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Silicon-doping induced strain of AlN layers: a comparative luminescence and Raman study

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Si-doped aluminum nitride layers show a shift of the near-band-edge luminescence at around 6 eV to lower energies for increasing Si concentration up to $\approx(1-3)\times10^{19}$ cm^{-3}. For higher concentrations, the luminescence shifts back to higher energies. This behavior is compared to concomitant shifts of the Raman-active E_2 vibrational mode and to X-ray diffraction data. It can be explained in terms of increasing tensile strain which finally relaxes due to the formation of cracks.

Aluminum nitride (AlN), representing the upper end of the technologically interesting alloy system aluminum gallium nitride (AlGaN), has a direct band-gap of ≈6.1 eV at low temperatures. This extremely wide gap could enable, e.g., future applications as a deep UV optoelectronic material. Indeed, Taniyasu et al. [1] recently demonstrated a light emitting diode made of Si- and Mg-doped AlN operating at ≈210 nm. This break-through is stimulating further work on the doping of AlN and its influence on crystal growth and optical properties. It is known from a number of works [2, 3] that doping AlN with Si leads to a red-shift of the near-band-edge luminescence. Nam et al. [2] explained this red-shift in terms of an electronic band-gap renormalization. In the present letter we give arguments that this shift is rather a consequence of tensile strain introduced by doping with Si. To show this we compared high-resolution X-ray diffraction (HRXRD) data and low temperature cathodoluminescence (CL) with Raman measurements, and the correlation of the results verified that the origin of the band-gap shift is doping-induced strain. A variety of AlN layers were grown by metal organic vapor phase epitaxy as described elsewhere in detail [4]. Two series of samples were grown at different growth temperatures of 1150 °C and 1190 °C, respectively. After deposition of a nucleation layer of AlN on the *c*-plane sapphire substrate an undoped AlN layer with a thickness of about 250 nm was grown, followed by a 250 nm to 350 nm thick Si-doped layer. The basic growth conditions of both the undoped and Si-doped layers were similar. The Si concentration was varied from 3×10^{17} cm^{-3} to 9×10^{19} cm^{-3} and measured by secondary ion mass spectroscopy (SIMS). For comparison, two undoped AlN reference samples were grown with a thickness of approx. 500 nm. The CL measurements were accomplished at 6 kV in a variable-temperature continuous helium-flow cryostat. The emitted light was focused on the entrance slit of a monochromator with attached liquid nitrogen-cooled charge-coupled device (CCD) camera. The electron beam spot diameter on the sample was around 0.5 mm, and the penetration depth was estimated to be ≈370 nm. In this case the spectral resolution was better than 3 meV at 6 eV. The Raman measurements were carried out in a confocal micro-Raman system with a 514 nm Ar$^+$-laser beam. The laser beam was focused with a microscope lens (×80, NA = 0.75) to about 0.75 µm spot diameter on the sample surface. To exactly calibrate our wave number scale we recorded simultaneously with the Raman signal various laser plasma lines. The spectra were recorded at room temperature in back-scattering geometry and detected by a DILOR XY800 triple-monochromator with an attached CCD camera. The

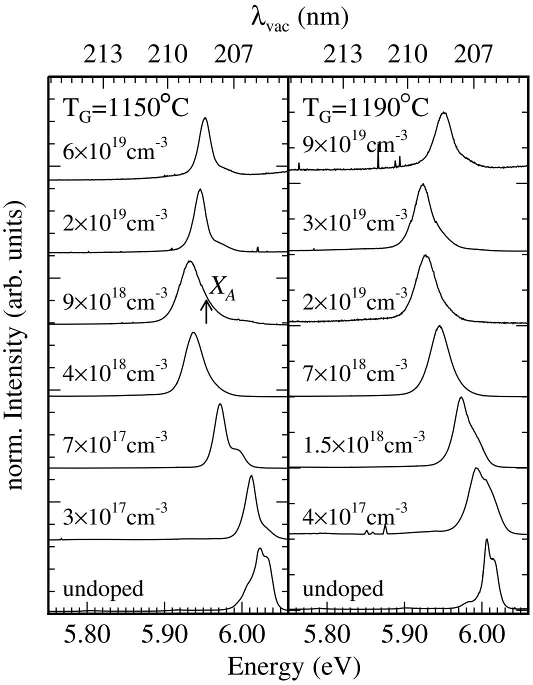

Figure 1 CL spectra of the Si-doped and the undoped AlN reference samples at $T \approx 10$ K. The dominant lines are from bound exciton recombination (including the double peak in the two lower spectra) while free exciton transitions are seen as high-energy shoulders (example marked by arrow). Left side: CL spectra of the series of AlN layers grown at 1150 °C. Right side: CL spectra of the series of AlN layers grown at 1190 °C.

