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Tellurium n-type doping of highly mismatched amorphous GaN$_{1-x}$As$_x$ alloys in plasma-assisted molecular beam epitaxy.

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- We report on n-type doping of amorphous GaN$_{1-x}$As$_x$ layers with Te in PA-MBE.
- We have used a low temperature PbTe source as a source of tellurium.
- Reproducible Te incorporation in amorphous GaN$_{1-x}$As$_x$ layers has been achieved.
- The optimal growth temperature window for efficient Te doping has been determined.
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Abstract.

In this paper we report our study on n-type Te doping of amorphous GaN$_{1-x}$As$_x$ layers grown by plasma-assisted molecular beam epitaxy. We have used a low temperature PbTe source as a source of tellurium. Reproducible and uniform tellurium incorporation in amorphous GaN$_{1-x}$As$_x$ layers has been successfully achieved with a maximum Te concentration of 9×10$^{20}$ cm$^{-3}$. Tellurium incorporation resulted in n-doping of GaN$_{1-x}$As$_x$ layers with Hall carrier concentrations up to 3×10$^{19}$ cm$^{-3}$ and mobilities of ~1 cm$^2$/Vs. The optimal growth temperature window for efficient Te doping of the amorphous GaN$_{1-x}$As$_x$ layers has been determined.
Introduction

In the so-called highly mismatched alloys (HMAs) the band anticrossing (BAC) model predicts that a wide range of direct energy gaps can be achieved through the modification of the conduction and valence bands [1,2]. For example, the energy gap of highly mismatched GaN$_{1-x}$As$_x$ alloys is expected to vary from 0.7 eV to 3.4 eV. An even larger modification of the electronic band structure is expected for the more extremely mismatched GaN$_{1-x}$Sb$_x$ and GaN$_{1-x}$Bi$_x$ alloys [1-3]. The large band gap range and controllable conduction and valence band edge positions make HMAs promising materials for solar energy conversion devices. For example, the HMAs may be suitable photoelectrodes for photoelectrochemical solar water splitting. This application requires a semiconductor with the bandgap of about >2.0 eV and the conduction and valence band edges straddling the H$_2$O redox potentials. At dilute doping levels, As, Sb and Bi form localized energy levels above the valence band in GaN. Our measurements of GaN doped with As and Sb have demonstrated that the localized As and the Sb levels lie at about 0.7 eV and 1.2 eV above the valence band edge of GaN, respectively [4,5]. The BAC model predicts that at higher concentrations of these group V elements the
interaction of the localized states with the valence band of GaN results in formation of a fully occupied narrow band of extended states that plays the role of a new valence band edge [1,2]. This has been shown to result in an abrupt reduction of the optical gap of the HMAs.

Previously we have achieved an enhanced incorporation of As, Sb and Bi in GaN by growing the alloy thin films at extremely low temperatures (down to about 100 °C) by plasma-assisted (PA-MBE) [6-11]. Although the layers become amorphous for high As, Sb and Bi content, optical absorption measurements are consistent with the predictions of the BAC model, indicating that the amorphous HMAs samples have a short-range order resembling random crystalline alloys. The large band gap range and controllable positions of the conduction and valence bands make these HMAs promising materials for efficient solar energy conversion devices. However, before such devices can be realised, it is essential to achieve controlled n- and p-doping of GaN$_{1-x}$As$_x$ alloys over a large composition range.

