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Si doping effects on (In,Ga)N nanowires

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Si doped (In,Ga)N nanowires (In content up to 0.4) are grown on Si(111) substrates by plasma-assisted molecular beam epitaxy. By increasing the Si doping level, coalescence between nanowires is reduced and a more uniform morphology is obtained. The Raman spectra from highly doped samples show a characteristic broad band in the optical phonon frequency range, which became more prominent at higher doping levels. This Raman band can be explained by plasmon-phonon scattering from a free electron gas with strong wave-vector nonconservation, providing evidence for successful n-type doping. The measured plasmon-phonon modes are explained by lineshape simulations taking into account the simultaneous contribution of both the charge-density fluctuation and the impurity induced Fröhlich scattering mechanisms. The according lineshape analysis allows for an estimate of the carrier concentration. © 2014 AIP Publishing LLC.

I. INTRODUCTION

(In,Ga)N alloys, which allow for blue/green light emitting devices, have led to the continuously increasing usage of solid state lighting. The band gap of these materials ranges from the ultraviolet (3.4 eV for GaN) to the near infrared region (0.63 eV for InN), which makes them highly interesting for other optoelectronic applications as well. However, with increasing In content the lattice mismatch between (In,Ga)N and GaN, the typical substrate/template, increases, resulting in misfit dislocations which degrade device performance. One way towards emission or absorption at green and longer wavelengths is the utilization of nanowires (NWs), which can accommodate lattice mismatch by lateral elastic relaxation. This can allow for growth on cost-effective, conductive, and scalable Si substrates. In particular, catalyst-free, self-induced NW growth by molecular beam epitaxy (MBE) is attractive since it allows GaN NWs with excellent structural and optical properties to be obtained and NW-based LEDs on Si substrates have been demonstrated. Consequently, increasing research efforts currently aim at realizing devices consisting of high In content (In,Ga)N NWs that emit light at longer wavelengths or harvest solar power. A crucial requirement for such devices is achieving intrinsic doping and the evaluation of the carrier concentration. So far, among III-N NWs grown by MBE Si doping has been investigated only for the n-type doping of the binary materials GaN and InN. Due to the geometry of NWs, it is very difficult and complicated to analyze the carrier concentration of NWs by Hall measurements. Here, we study the Si doping of ternary (In,Ga)N NWs grown by MBE and estimate the carrier density using Raman spectroscopy.

II. EXPERIMENT

Prior to growth, the native oxide of the Si substrates was removed in situ by Ga deposition followed by annealing until the formation of a clean Si(111) reconstructed surface was confirmed by reflection high-energy electron diffraction. After nitridation of the Si substrate for 5 min, (In,Ga)N NW growth was carried out by plasma-assisted MBE using the self-induced method for 1.5 h with a Ga flux of 1.6 nm/min, an In flux of 1.9 nm/min and a N flux of 10 nm/min. The substrate temperature was varied in the range between 500 and 640°C in order to modify the In incorporation. For Si doping, effusion cell temperatures were used. Some samples were grown with Mg co-doping in order to achieve electrical compensation of the n-type doping. The NW morphology was analyzed with a scanning electron microscope (SEM) and the interface between NWs and the Si substrate was investigated by high resolution transmission electron microscopy (HRTEM). The In content of the NWs was determined by X-ray diffraction using Vegard’s law. The incorporation of Si into the NWs was examined by micro-Raman spectroscopy using optical excitation at 3.06 eV (laser diode) or 3.81 eV (He-Cd laser). The Raman signal was dispersed by an 80-cm Jobin-Yvon spectrograph and detected with a liquid N2-cooled CCD. The measurements were performed at room temperature in backscattering geometry, i.e., along (perpendicular to) the NWs’ c-axis for as-grown (dispersed) NWs. The Raman spectra of the dispersed NWs were recorded from NW bunches without a well-defined polarization configuration. In some cases, NWs were dispersed on MgO substrates, in which first-order Raman scattering is forbidden by selection rules. This was done in order to record Raman spectra without the strong contribution of the optical-phonon line from Si.