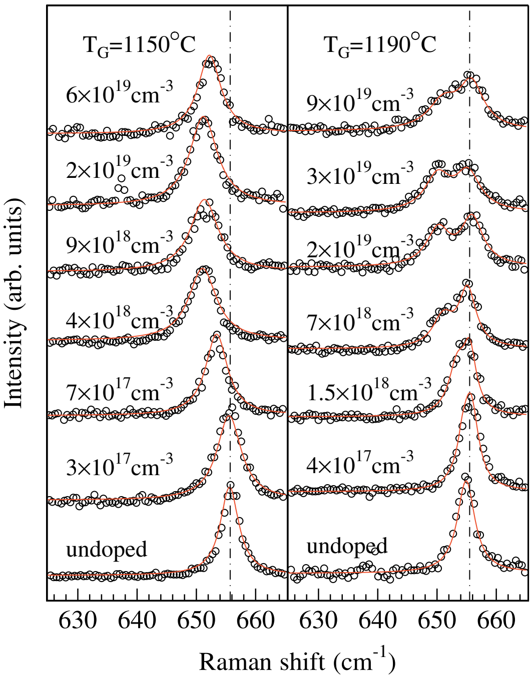

Figure 2 (online colour at: www.pss-rapid.com) Raman spectra of the E_2^{high} mode for the Si-doped and the undoped AlN reference samples. The vertical lines mark the position of the E_2^{high} mode of unstrained AlN.

overall spectral resolution and accuracy of this system is therefore better than 0.5 cm^{-1}.

Figure 1 shows near-band-edge CL spectra of the Si-doped AlN layers and of the undoped reference samples. Each spectrum consists of bound and free exciton (X_A) transitions, the latter being only visible as weak high-energy tails.[1] Starting from the peak position of the undoped AlN reference samples at ≈6.01 eV, we observe in both sample series a similar monotonic shift of the luminescence peak towards lower energies for increasing Si concentrations up to (1–3) × 10^{19} cm^{-3}. For the higher doping levels of 6 and 9 × 10^{19} cm^{-3} the shift reverses back to higher energies. Figure 2 shows the corresponding Raman E_2^{high} modes for both sample series. For the samples grown at lower temperatures the AlN E_2^{high} mode shifts to lower wavenumbers for Si concentrations up to 9 × 10^{18} cm^{-3}, and again shifts back for the higher doping levels. The samples grown at 1190 °C exhibit basically the same behavior, but show additionally a non-shifting high-energy component at the initial position of 656 cm^{-1} which is assumed to originate from the undoped AlN buffer layer. The low energy component shifts down for Si concentrations up to 3 × 10^{19} cm^{-3}, and shifts back again at the highest doping level of 9 × 10^{19} cm^{-3}. In HRXRD measurements [4] the samples grown at 1190 °C also showed a doublet peak structure like the Raman spectra. This indicates different strain in the underlying undoped buffer and the top Si-doped AlN layer. For the samples grown at lower temperature, we found only one single shifted peak, similar to the Raman measurements. For these samples we therefore cannot separately identify the strain in the buffer layer. Altogether, for both series of samples we observe that either the single E_2^{high} mode (1150 °C series) or the corresponding low-energy component of the doublet peak (1190 °C series) show a behavior in full analogy to the near-band-edge CL luminescence.

To evaluate the correlation quantitatively we performed line shape fits to the Raman spectra as well as to the near-band-edge emission spectra. For the Raman spectra shown in Fig. 2 we used one or two Lorentzian lines to fit the single or doublet E_2^{high} mode, respectively. The wave number scale was calibrated against the Ar$^+$-laser plasma line at 520.3 cm^{-1} recorded together with the sample spectra yielding the position of the E_2^{high} mode to better than 0.5 cm^{-1}. The fits to the measured spectra are shown as solid lines in Fig. 2. For the CL spectra we proceeded in the following way: The bound and free components in Fig. 1 have been decomposed by fitting either Gaussian or Lorentzian shapes to them. The free exciton component could always be satisfactorily fitted by a Gaussian shape.

