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In this work, we report a p- to n-type conductivity transition of GaInNAs (1.0 eV bandgap) layers in p-i-n dilute nitride solar cells continuously controlled by the V/III ratio during growth. Near the transition region, we were able to produce GaInNAs layers with very low effective electrically active doping concentrations resulting in wide depleted areas. We obtained internal quantum efficiencies (IQEs) up to 85% at 0.2 eV above the bandgap. However, the high IQE comes along with an increased dark current density resulting in a decreased open circuit voltage of about 0.2 V. This indicates the formation of non-radiant defect centers related to the p-type to n-type transition. Rapid-thermal annealing of the solar cells on the one hand helps to anneal some of these defects but on the other hand increases the effective doping concentrations. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4909507]

There is a vital demand for high efficiency solar cells for space applications or terrestrial concentrator photovoltaic. Besides novel upcoming production techniques like direct wafer bonding,[1] the growth of monolithic GaInP/(In)GaAs/Ge still holds significant potential for optimization. It is well known that the integration of an additional dilute nitride middle junction based on GaInN(Sb)As with a bandgap of 1.0 eV, lattice matched to Ge/GaAs, could improve these devices even further.[2–5] However, the growth of high quality GaInNAs still holds significant challenges and minority carrier diffusion lengths comparable to those typically achieved in GaAs could not be reached.[6,7] The reason for the poor electronic properties lies in the incorporation of the highly electro negative N atom into the (In)GaAs crystal lattice, which gives rise to the formation of various crystal defects. Some of them can be annealed by a thermal treatment, but others are stable to at least some extend.[8,9] Not all of the defects have been identified yet but there is evidence for the formation of As_{Ga}-antisites,[10,11] N interstitials,[9,12] N-N chain ordering,[13,14] or Ga-vacancies.[15–17] Especially, Ga-vacancy defects are known to be responsible for the relatively high ($\sim10^{16} cm^{-3}$) electrically active p-type doping concentration usually found in MBE grown non-intentionally doped (NID) GaInNAs layers. This doping concentration is too high to produce wide depletion layers in p-i-n structures which are used to deal with the low diffusion lengths. However, there are also reports on n-type NID-GaInNAs layers[3] and even transition phenomena from n-type to p-type could be observed in NID-GaInNAs layers with 1.15 eV band gap depending on the substrate temperature during growth.[18] Consequently, the precise control of the electrically active defect formation is critical for the current generation in a GaInNAs solar cell. In this context, we report on the growth of 1.0 eV GaInNAs solar cells, where we were able to adjust the GaInNAs layers from n-type to p-type by increasing the V/III ratio. GaInNAs layers with a

very low effective doping concentration (N_{eff}) were obtained near the transition region, leading to an efficient carrier collection and high internal quantum efficiencies (IQEs). However, this comes along with a strongly increased dark current due to an increased non-radiant recombination rate.

The structures used for this work were grown in a 3 in. EIKO MBE system with standard solid sources, aside from N which was provided as atomic species by a RF plasma source. The flux ratios in this study were obtained by a VARIAN beam-flux monitor (BFM) measuring the beam equivalent pressure (BEP) at the substrate position. It has to be noted that these values are depending on the geometric alignment of the effusion cells and can differ notably from machine to machine. In addition, the substrate temperature during growth affects the effective group V flux as some fraction is desorbed from the growth surface.

External quantum efficiency (EQE) measurements were performed by illuminating the solar cells with light of a Xenon lamp that was spectrally filtered by a grating monochromator. The photon flux used to obtain the EQE from the measurement current was calculated from the power spectrum of the filtered light recorded with a power meter (Coherent FieldMaster-GS with Ge-detector). The power meter is factory calibrated and the signal-to-noise ratio during the measurements was in the range of 10^2–10^3. There was no bias voltage applied. The IQE was obtained by dividing the EQE by (1-Reflection). The reflection was measured in the range of 250–1500 nm using a UV/VIS-IR spectrophotometer (Perkin Elmer). Current-voltage (I-V) photovoltaic measurements were performed in darkness and under illumination using the full spectrum of a Xenon lamp shining on the solar cell. All measurements were performed at 25 °C.

Figure 1(a) summarizes the sample layout. The substrates were Zn-doped GaAs (100) wafers with 6° offcut to (111)B. As p-side of the double-heterostructure p-i-n diode, we used a 100 nm thick C-doped GaAs layer with a doping density equal to $1 \times 10^{17} cm^{-3}$ on which the 1500 nm thick

