^0\) have reported band-gap values as high as 3.64 and 3.7 eV for their $a$-GaN films deposited by rf sputtering of Ga targets under mixed ambient of Ar\(_2\), N\(_2\), and H\(_2\). The largest band-gap value of 3.47 eV, which was obtained in the present case for the film deposited at 300 °C, is thus attributed to its dominantly amorphous nature, though it could still be affected by the presence of arsenic in the film.

As mentioned earlier, the arsenic content of the films deposited above the substrate temperature of 300 °C is significantly low (1–5 at. %) and the films are predominantly polycrystalline GaN. It is seen from Fig. 6(a) that with increase in substrate temperature above 300 °C, the band gap monotonically decreases from the value of 3.47 eV to nearly the value of 3.37 eV for the GaN film deposited at 700 °C. This variation in the band gap has been explained by assuming the presence of amorphous phase in polycrystalline GaN films deposited above 300 °C which monotonically decreases with increase in substrate temperature. This conjecture has been substantiated by the following analysis.

In the subsequent analysis, it has been assumed that the film deposited at 250 °C is completely amorphous, while that deposited at 700 °C is completely polycrystalline GaN. The dispersion of optical constants obtained by fitting of the ellipsometric data of GaN films deposited at 250 °C has been assumed to be the dispersion relation for ($a$-GaN), while the dispersion of optical constants for GaN film deposited at 700 °C has been assumed to be the dispersion relation for ($c$-GaN). The ellipsometric data for all the other films have been fitted by assuming these films to be mixtures of $a$-GaN and $c$-GaN and the Bruggemann EMA model has been used to determine the effective dispersion constant of the film. By fitting the ellipsometric data in this manner, the relative fraction (ratio) of $a$-GaN and that of $c$-GaN have been determined for all the films deposited above 300 °C. The ratio of amorphous to crystalline phase present in the films as obtained by the above method is plotted as a function of substrate temperature in Fig. 6(b). It is found that the crystalline phase begins to appear in the films deposited at substrate temperature of 300 °C, while the films deposited at 600 °C and above are completely polycrystalline in nature.

Finally, the refractive index at 1200 nm and the band-gap values of the films deposited above 300 °C are plotted in Figs. 7(a) and 7(b) as a function of the fractional amorphous content (i.e., ratio of amorphous to crystalline phases) of the samples which is more relevant to material properties. The correspondence between the amorphous content of the films and the measured band gap given in Fig. 7(b) clearly shows that the above conjecture is justified and the decrease in band gap of the films deposited at substrate temperatures above 300 °C can be attributed to the removal of the amorphous phase from polycrystalline GaN films at higher substrate temperatures. However, as can be seen from Fig. 7(a), the refractive index values do not monotonically increase with the decrease in amorphous content of the films and are also sensitive to the degree of orientation of the polycrystalline films, because the presence of crystallites with different orientations leads to lower refractive index values for films deposited at substrate temperatures in the range of 400–550 °C.

IV. CONCLUSION

SE measurements have been carried out on GaN films deposited by reactive rf sputtering of GaAs target in 100% nitrogen ambient at different substrate temperatures ranging from room temperature to 700 °C. With increase in substrate temperature, the structure of the films changes from arsenic-rich amorphous to nearly arsenic-free oriented polycrystalline hexagonal GaN. A generalized dispersion model for optical constants proposed by Adachi et al. for crystalline and amorphous materials has been used for ellipsometric analysis of the films. Best fits have been obtained for all the films with a two-layer sample structure consisting of a bulklike layer on the substrate and a surface roughness layer on top,
having a void fraction of 50%. It is found that the thickness of the surface layer increases with the increase in substrate temperature and correlates very well with the surface roughness of the films measured from the AFM images. From the best-fit parameters of the dispersion model, refractive index, extinction coefficient, and band-gap values have been calculated for all the films. The refractive index of the films is relatively lower for the amorphous films deposited below 300 °C. The fluctuation in refractive index of films deposited above 300 °C with substrate temperature correlates well with the dependence of their growth rate on substrate temperature, which has been earlier attributed to change in preferred orientation of crystallites. Polycrystalline GaN films with (1010) and (0002) oriented crystallites show refractive index value of 2.2 at 1200 nm, which is slightly lower than the reported values of 2.25–2.3 for epitaxially grown GaN films. The increase in band gap of the films with initial increase in substrate temperature correlates well with the earlier reported observation of reduction in arsenic content in the films with increase in substrate temperature. The largest band-gap value of 3.47 eV for the film deposited at 300 °C is attributed to the dominating presence of $a$-GaN phase in the film. Above 300 °C, the band gap monotonically decreases with increase in substrate temperature and the nearly arsenic-free GaN film deposited at 700 °C exhibits a band gap of 3.37 eV, close to the reported value for hexagonal GaN. The decrease in band gap with increase in substrate temperature is attributed to the reduction in amorphous content of GaN films with increase in substrate temperature.

ACKNOWLEDGMENTS

The financial support for this work received from the Board of Research in Nuclear Sciences, Department of Atomic Energy, Government of India, is gratefully acknowledged. The authors also wish to thank Dr. S. C. Sabharwal, Head, Spectroscopy Division, Bhabha Atomic Research Centre, for his encouragement during this work. FIST (Physics)-IRCC central SPM Facility of IIT Bombay is acknowledged for providing the facilities for AFM measurements.

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