Recently, we have demonstrated a successful p-type doping of amorphous GaN$_{1-x}$As$_x$ alloys with Mg [12]. The room temperature p-type conductivity has increased monotonically with increasing of Mg content, up to a maximum value of about 4.86 S/cm for 8 atomic % Mg content. We have found that achieving the p-type conductivity of GaN$_{1-x}$As$_x$ layers, requires growth under Ga-rich conditions [12]. These conditions result in the formation of As-rich crystalline GaAs:N inclusions inside the amorphous GaN$_{1-x}$As$_x$ matrix, which can be observed in the X-ray diffraction (XRD) and transmission electron microscopy (TEM) [12]. The role of these inclusions on the hole transport will require further studies. However, since the fraction of the GaAs:N is relatively low we believe the hole transport predominantly occurs in the As derived valence band of GaN$_{1-x}$As$_x$. 
We have also shown that it is possible to achieve n-type doping of amorphous GaN$_{1-x}$As$_x$ alloys with Te [12]. In MBE studies of GaAs:Te it was demonstrated many years ago that tellurium tends to accumulate on the surface by displacing arsenic atoms and forming a stable surface compound, presumably GaTe [13,14]. The build-up of a high surface concentration of Te on GaAs during MBE growth makes the doping process extremely difficult to control. However, Te doping in GaAs has been successfully achieved using PbTe as a doping source [13,14]. This is because Pb itself has a unity sticking coefficient on GaAs at room temperatures, but rapidly desorbs at temperatures above 250 °C.

In this paper we present a systematic study of the growth conditions affecting Te doping of amorphous GaN$_{1-x}$As$_x$ layers grown by PA-MBE. We show that controlling of the fluxes of Te and As and the growth temperatures are essential for efficient n-doping of the GaN$_{1-x}$As$_x$ alloy with specific composition.

II. EXPERIMENTAL DETAILS
GaN$_{1-x}$As$_x$ samples were grown by plasma-assisted molecular beam epitaxy (PA-MBE) in a MOD-GENII system. The system has a HD-25 Oxford Applied Research RF activated plasma source to provide active nitrogen and elemental Ga is used as the group III-source. In all experiments we have used arsenic in the form of As$_2$ produced by a Veeco arsenic valved cracker. A low temperature PbTe source has been installed in the system for the studies of n-type doping. The MBE system is equipped with reflection high energy electron diffraction (RHEED) for surface reconstruction analysis. For the growth of all GaN$_{1-x}$As$_x$ samples, we have used the same active nitrogen flux (total N$_2$ beam equivalent pressure (BEP) $\sim$1.5×10$^{-5}$ Torr, RF power 200 W) and the same deposition time of 2 hours. All layers were grown on 2-inch (0001)
sapphire substrates.

Note that in MBE the substrate temperature is normally measured using an optical pyrometer. However, because we have used uncoated transparent sapphire the pyrometer measures the temperature of the substrate heater, but not the substrate. Therefore in this study our estimate of the growth temperature is based on a thermocouple reading [6-9].

We have used a wide range of in-situ and ex-situ characterisation techniques to study the surface morphology, composition, structural, electrical and optical properties of the GaN$_{1-x}$As$_x$:Te layers. The morphology of the samples was studied in-situ using RHEED and ex-situ using atomic force microscopy (AFM). The structure and orientation of the GaN$_{1-x}$As$_x$ layers were determined by X-ray diffraction (XRD) using a Philips X’Pert MRD diffractometer. Microstructural information on the GaN$_{1-x}$As$_x$ alloys was obtained using transmission electron microscopy (TEM) techniques. Microscopic crystallinity and phase separation were studied by directly comparing the selective area electron diffraction patterns (SAD) with XRD measurements. The As content and uniformity in the GaN$_{1-x}$As$_x$ films were measured by electron probe microanalysis (EPMA) using a Cameca SX100 and by combined Rutherford backscattering spectrometry (RBS) and particle-induced x-ray emission (PIXE) measurements using a 3.04 MeV $^4$He$^{++}$ beam. The band gap of the thin films was measured by optical transmission and reflection using a Perkin Elmer Lambda 950 Spectrophotometer over the wavelength range of 190-3000 nm. Hall effect measurements in the van der Pauw configuration were used to determine the electrical properties of the deposited films.

