A 300 nm thick epitaxial AlInN film with a highly flat surface grown almost perfectly lattice-matched to c-plane free-standing GaN substrate

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Single-layer AlInN films with a film thickness of approximately 300 nm were grown on a c-plane free-standing (FS) GaN substrate by metalorganic chemical vapor deposition. The result showed that a highly flat-surface AlInN film with a small root-mean-square-square surface roughness of less than 0.5 nm was realized by adjusting its alloy composition to an almost perfectly lattice-matched to FS-GaN. As for the highly flat-surface AlInN film, the optical constants were evaluated in whole visible wavelength by spectroscopic ellipsometry. Then, its energy bandgap energy was determined to be 3.92 eV. © 2019 The Japan Society of Applied Physics

1. Introduction

Ternary AlInN alloys have a highly useful feature of being lattice-matched to GaN in addition to their attractive bandgap nature of extremely wide range from 0.7 eV for InN to 6.2 eV for AlN. Based on those properties, they have often been utilized as component materials for GaN-based electronic and optical devices.1–14 Cladding layers in GaN-based laser diodes (LDs) are one of the most promising applications for AlInN alloys. For one thing, AlInN alloys show a large refractive index contrast to GaN or InGaN in whole visible wavelength.14–16 For another, AlInN alloys have an alloy composition lattice-matched to c-plane GaN, unlike conventional cladding layer materials for GaN-LDs, such as GaN/AlGaN superlattices or single-layer AlGaN films.17,18 Thus, we have conducted researches for achieving thick and flat-surface AlInN films applicable to cladding layers in GaN-LDs. Most recently, we grew approximately 300 nm thick single-layer AlInN epitaxial films on a c-plane GaN-on-sapphire template by metalorganic chemical vapor deposition (MOCVD).15,16 Then, an AlInN film grown lattice-matched to GaN on sapphire showed a relatively flat surface with a root-mean-square (RMS) roughness of 1.8 nm, although there were a certain number of surface pits originating from threading dislocations of the underlying GaN film.15,16 This result indicates that an extremely flat surface with few pits will be obtained by growing an AlInN film lattice-matched to a low-dislocation-density GaN substrate. In this study, therefore, we attempted to grow thick AlInN epitaxial films on a free-standing (FS) GaN substrate instead of GaN-on-sapphire templates. Optical constants and energy bandgaps for an AlInN epitaxial film were also evaluated.

2. Experimental methods

AlInN films with a film thickness of approximately 300 nm were grown on a 2 in. diameter c-plane FS-GaN substrate by MOCVD with a laminar-flow reactor. As for the FS-GaN substrate, the threading dislocation density was less than 5 × 106 cm−2, and the surface roughness was less than 0.2 nm in RMS. During the AlInN growth, the trimethyl-aluminum, trimethyl-indium and NH3 gases were supplied into the reactor with a N2 gas flow under a constant reactor pressure of 13.3 kPa. The growth temperature was in the rage from 800 °C to 860 °C, and the growth rate was maintained at approximately 0.6 μm h−1. Alloy compositions of AlInN films were derived by applying the measured lattice constants to an equation (c − c0)/c0 = −2 (C13/C33) (a − a0)a019 where, a0 and c0 are the room-temperature lattice constants of free-relaxed crystals, a and c are the measured lattice constants, and C13 and C33 are the elastic stiffness constants. Here, a0 and c0 of AlInN were determined according to Vegard’s law20,21 using the reported lattice constants,22 a and c were estimated using main peaks in XRD (θ−2θ) scans taken for symmetric (0002) and asymmetric (1012) planes, and C13 and C33 were obtained by assuming a linear interpolation between reported values for AlN and InN.23 The surface morphology and roughness were evaluated by atomic-force microscopy (AFM). The film thicknesses, optical constants and energy bandgaps for AlInN films were estimated via spectroscopic ellipsometry (SE) analyses.

3. Results and discussion

3.1. Characterization of epitaxial AlInN films grown on FS-GaN

Figures 1(a) and 1(b) show the in-plane lattice constants a and in-plane lattice strains εxx, respectively, for 300 nm thick AlInN films with different alloy compositions grown on the FS-GaN substrate. Here, surface AFM images for the respective AlInN films are shown as Figs. 1(c)–1(f), which also denote their respective InN molar fraction xIn in AlInN and RMS roughness values. In Fig. 1(a), a blue solid line represents a-axis lengths for perfectly-relaxed AlInN crystals estimated by Vegard’s law. For comparison, the figure also shows results obtained for an AlInN film grown nearly lattice-matched to GaN grown on sapphire.15,16 As obvious in Fig. 1(a), the a-axis lengths of AlInN films were almost perfectly consistent with an intrinsic a-axis length of FS-GaN, 3.189 Å, regardless of their alloy compositions. This means that no lattice relaxation occurred for AlInN films within the range from 0.152 to 0.213 in xIn. Further, an alloy composition of AlInN lattice-matched to FS-GaN was estimated to be xIn = 0.180. Correspondingly, as seen in Fig. 1(b), the in-plane lattice strain linearly changed with the change in the alloy composition, and the in-plane lattice strain reversed its direction at the lattice-matching
composition, $x_{\text{In}} = 0.180$. Compared to our previous results$^{16}$ there is no large contradiction except that the $a$-axis length and an alloy composition for lattice matching were 3.183 Å and $x_{\text{In}} = 0.166$, respectively, for on GaN-on-sapphire templates. For more precise discussion, we also calculated lattice-matching alloy compositions at the growth temperatures ($T_g$) by utilizing thermal expansion coefficients reported for III-nitrides.$^{24,25}$ The result confirmed that variation of the lattice-matching alloy compositions at $T_g$ was as small as less than 0.001 in the $x_{\text{In}}$ increase. This indicates that the difference in thermal expansion coefficients between AlInN and GaN was not so large and its effect on in-plane lattice strains was negligible.

