RAMAN ANALYSIS OF Al_xGa_{1-x}N FILMS

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ABSTRACT

Raman analysis of the E2 mode of $Al_xGa_{1-x}N$ in the composition range $0 \le x \le 1$ is presented. The lineshape was observed to exhibit a significant asymmetry and broadening toward the high energy range. The spatial correlation model is discussed, and is shown to account for the lineshape. The model calculations also indicate the lack of a long-range order in the CVD (chemical vapor deposition) alloys. These results were confirmed by X-ray scattering: the relative intensity of the superlattice line was found to be negligible. The line broadening of the E2 mode was found to exhibit a maximum at a composition x~0.5 indicative of a random disordered alloy system. The stress state of the alloys was found to be tensile and was attributed to the difference in the thermal expansion coefficients of the SiC substrate and the film.

INTRODUCTION

Raman spectroscopy has been proven in the past to be a powerful method in studying alloy systems among which are $Al_xGa_{1-x}As$, $In_xGa_{1-x}As$, and many more [1-2]. Raman scattering from a perfect crystal, which consists of a lattice with translational symmetry, involves phonons with wavevector $q \cong 0$ near the Brillouin zone (BZ) center [3]. The alloying may destroy the configurational translational symmetry, and the phonons of $q \ge 0$ may be allowed to participate in the Raman scattering. As a result the Raman lineshape changes, and an investigation of the line characteristics may yield valuable information on the microstructure state of the alloy.

In this paper we present observations and analytical study of an asymmetric E2 Raman lineshape of $Al_xGa_{1-x}N$ films. The asymmetry of the line is shown to agree with the spatial correlation model which is based on the relaxation of the q \equiv 0 selection rules due to the alloying. The calculations indicated that the $Al_xGa_{1-x}N$ lattice lacks a long range order, a result which was confirmed by X-ray diffraction: the superlattice diffraction line was found to exhibit a very weak relative intensity. Moreover, the functional behavior of the E2 linewidth with respect to the composition x in the range 0 - 1 indicated a random distribution of the alloy constituents with maximum disorder at composition x~0.5.

In general, stress may be analyzed via the Raman peak position. However, the peak position of the alloy depends on the convoluted effects of the stress, the relaxation of the $q \equiv 0$ selection rules, and the mode-type. These effects are functions of the composition; the stress is also a function of the lattice constants and the thermal expansion coefficients of the film-substrate system. Thus, in a sample of known spatially uniform composition, and with structural defects due to stress, the stress-type may be analyzed by acquiring spectra at a defect and at a defect-free region. Our analysis using this approach indicates that the AlGaN alloys are under tensile stress. The stress is suggested to be due to the difference in thermal expansion coefficients of the film and the SiC substrate.

EXPERIMENT

Raman spectra were acquired in a backscattering geometry in which the E2 is an allowed Raman mode from the c-face of the Wurtzite structure [4]. In the experiments the 488 nm line of an Ar⁺ ion laser was utilized and the data were acquired at sample temperatures of 300K and 10K. The data for the lineshape investigation were acquired in a macro mode of laser spot size ~ 2 mm; for the stress measurements the micro mode of spot size ~ 3 μ m was utilized. The experimental

error in the linewidth and peak position measurements is ± 1.5 cm⁻¹ and 0.5 cm⁻¹ respectively. The Al_xGa_{1-x}N films were grown via the organometallic chemical vapor deposition (OMCVD) method at ~ 1100 °C on 6H-SiC(0001) substrates with a 100 nm AlN buffer layer. The thickness of the films is ~ 2 µm and the composition, x, which was determined via Rutherford backscattering (RBS), energy dispersive X-ray (EDX), and Auger spectroscopy, is: 0.06, 0.12, 0.22, 0.32, and 0.70. The Raman data points for x=0 and x=1 were obtained from GaN film and AlN crystallite respectively.

RESULTS AND DISCUSSION

The Configurational Disorder in AlGaN Films

Figure 1 shows the room-temperature Raman spectra of the E2 line from Al_xGa_{1-x}N films of compositions 0.06, 0.12, 0.22, and 0.70, which exhibit linewidths Γ of 8, 13, 16, and 19 cm⁻¹ respectively. As depicted in the figure, the spectral lineshape for films of x>0.06 exhibit asymmetric broadening and a peak shift toward higher frequency. Possible line broadening mechanisms applicable to alloys include thermal broadening, activation of a symmetry forbidden zone-center (q \equiv 0) mode which lies in the same frequency range as the investigated line, and broadening due to activation of a collection of modes of wavevectors q≥0. The last two broadening mechanisms result from the elimination of the translational symmetry of the lattice due to alloying.