III. RESULTS AND DISCUSSION
In order to achieve n-type conductivity in Te-doped amorphous GaN$_{1-x}$As$_x$, the layers have to be grown under Ga-rich conditions as described above. Therefore, in the current study we used a constant Ga flux with a BEP $\sim 2 \times 10^{-7}$ Torr and operated the HD-25 nitrogen source at 200W with a N$_2$ BEP of $\sim 1.5 \times 10^{-5}$Torr. The arsenic flux range was selected in order to maintain the composition of the GaN$_{1-x}$As$_x$ layers at around 60 mol%. Initially we grew several sets of samples at a growth temperature of $\sim 280$ °C with an As BEP of $\sim 6 \times 10^{-6}$ Torr. RBS data confirms that the GaAs content in this set of layers was about 60 mol% (x=0.6) and the optical band gap of the GaN$_{1-x}$As$_x$ layers was $\sim 1.3$ eV as measured by absorption studies. The RHEED patterns demonstrated the formation of an amorphous layer during the first few minutes of the growth. The GaN$_{1-x}$As$_x$ layers remained amorphous during the whole duration of the growth. Different fluxes of PbTe were used in order to investigate n-type doping, but we did not observe any significant changes in the RHEED pattern for the entire range of PbTe fluxes studied.

RBS data demonstrate a uniform incorporation of tellurium through the bulk of the GaN$_{1-x}$As$_x$:Te layers. Figure 1 shows the dependence of the Te concentration in the GaN$_{1-x}$As$_x$ layers measured by RBS against the PbTe flux. The thickness of the GaN$_{1-x}$As$_x$:Te layers was in the range 0.6 - 1 µm as measured by RBS, with the majority of the layers having a thickness $\sim 0.9$ µm. We have observed a gradual increase of the Te incorporation up to $\sim 4 \times 10^{20}$ cm$^{-3}$ as the PbTe flux increased. At the same time the RBS measurements show that Pb is not efficiently incorporated into the bulk of the GaN$_{1-x}$As$_x$ layers, with Pb concentration lower than $1.3 \times 10^{20}$ cm$^{-3}$ for the highest PbTe fluxes.

XRD measurements on these samples did not show any GaN related peaks, confirming the amorphous structure of the grown GaN$_{1-x}$As$_x$ layers. However, as we have reported previously
[12], a weak feature corresponding to the (111) diffraction peak of zinc blende GaAs:N can be detected. This indicates the presence of small crystalline GaAs:N inclusions in the amorphous GaN$_{1-x}$As$_x$:Te film. The presence of these inclusions has been confirmed by detailed TEM results that will be published separately.

Figure 2 presents dependence of the resistivity and electron concentration as a function of the Te concentration measured by RBS. Hall effect measurements demonstrate that both undoped and Te-doped GaN$_{1-x}$As$_x$ layers exhibit n-type conductivity. The resistivity drops abruptly for Te concentrations above $10^{19}$ cm$^{-3}$. At the same time we observe an increase in the electron concentrations up to $6\times10^{18}$ cm$^{-3}$. For Te doping higher than $2\times10^{20}$ cm$^{-3}$, a decrease in the electron concentration is observed. This may suggest deactivation of Te donors or formation of compensating native defects at this high Te doping level. The electron mobilities for all of the Te doped samples are very low, ranging from 0.4 - 1.1 cm$^2$/Vs. These values are reasonable given the amorphous structure of the GaN$_{1-x}$As$_x$ matrix.

Since the electrically active Te donors substitute the anion sites it is expected that the efficiency of the Te incorporation will depend on the As to N ratio. We have studied the influence of the As$_2$ flux during growth on the efficiency of the Te doping by changing the As$_2$ flux BEP from $1.0\times10^{-6}$ Torr to $6.4\times10^{-6}$ Torr. The lower range of arsenic fluxes was limited to $1.0\times10^{-6}$ Torr to avoid the formation of metallic droplets on the surface of the GaN$_{1-x}$As$_x$:Te layers. Figure 3a shows tellurium incorporation measured by RBS as a function of the Te flux used during the growth for three different arsenic fluxes. For all three As$_2$ fluxes we have achieved efficient incorporation of Te into the GaN$_{1-x}$As$_x$ layers. We observed a gradual increase of the Te incorporation as the PbTe flux increased. At the same time there is a clear increase in Te incorporation with decreasing As$_2$ flux. The maximum Te concentration achieved at the
The lowest arsenic flux was \(~9 \times 10^{20} \text{ cm}^{-3}\).