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[1] We made sure that these tails are due to free exciton recombination by recording spectra at higher temperatures observing that the tails grow in succession stronger albeit these spectra are unsuitable for line fits due to the strong overlap of the bound and free components.

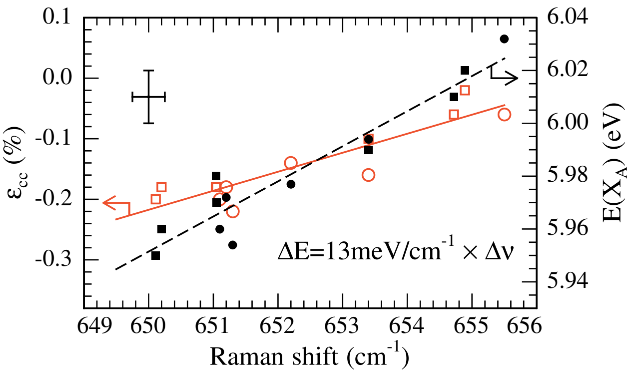

Figure 3 (online colour at: www.pss-rapid.com) Correlation of the strain ε_{cc} (open symbols) measured by HRXRD and the free exciton (X_A) energy position (full symbols) with the Raman shift of the lower component of the E_2^{high} mode. The experimental error of the X_A-to-E_2 correlation is indicated in the upper left corner. Samples with $T_G = 1150$ °C are represented by circles, samples with $T_G = 1190$ °C by squares. The solid and the broken line are least square fits to the data.

As both spectral components are relatively broad, the uncertainty in determining their positions was as large as ≈10 meV. For all Si-doped samples the fits yielded localization energies of the donor bound exciton transitions ranging from 22 meV to 29 meV. In the literature, similar values were found for Si-doped AlN samples grown on sapphire [2] and 6H-SiC [3]. The positions of the free exciton transition X_A are plotted against the E_2^{high} Raman mode in Fig. 3. A linear correlation of the two energies is obvious and is described by a regression line with slope $\Delta E(\mathrm{CL}) = 13\ \mathrm{meV/cm^{-1}} \times \Delta\nu\ (\mathrm{Raman})$.

Basically, various effects can lead to a decrease of the emission energy of highly doped samples. Bandgap renormalization e.g. is an effect expected to happen at donor concentrations approximately above the critical density of Si in AlN, $n_c \approx 1.3 \times 10^{21}\ \mathrm{cm^{-3}}$ [5]. This very high density is the reason that the redshift of our CL bands cannot be explained by bandgap renormalization as was the case in Ref. [2]: Our samples have donor densities far below n_c and they do show free exciton emission which would be quenched above n_c. The occurence of free exciton recombination furthermore excludes self-absorption effects in the CL spectra as a possible interpretation of the spectral shifts. Another possible explanation for the redshift is the occurrence of potential fluctuations (or alloying) for higher silicon doping concentrations. Increasing potential fluctuations, however, can only lead to a downshift of the emission energy but can never account for the final upshift for the highest Si concentrations. An important finding is that the tensile strain as determined by HRXRD correlates linearly with the observed Raman shift (see Fig. 3). Thus, the only explanation for the CL shift consistent with the experimental data is in terms of strain effects caused by the Si doping. The decrease of such strain above a doping level of $(1-3) \times 10^{19}\ \mathrm{cm^{-3}}$ comes unexpected. A clue to this observation is given by scanning electron microscopy studies on our layers revealing cracks on the surface of these highly doped samples. The formation of cracks relaxes the strain in the layers, and therefore the near-band-edge emission shifts back towards the position observed in the undoped layer. Alternatively, the strain can be calculated from the position of X_A using the equations and deformation potentials given by Wagner and Bechstedt [6]. For the Raman data the strain was computed using averaged phonon-deformation potentials from Sarua et al. [7] and Wagner and Bechstedt [6]. The strain values calculated from the luminescence and from the Raman shift coincide within an error margin of 4%. Hence, we obtain an excellent correlation of the strain as determined by HRXRD, the shift of the Raman E_2^{high} mode, and the CL free exciton emission. We note that based on the strain values obtained from the Raman data we calculate a biaxial stress coefficient of $\partial E/\partial\sigma_\perp = -49$ meV/GPa which is in agreement with that of Pantha et al. [8]. In summary, our data clearly correlate the shift of the near-band-edge luminescence towards lower energies to tensile strain originating from the doping of AlN with Si.

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