To investigate the thermal contribution to the line broadening, Raman spectra were acquired at T=10K, and no significant change was observed between the shapes and linewidths of the room and cold temperature spectra. Thus the linewidth in our sample is not strongly affected by temperature. The only effect of the low temperature is the shifting of the peak position by ~ 2 cm⁻¹ toward higher frequency, which was also previously observed in GaN films [5] and crystals [6] and was attributed there to the thermal contraction of the bonding.

The second possible mechanism is the activation of a $q \equiv 0$ symmetry forbidden mode which might be convoluted with the E2 line and cause the asymmetric broadening. However, the only mode in the frequency range of the E2 line that is forbidden in the back-scattering geometry is the A1(TO) mode of GaN at ~560 cm⁻¹ which lies at a lower frequency.

A more plausible mechanism to account for the high frequency asymmetric linewidth in our Raman spectra is the spatial correlation model, also known as the confinement model. The model was developed to explain the asymmetry line in BN [7] and Si [8] and has been successfully applied to quantify the lineshape behavior of Ga1-xAlxAs and Ga1-xInxAs alloy systems [1]. The foundation of the model lies in attributing the relaxation of the q=0 Raman selection rules to the phonon confinement in a finite domain of size L. The size of L in an alloy system may be viewed as the average size of the ordered domains which are embedded in the configurational-disordered matrix. According to the model, as L gets smaller, the range of wavevectors Δq becomes larger: a wider range of frequencies are allowed to participate in the Raman scattering, and as a result the Raman lineshape exhibits a change. The lineshape-change depends on the phonon dispersion curve $\omega(q)$; for a curve of negative slope the line asymmetry is toward lower frequencies and for a positive slope the asymmetry is toward higher frequencies. The peak position also shifts accordingly. However, the position is a function of the stress and the alloy-mode as well: an alloy can be categorized as being a one- or two- mode type [9] and the behavior of the peak position depends on the type. The deconvolution of the peak position is left to a future investigation; at present we address merely the origin of the asymmetric lineshape and line broadening.

The Raman intensity $I(\omega)$ for the spatial correlation model may be expressed as [1, 7-8]

$$I(\omega) \propto \int \exp\left(\frac{-q^2 L^2}{4}\right) \times \frac{d^3 q}{\left[\omega - \omega(q)\right]^2 + \left(\frac{\Gamma_0}{2}\right)^2}$$
(1)

where q is in units of $2\pi/a$, a is the lattice constant, and Γ_0 is the linewidth of the material of composition x=0 which is GaN in this study. Our GaN films exhibit linewidths in the range of



FIG. 1. The Raman spectra of the E2 mode of films of various composition x. The solid lines were calculated from the spatial correlation model (Eq. 1).

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FIG. 2. The (0002) x-ray diffraction of film of x=0.22. The inset shows the very weak (0001) superlattice line.

FIG. 3. The E2 Raman linewidth as a function of composition x.

 $3-5 \text{ cm}^{-1}$ depending on the film quality. For the calculations we used the upper range value to account for the stress in the alloy which was inferred from the appearance of cracks in the films. In the calculation we assumed a spherical correlation domain and BZ.

To evaluate Equation 1 we fitted the phonon dispersion curves, which have been calculated by Azuhata et al [10], in the vicinity of BZ center. In their calculations the E2 mode along the Δ direction exhibits a doubly degenerate behavior and is a weak function of q, thus having no effect on the line broadening mechanism. In contrast, the E2 curves along the Σ and T directions both split into a lower and an upper branch, where the former is a decreasing function of q and the later is an increasing function; these curves are expected to influence the Raman lineshape. Our calculations of Eq. 1 best concur with the phonon dispersion curve of the form: $\omega(q) = A + Bq^2$ (in units of cm⁻¹ and with A=568 and B=100) which is the approximated behavior of the upper branch of the Σ and T curves in the vicinity of the zone center. However, when we included the contribution to the lineshape arising from the lower branches of the dispersion curves the fit was not ideal. Similar behavior has been previously observed in the calculation of BN lineshape [7]. The reason for the dominance affect of the upper branches in our calculations is under investigation.