Further evidence for a complex interrelatedness between different growth parameters is shown in Figure 3b that presents RBS measured GaAs mole percent in GaN$_{1-x}$As$_x$:Te layers as a function of PbTe flux for 3 different arsenic fluxes. At high arsenic fluxes the Te incorporation does not have a significant influence on the alloy composition of the GaN$_{1-x}$As$_x$ layers. The constant composition of about 60% GaAs mole fraction is close to the intended composition set by the As and N fluxes. It is worth noting that at this composition GaN$_{1-x}$As$_x$ has the direct energy gap of 1.5 eV, which is close the optimum gap for efficient utilization of the solar spectrum. At the lowest As$_2$ flux of BEP~1.0×10$^{-6}$ Torr we have observed a clear decrease in the arsenic incorporation with increasing PbTe fluxes. This behaviour could be understood by noting that the Ga-N bond (2.24 eV/bond [15]) is significantly stronger than the Ga-As bond (1.63 eV/bond [15]). As a result there is a preferential incorporation of nitrogen over arsenic in the GaN$_{1-x}$As$_x$ layers. We were unable to find reliable published data on the energy of the Ga-Te bond. We expect that the value must be higher than that for the Ga-As bond, because the experimental data demonstrate that Te replaces As on the growth surface during MBE of GaAs:Te [13,14]. Therefore, we suggest that at low arsenic fluxes the probability of bonding Te to Ga increases due to the higher quantity of free Ga atoms on the growth surface. This will result in an increase of tellurium incorporation and in a decrease in the arsenic incorporation to GaN$_{1-x}$As$_x$:Te layers. Therefore, the need to control the alloy composition requires high enough As$_2$ fluxes. Consequently, although the low As$_2$ flux of 1.2×10$^{-6}$ Torr improves the Te incorporation it does not allow a control of the GaN$_{1-x}$As$_x$ alloy composition.

Resistivities of the GaN$_{1-x}$As$_x$:Te films as a function of PbTe BEP grown under different As fluxes are shown in Figure 4. The figure demonstrates that we can reproducibly control n-type
doping of GaN$_{1-x}$As$_x$ layers by changing the PbTe flux during growth for the whole range of arsenic fluxes studied. Increasing PbTe flux during the MBE growth increases Te incorporation and resulting in a decrease of the resistivity. The observed behaviour is similar for the 3 different arsenic fluxes. The lowest resistivity is observed for the lowest arsenic flux and that probably relates to the highest Te incorporation under these growth conditions as shown in Fig.3a. We have demonstrated Hall electron concentrations in the GaN$_{1-x}$As$_x$ layers up to $3 \times 10^{19}$ cm$^{-3}$. It should be noted however that the reduced resistivity of the film grown at the lowest As$_2$ flux comes at the price of reduced capability to control the alloy composition that is essential for all practical applications of GaN$_{1-x}$As$_x$. The electron mobility in all samples was weakly dependent on the doping level and remained very low at $\sim 1$ cm$^2$/Vs.

Finally we have investigated the effect of the PA-MBE growth temperature on the electrical properties of the Te doped GaN$_{1-x}$As$_x$. For this study we have used constant As$_2$ flux of $3.2 \times 10^6$ Torr that, as is shown in Figs. 3 and 4 has provided alloy with well defined composition and good electrical properties. Figure 5 presents dependencies of the Te concentration and alloy composition on the temperature for fixed As$_2$ and Te fluxes. There is a fixed temperature growth window where we can achieve n-type doping of GaN$_{1-x}$As$_x$ with PbTe flux. At growth temperatures below $\sim 250$ °C we cannot see any effect of the PbTe flux on the transport properties of GaN$_{1-x}$As$_x$ layers, probably because the temperature of the surface is too low for decomposition of the PbTe. This temperature is practically identical to the minimum growth temperatures for efficient Te doping of GaAs layers in MBE [13,14]. Also, as shown in Fig. 5, we have observed a decrease in the incorporation of Te and As in GaN$_{1-x}$As$_x$ at growth temperatures above $\sim 400$ °C. This is consistent with our previous papers on the growth of amorphous GaN$_{1-x}$As$_x$ layers that have shown reduced incorporation of As with increasing growth temperature [6,7]. However, it is still unclear whether the decrease in
the Te incorporation with increasing growth temperature is related to the reduced arsenic incorporation at higher growth temperatures.