III. RESULTS AND DISCUSSIONS

The SEM images of (In,Ga)N NWs grown at different temperatures (Tsub = 640, 590, 540, and 500°C) with different Si fluxes (undoped, TSi = 1100, and 1300°C) are displayed in Fig. 1. The average In-contents of the samples, as determined by XRD, are presented in Fig. 2. Without Si doping, with decreasing substrate temperature, the In content of the (In,Ga)N NWs increases accompanied by a tendency for...
lateral growth and coalescence [see Figs. 1(a), 1(d), 1(g), and 1(j)], as already observed previously. With Si doping, for all substrate temperatures coalescence is reduced and the NWs are more uniform, even at the lowest Tsub of 500 °C. This impact of Si doping on the NW morphology is quite different from what has been found for GaN NWs, where a decrease in height and density as well as a reverse tapered shape (increase of diameter from bottom to top) were observed. The decrease in the density of Si-doped GaN NWs was explained by the prevention of NW nucleation due to the formation of an additional ~3-nm-thick SiN layer on top of the ~2-nm-thick SiN layer generally grown on Si substrates in the case of undoped NW growth. Fig. 3 shows a typical HRTEM image of the interface between an (In,Ga)N NW and the Si substrate. Apart from the commonly observed ~2 nm thick SiN layer, no additional SiN layer was found. The reason why in this case an additional SiN layer did not form under Si doping may be related to the much lower substrate temperature used for the growth of (In,Ga)N NWs. As a consequence, the nucleation of (In,Ga)N NWs is much faster than that of GaN NWs. Thus, (In,Ga)N NW nucleation might dominate over SiN formation. In addition, in growth experiments by metal organic vapor phase epitaxy, it was found that the formation of SiN was less efficient at low temperature.

An improved morphology has also been observed for Si-doped InN NWs. Changes in NW morphology upon the
addition of dopants are usually attributed to the modification of adatom diffusion lengths. For ternary alloys, the situation is more complex since the composition of the NWs may also be affected. Indeed, the In content is significantly reduced for the highest $T_{Si}$ of 1300°C, probably due to the additional heating of the substrate by the Si cell. As pointed out above, a lower In content is typically associated with less coalescence. However, the comparison of samples (d) and (l) shows that well isolated NWs with higher In content are obtained with Si doping. Therefore, Si doping has a clear beneficial impact on the morphology of (In,Ga)N NWs.

The incorporation of Si into (In,Ga)N NWs was investigated by micro-Raman spectroscopy under near-resonant conditions. Raman spectroscopy is an established tool to investigate electron gases in doped semiconductors via coupled longitudinal optical (LO)-phonon plasmon modes. In binary semiconductors, the analysis of the two coupled modes $L^{-}$ and $L^{+}$ can be utilized to determine the carrier density and mobility. In the case of strong wave-vector nonconservation, however, a broad spectral feature between the transverse optical (TO) and LO phonon frequencies dominates the Raman scattering from the free carrier gas instead of the two separated $L^{-}$ and $L^{+}$ modes.

First, low In content samples grown at 640°C with $T_{Si} = 1100$, 1200, and 1300°C were analyzed. Figs. 4(a)–4(c) show the Raman spectra acquired in backscattering configuration along the c-axis of the NWs with 3.81 eV excitation after the subtraction of a smooth and featureless photoluminescence background. The Raman scattering from the lightly doped sample ($T_{Si} = 1100$ °C) reveals, in addition to the signal from the Si substrate, only the expected phonon modes, i.e., the LO and $E_{2}(high)$ modes. Since the coupling of light into and out of the NWs takes place predominantly through their sidewalls, the $E_{2}(LO)$ instead of the $A_{1}(LO)$ phonon mode is observed. Note that (In,Ga)N exhibits one-mode behavior for both $E_{2}(high)$ and LO phonon modes. The spectra of the more heavily doped samples exhibit a broad band between 560 and 730 cm$^{-1}$, which becomes more pronounced with increasing doping level. This broad Raman band can be explained by plasmon-phonon excitations under the condition of strong wave-vector nonconservation, as reported previously for p-type GaAs, n-type cubic GaN, and n-type InN layers. One reason for the breakdown of the wave-vector conservation is given by the elastic scattering by ionized impurities. In NW geometries, the spatial confinement of free electron gases in the radial direction causes an additional contribution to the wave-vector nonconservation.