When focusing on their surface morphologies, it is obvious that they drastically varied depending on their alloy compositions. Most noteworthy is that a highly flat surface with an extremely small RMS value of less than 0.5 nm was realized at $x_{\text{In}} = 0.179$, as seen in Fig. 1(e), which is very close to the lattice-matching composition, $x_{\text{In}} = 0.180$. This RMS roughness value is the smallest ever reported for thick AlInN films with thicknesses of 300 nm or greater. In the past researches, we have reported an RMS value of approximately 1.8 nm for a 300 nm thick AlInN film almost perfectly lattice-matched to GaN on sapphire ($x_{\text{In}} = 0.164$), as seen in Fig. 1(g)$^{15,16}$. On the other hand, an AlInN film with in-plane compressive strain ($x_{\text{In}} = 0.213$) showed a granular surface morphology with a large RMS value of greater than 5 nm, as seen in Fig. 1(f). This seemed to be very similar to those for AlInN films grown on GaN-on-sapphire templates that we have reported$^{16}$. For AlInN films with in-plane tensile strain ($x_{\text{In}} = 0.152$ and 0.171), however, numerous “micro gaps” like cracks were observed on their surfaces, as seen in Figs. 1(c) and 1(d). This phenomenon is quite different from that seen for on GaN-on-sapphire templates in our previous report$^{16}$.

Figure 2 shows XRD $\omega-2\theta$ profiles taken around (0002) reflections for the same samples as in Fig. 1. For comparison, the XRD profile obtained for the AlInN film nearly lattice-matched to GaN grown on sapphire$^{15,16}$ was also drawn as a black line. As seen in this figure, clear periodical fringe peaks, which reflect the steepness of their surfaces and interfaces, were observed for samples with $x_{\text{In}}$ of 0.152, 0.171, and 0.179. The fringe peaks are also observed for the reference sample grown on GaN on sapphire. In contrast, there were no fringe peaks observed for the sample with a granular surface morphology ($x_{\text{In}} = 0.213$). Further, its XRD profile showed that a kind of phase separation occurred in the AlInN film, which is clarified by a distinctive sub-peak at a shoulder part of the main peak from the AlInN film. The tendency mentioned above seemed to be almost the same as the result obtained for AlInN films grown on GaN-on-sapphire templates in our previous report$^{16}$.

3.2. Discussion on surface morphology variation of AlInN films grown on FS-GaN

We have reported that the surface morphology for 300 nm thick AlInN films grown on GaN-on-sapphire templates drastically varied around a lattice-matching composition as a boundary.$^{16}$ That is, their surfaces were relatively flat at low
InN molar fractions. However, once the InN molar fraction exceeded the lattice matching composition, they turned into a granular surface morphology originating from a columnar polycrystalline microstructure. From this, it is understood that the highly flat-surface morphology obtained in this study \[x_{\text{In}} = 0.179\] in Fig. 1(e) is attributed to its strain-less crystal resulting from almost perfectly lattice-matching composition. Further, the granular surface morphology observed for the sample with in-plane compressive strain \[x_{\text{In}} = 0.213\] in Fig. 1(f) probably reflects the columnar polycrystalline microstructure as ever reported.\[16,26,27\] The phase separation of AlInN observed by XRD is also consistent to our previous result, in which the InN content was observed to decrease in the columnar polycrystalline region.\[16,27\] On the other hand, the surface morphologies for samples with in-plane tensile strain \[x_{\text{In}} = 0.152\] and 0.171 in Figs. 1(c) and 1(d) were found to be far different from those grown on GaN-on-sapphire templates.\[16\] That is, in the case of AlInN films grown on GaN-on-sapphire templates, their surface morphology consisted of flat areas and a certain number of pits as seen in Fig. 1(g). Further, the observed surface pits have been confirmed to originate from threading dislocations in the underlying GaN-on-sapphire templates.\[15\] Here, we speculate that the pits or dislocations in AlInN films functioned to release the increased in-plane stress. In contrast, regarding AlInN films grown on low-dislocation-density FS-GaN substrates, the number of dislocations is too small to provide the same function. Thus, we concluded that the micro gaps generated to release the in-plane stress instead of pits or dislocations. Figures 1(c) and 1(d) also showed that the micro gaps increased with the decrease in the InN molar fraction, which will also confirm the validity of our speculation. From Figs. 1(b)–1(d), the generation of micro gaps is found to occur even under a relatively small lattice strain less than 0.2\%. This may indicate that the compositional range for achieving highly flat AlInN films on FS-GaN substrates is much narrower than on GaN-on-sapphire templates.