Results in Fig 6 show the temperature dependence of the resistivity for the samples from Fig. 5. The low resistivity is obtained only for the growth temperatures between 280 °C and 330 °C. At temperature higher than 350 °C the resistivity increases abruptly by more than an order of magnitude indicating increasing fraction of electrically inactive Te atoms in the material.

Conclusions

In this paper we have studied n-type Te doping of amorphous GaN$_{1-x}$As$_x$ layers grown by PA-MBE. A low temperature PbTe was used as a source of tellurium. We have carried out a systematic investigation of the effects of varying Te and As fluxes as well as the substrate temperature on a growth of GaN$_{1-x}$As$_x$ films with controlled n-type conductivity. We have successfully identified the range of the growth parameters for reproducible and uniform tellurium incorporation in amorphous GaN$_{1-x}$As$_x$ layers with x ≈ 0.6. Tellurium incorporation resulted in n-doping of GaNAs layers with resistivity changes over 4 orders of magnitude, Hall electron concentrations up to 3×10$^{19}$ cm$^{-3}$ and mobilities of ~1 cm$^2$/Vs. The optimal temperature growth window for efficient Te incorporation into GaN$_{1-x}$As$_x$ layers was found to be between 250 °C and 400 °C, although the highest n-type conductivity has been observed in a more limited temperature range from 280 °C to ~330 °C. The successful synthesis of n-type doped GaN$_{1-x}$As$_x$ provides a unique opportunity to study doping and charge transport in ionic amorphous material. Also in combination with previously reported p-type doping it offers a potential for realizing p-n junction in a non-crystalline semiconductors.
Acknowledgements

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References


**Figure Captions**

Figure 1. Tellurium concentration in GaN$_{1-x}$As$_x$:Te layers measured by RBS as a function of the PbTe flux (BEP) used in the growth. MBE growth temperatures were ~280 °C, Ga BEP ~2.3×10$^{-7}$ Torr and As$_2$ BEP ~6.4×10$^{-6}$ Torr.

Figure 2. Resistivity (a) and electron concentration (b) in GaN$_{1-x}$As$_x$:Te layers as a function of Te concentration measured by RBS. MBE growth temperatures were ~280 °C, Ga BEP ~2.3×10$^{-7}$ Torr and As$_2$ BEP ~6.4×10$^{-6}$ Torr.

Figure 3. Tellurium concentration (a) and GaAs content (b) in GaN$_{1-x}$As$_x$:Te layers as a function of the PbTe flux (BEP) used in the growth for 3 different arsenic fluxes. MBE growth temperatures were ~280 °C and Ga BEP ~2.3×10$^{-7}$ Torr.

Figure 4. Resistivity of GaN$_{1-x}$As$_x$:Te layers as a function of the PbTe flux (BEP) used in the growth for 3 different arsenic fluxes. MBE growth temperatures were ~280 °C and Ga BEP ~2.3×10$^{-7}$ Torr.

Figure 5. RBS Tellurium concentration (left) and GaAs content (right) in GaN$_{1-x}$As$_x$:Te layers as a function of MBE growth temperatures. Ga BEP ~2.3×10$^{-7}$ Torr, PbTe BEP ~ 1.1×10$^{-8}$ Torr and As$_2$ BEP ~3.2×10$^{-6}$ Torr.

Figure 6. Resistivity of GaN$_{1-x}$As$_x$:Te layers as a function of MBE growth temperatures. Ga BEP ~2.3×10$^{-7}$ Torr, PbTe BEP ~ 1.1×10$^{-8}$ Torr and As$_2$ BEP ~3.2×10$^{-6}$ Torr.
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