In order to simulate the experimental spectra, the contribution of the charge-density fluctuation (CDF) and the impurity-induced Fröhlich (IIF) mechanisms were taken into account. The details of the lineshape calculations are given in Refs. 29 and 35. We use the following parameters close to those of GaN: effective electron mass 0.2 $m_{0}$, dielectric constant $\varepsilon_{\infty} = 5.3$, TO phonon frequency $\omega_{TO} = 558$ cm$^{-1}$, and LO phonon frequency $\omega_{LO} = 728$ cm$^{-1}$. The best fits were obtained with plasmon damping constant $\Gamma = 50$ cm$^{-1}$, phonon damping constant $\gamma = 10$ cm$^{-1}$, and cutoff wave vector $q_{max} = 20q_{PT}$, where $q_{PT}$ is the Fermi-Thomas screening wave-vector. Theoretical lineshapes for Fermi energies $E_{F}$ ranging from 75 to 300 meV (corresponding to electron concentrations $n = 8.3 \times 10^{18}$–6.7 $\times 10^{19}$ cm$^{-3}$) with respect to conduction band minimum are shown in Fig. 5 for the CDF and the IIF mechanisms. The strong feature in the calculated CDF spectra at $\omega_{TO}$ is an artifact caused by the fact that in the lineshape function given by Eq. (2.108) in Ref. 29, the singularity in the prefactor $S(\omega) = (\omega_{LO}^{2} - \omega^{2})/(\omega_{TO}^{2} - \omega^{2})^{2}$ (without phonon damping) is not fully compensated by the corresponding minimum in the energy-loss function Im$[-1/\varepsilon(q,\omega)]$ for the case of large plasmon damping. The simulated IIF spectra [cf. Fig. 5(b)] exhibit a lineshape similar to the bare $E_{2}(LO)$ phonon mode and vary only slightly with $E_{F}$. In contrast, the CDF spectra strongly depend on $E_{F}$ as indicated by the arrow in Fig. 5(a) where a broad peak around 670 cm$^{-1}$ becomes dominant with increasing $E_{F}$ (also see Ref. 35). This trend resembles the change observed in the experimental Raman spectra with increasing Si doping. Satisfactory lineshape fittings for Raman shifts $> 600$ cm$^{-1}$ are obtained for the heavily doped samples ($T_{Si} = 1200$ and 1300°C) using a superposition of CDF and IIF spectra [see Figs. 4(b) and 4(c)]. As a result of the fitting procedures, the Fermi energies ($E_{F}$) (carrier concentrations) for the two heavily doped samples are deduced to be 100 and 150 meV ($n = 1.3 \times 10^{19}$ and 2.4 $\times 10^{19}$ cm$^{-3}$), respectively. One would expect much more than an increase by a factor of two in...
carrier concentration for an increase in the Si cell temperature by 100 °C. Consequently, our observations indicate that for the largest Si fluxes the solubility limit of Si in GaN under nitrogen-rich growth conditions is already reached. Note that the weighting factor used in Eq. (2.124) of Ref. 29 to describe the wave-vector nonconservation constitutes an approximation, which might lead to a significant overestimation of the carrier densities extracted from the lineshape fitting. The degree of this overestimation could only be determined by independent electrical measurements. However, the obtained values can be utilized to determine trends such as the relation between Si cell temperature and carrier density, as shown in Fig. 4.

In addition to the low In content samples, high In content samples grown at 500 °C [undoped, Si-doped (TSi = 1300 °C), and co-doped (TSi = 1300 °C and TMg = 240 °C)] were investigated under 3.06 eV excitation. The Raman spectra from the as-grown samples shown in Figs. 6(a1)–6(a3) are dominated by optical-phonon scattering (520 cm⁻¹) from the Si substrate. However, the comparison of the spectrum from the undoped sample (j) with that of the heavily doped sample (l) reveals again an additional doping-induced broad band between the TO and LO phonon frequencies, as indicated by the arrow in Fig. 6. Raman spectra recorded from NWs dispersed on MgO substrates are displayed in Figs. 6(b1)–6(b3). Unfortunately, for NWs with high In content the lineshape analysis is complicated by the contribution of the so-called S band, which is related to disorder and the broadening of all Raman excitations due to fluctuations in the In content. Therefore, only the spectrum of the undoped sample was evaluated by a lineshape analysis. This analysis reveals the contributions of a broad superimposed E₁(TO) or E₂(high) band as well as the E₂(LO) peak and the S band. The lineshape of the heavily doped sample [cf. Fig. 6(b2)], in comparison, can only be explained by taking into account an additional contribution in the range between the TO and LO phonon frequencies [indicated by the arrow in Fig. 6(b2)], in accordance with the result obtained from the as-grown samples.

In order to exclude surface-optical phonon modes as a possible alternative explanation for the doping-induced broad Raman band, the spectra were compared with those recorded with as grown NWs immersed in paraffin oil (Nujol, dielectric constant ε = 2.3). The change in dielectric constant of the environment around the NWs did not cause any modification of the spectra [see Fig. 6(a2), without (black) and with (red curve) Nujol], in contrast to the expectation for surface-optical phonon modes. We therefore conclude that surface-optical phonon modes are not responsible for the broad Raman band. Also, surface and confined modes, which are defined only for the effective medium formed by NW ensembles, can be ruled out as the origin of the broad Raman band because the band appears at the same position for the as-grown and dispersed NWs [see Figs. 6(a2) and 6(b2)]. Furthermore, the Raman spectra of the samples heavily co-doped with Si and Mg resemble those of undoped NWs [see Figs. 6(a3) and 6(b3)], in accordance with the expected electrical compensation. We note that the morphology of co-doped sample is similar to Si doped sample (l). It is noteworthy that the highly doped samples (f) and (i) also exhibit the additional broad Raman band (not shown here). Consequently, our Raman results demonstrate the incorporation of Si atoms as donors into (In,Ga)N NWs leading to the formation of a free carrier gas.

IV. CONCLUSION

In conclusion, we have investigated Si-doped (In,Ga)N NWs grown by MBE on Si(111) substrates. The NW
morphology was improved by Si doping even at the lowest substrate temperature of 500 °C. Electrically active Si incorporation was demonstrated by a Raman scattering analysis. These results constitute an important step towards the fabrication of (In,Ga)N NW based devices.

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