The calculated lines and the Raman data for samples of composition 0.12 and 0.22 are presented in Figure 1. As depicted in the figure the asymmetric Raman data concur with the spatial correlation model, where the small deviation ~ 560 cm⁻¹ may be attributed to the activated A1(LO) mode. The ordered domain size, L, was determined from our calculations to be $\sim 2.5 - 3.5$ nm; a relatively small value suggesting the lack of a long range order in the alloy system. In order to further investigate this hypothesis a film of composition x=0.22 was characterized by XRD: the scan is presented in Figure 2. The figure shows the diffraction peak of the (0002) planes of the AlGaN (superimposed is also the SiC substrate peak) and the inset presents the weak (0001) diffraction peak. The (0001) is a forbidden reflection in the WZ structure and appears as a superlattice line only when lattice ordering exists [11]; the intensity ratio (0001)/(0002) is a measure of the extent of the order [12]. Al_xGa_{1-x}N films which were grown by molecular beam epitaxy have been reported by Korakakis et al [11] to exhibit a long range order; the intensity ratio of their XRD lines is ~ 0.05 in contrast to our much smaller intensity ratio of ~ 0.002. Thus the XRD confirms the Raman analysis, indicating that the alloys in this study do not exhibit significant long range ordering. More insight into the alloy micro-structure may be obtained from the Raman linewidth behavior. Figure 3 presents the Raman linewidth of the E2 mode as a function of the composition. The linewidth behavior follows a pattern which exhibits a maximum at composition $x \sim 0.5$, a value at which a maximum disorder should be expected in a random system. Thus our data suggest that the distribution of the alloy constituents for the most part is random.

The Stress State of the AlGaN Films

The morphology of our AlGaN films consists of uniformly distributed crack density which is indicative of the high stress state present in the films. In general, stress may be analyzed via the shifting of the Raman peak position. However, as mentioned the Raman peak position of the alloy depends on the combined effects of the stress, the relaxation of the q \cong 0 selection rules, and the mode-type. All these effects are functions of the composition; the stress, however, is also a function of the lattice constants and the thermal expansion coefficients of the film-substrate system.

In order to determine the stress-type in the alloy we took advantage of the film morphology: Micro-Raman spectra were acquired at a crack region, where the film is relatively relaxed, and at a region remote from the crack, where the film is strained. Figure 4 shows characteristic spectra of the relaxed and strained regions. The linewidth of both spectra is ~16 cm⁻¹ implying that no significant spatial variation of composition, x, occurs across the film. Since the composition is similar in the relaxed and the strained regions, the Raman peak position is influenced mainly by the stress effects due to the film-substrate thermal and lattice mismatch. As can be observed in the figure, the peak position of the strained region suggesting that the original stress state of the film (before relaxation via cracking occurs) is tensile.

A source of the tensile stress in the alloys may be the difference in the thermal expansion coefficients, α , of the film, the buffer-layer, and the substrate at the elevated temperature (1400 K)



FIG. 4. The Raman spectra of the E2 mode acquired at a relaxed and at a strained region of AlGaN film of composition x=0.22.



FIG. 5. Raman spectra of (a) AlN film grown on SiC substrate and (b) AlN crystal.

at which our films were grown. The α 's of GaN and SiC at this temperature range have not yet been measured. However, at ~750 K the thermal expansion coefficients along the a axis (α_a) and c axis (α_c) have been measured [13]; for GaN, α_a =6.2 and α_c =6.1, and for SiC α_a =4.2 and α_c =4.0, where α is in units of 10⁻⁶ K⁻¹. The average thermal expansion coefficients of AlN at 750 K and 1200 K have been reported to be 5.8 and 6.2 10⁻⁶ K⁻¹ respectively [14]. The smaller value of the SiC thermal coefficient relative to that of the alloy constituents thus may be the cause of the tensile stress in our films. To acquire further insight into this issue, the Raman spectra of AlN film, grown under similar conditions as the alloys, was compared to that of AlN crystallite. The spectra are presented in Figure 5 (the spectrum of the crystallite was acquired with a backscattering geometry from the a-face for which the E1(TO) is an allowed mode as well). As can be seen in the figure, the AlN Raman peak of the film exhibits a tensile shift of ~4 cm⁻¹ relative to the peak position 656 cm⁻¹ of the crystal. A result suggestive of the presence of stress in the film due to the different coefficients of thermal expansion.

CONCLUSIONS

The asymmetric behavior of the E2 Raman lineshape of $Al_xGa_{1-x}N$ alloys was attributed to the activation of phonons of $q \ge 0$ arising from the disordered state of the alloys. The line broadening of the E2 Raman mode exhibits a maximum at composition $x \sim 0.5$ which is consistent with a random distributed system. X-ray diffraction supports these findings: the superlattice relative line-intensity is weak. The alloy exhibits tensile stress which is suggested to be due to interfacial thermal mismatch.

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