### 3.3. Optical constants and energy bandgaps for epitaxial AlInN films grown on GaN-on-Sapphire

Regarding the highly flat-surface AlInN epitaxial film with \[x_{\text{In}} = 0.179\], its optical constants and energy bandgap were estimated by SE analysis, in the same way as in our previous work.\[15,16\] Figures 3(a) and 3(b) show the measured and fitted waveforms of the amplitude ratio \(\Psi\) and the phase parameter \(\Delta\), which represent the complex reflectance ratio
\[
\frac{r_p}{r_s} = \tan \Psi \cdot e^{i\Delta}
\]
using the complex field reflectance for \(s\)- and \(p\)-polarized lights, \(r_p\) and \(r_s\). Here, because of a roughened backside surface of the FS-GaN substrate, the measured waveforms do not include the interference from GaN unlike the case of using GaN-on-sapphire templates. The model fitting was conducted by using the Tauc–Lorentz oscillator model,\[28\] and the results showed that the fitted waveforms are in good agreement with the measured ones. Thus, the refractive index \(n\) and extinction coefficient \(k\) were derived, as seen in Fig. 4. Here, the past research results for AlInN films grown on GaN-on-sapphire templates\[14–16\] are also plotted. The bandgap energy \(E_g\) was estimated from the extended Tauc formula \((\alpha E)^2 \cong (E - E_g)\)\[14–16,29\] for photon energy \(E\), where the light absorption coefficient \(\alpha\) is given by \(\alpha = 4\pi k/\lambda\) using the derived \(k\) and the incidence wavelength \(\lambda\). Figure 5 plots the relationship between \((\alpha E)^2\) and \(E\). From the intersection of the tangent of the drawn curves with the energy axis, the energy gap \(E_g\) of the AlInN film almost perfectly lattice-matched to FS-GaN \((x_{\text{In}} = 0.179)\) was estimated to be 3.92 eV.

Fig. 3. (Color online) Waveforms of (a) \(\Psi\) and (b) \(\Delta\) obtained at different incidence angles of 60°, 70° and 80° obtained by SE measurements for a 300 nm thick AlInN film \((x_{\text{In}} = 0.179)\) grown on a c-plane FS-GaN substrate by MOCVD. The blue and red lines show the measured and the fitted waveforms, respectively.

Fig. 4. (Color online) Spectra of (a) refractive index \(n\) and (b) extinction coefficient \(k\) determined for an AlInN film with \(x_{\text{In}}\) of 0.179. For comparison, past research results\[14–16\] grown on GaN-on-sapphire templates are also plotted.
to release the increased in-plane tensile stress in AlInN dislocations. It was considered that those micro gaps generated on the surfaces showed a granular surface morphology probably resulting from a columnar polycrystalline microstructure. This phenomenon is quite similar to those ever reported for AlInN films with lower InN molar fractions shown a different tendency from that observed for AlInN films drastically varied around the lattice-matching composition. In the case when the InN molar fraction is higher than the lattice-matching composition (xIn = 0.179). In addition, it was confirmed that the surface morphology of AlInN films drastically varied around the lattice-matching composition. In conclusion, 300 nm thick AlInN films grown on GaN-on-sapphire template is also plotted.

4. Conclusions

In conclusion, 300 nm thick AlInN films were grown on a c-plane FS-GaN substrate by MOCVD. A highly flat-surface AlInN film with an RMS roughness value of less than 0.5 nm were obtained for an almost perfectly lattice-matching alloy composition (xIn = 0.179). In addition, it was confirmed that the surface morphology of AlInN films drastically varied around the lattice-matching composition. In the case when the InN molar fraction is higher than the lattice-matching composition, their surfaces showed a granular surface morphology probably resulting from a columnar polycrystalline microstructure. This phenomenon is quite similar to those ever reported for AlInN films grown on GaN-on-sapphire templates. However, AlInN films with lower InN molar fractions showed a different tendency from that observed for GaN-on-sapphire templates. That is, they showed numerous “micro gaps” on their surfaces instead of pits originating from dislocations. It was considered that those micro gaps generated to release the increased in-plane tensile stress in AlInN films. The optical constants of the highly flat-surface AlInN film with xIn of 0.179 were estimated by SE measurement, and the bandgap energy was derived to be 3.92 eV.

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Fig. 5. (Color online) Absorption spectra determined for an AlInN film with xIn of 0.179. For comparison, a past research result for an AlInN film grown on GaN-on-sapphire template is also plotted.

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