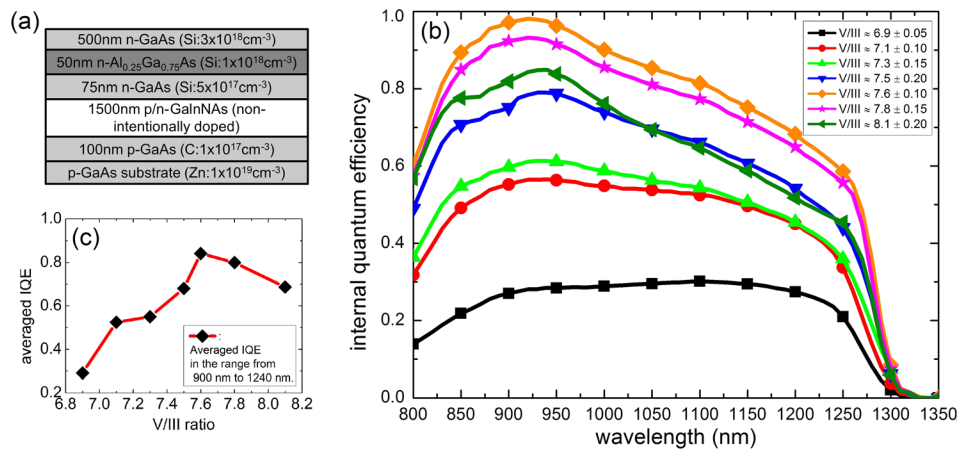a)fabian.langer@physik.uni-wuerzburg.de

FIG. 1. (a) Schematic layout of the GaInNAs solar cells. The GaInNAs layer is lattice matched to GaAs and NID. The pn-transition of the p-i-n diode lies—depending whether the GaInNAs is p- or n-type—either between the n-GaAs/p-GaInNAs or between the n-GaInNAs/p-GaAs. (b) IQE spectra of GaInNAs solar cells grown with different V/III ratios (see legend). The shape of the curve representing the cell with the lowest V/III (black) suggests an n-type GaInNAs configurations and changes with increasing V/III to p-type GaInNAs. (c) Averaged IQE values in the range from 900 nm to 1240 nm. The almost compensated cell with a V/III ≈ 7.6 (orange) reaches 84% quantum efficiency.

1.0 eV GaInNAs layer was deposited. The GaInNAs layer was NID and lattice matched to GaAs with an In(N) concentration of 7.8%(2.8%). The n-side of the p-i-n diode was 75 nm thick Si-doped GaAs with a doping density equal to 5×10^{17} cm^{-3} on top of the GaInNAs layer. In addition, we integrated a 50 nm thick Si-doped $Al_{0.25}Ga_{0.75}As$ layer that serves as a hole barrier. The samples were finalized with 500 nm highly n-type Si-doped GaAs. We investigated several different group V (i.e., essentially the As flux) to group III (considering both In and Ga fluxes) flux ratios during the GaInNAs growth of the specific samples. The growth temperature of the GaInNAs layer was 440 °C and all samples—unless otherwise noted—were subjected to a post-growth rapid thermal annealing (RTA) at 700 °C for 20 min.

The solar cells were fabricated with 1.0 cm^2 active areas. The front contacts are 15 μm broad annealed Ni/Au-Ge/Ni/Au fingers covering the active material and the back contacts are a planar metallization of Au-Ge/Ni/Au. The electrical isolation of the p-i-n-junctions was realized by chemical wet etching. As a reference, we have grown a GaInNAs solar cell with a V/III ratio ≈9.5. Another solar cell with a reduced V/III ≈ 7.6 was grown, using identical growth parameters otherwise. Figure 2 shows the illuminated (empty rectangles) and dark (filled triangles) I-V characteristics of those two solar cells. The black curves are measurements of the reference cell and the red ones are from the cell with the reduced V/III ratio. There are clear differences between the two cells. First of all, the open-circuit voltage (V_{OC}) of the reference cell is 0.39 V, which is a common value for 1.0 eV GaInNAs solar cells,[3,19] whereas the cell with the reduced V/III only reaches 0.21 V. Also the photo current density (J_{SC}) is disparate for both cells. The reference cell produces 6.6 mA/cm^2 (fill factor (FF) 59%), but the cell with the reduced V/III has a higher density of 9.1 mA/cm^2 (FF 42%). Other published results report FFs for 1.0 eV GaInNAs solar cells up to 70%.[3,4,20] Especially, the FF of the cell with the reduced V/III is much lower. The fitted diode parameters of the dark curves reveal a significantly lower dark current density (J_0) of 2.2×10^{-4} mA/cm^2 (ideality factor n = 1.49) for the reference cell compared to 2.3×10^{-2} mA/cm^2 (n = 1.36) for the cell with lower V/III

ratio. The increased J_0 can be regarded as a sign of shortened lifetime of the photo generated carriers due to increased Shockley-Read-Hall recombination in the GaInNAs. It is very likely that the lowered V/III during the growth of the GaInNAs material promotes the formation of crystal defects like As-vacancies. It has to be noted that with further lowering of the V/III ratio in the range of ≈6.0, the GaInNAs growth gets amorphous. At this point, it is very counter intuitive that the formation of defects—which are strongly increasing J_0—can increase the J_{SC}. But this finding seems possible if these defects are reducing N_{eff} in the GaInNAs layer and therefore increase the depletion layer width. The increased influence of field-assisted collection can also be seen at the dark I-V curves shifted by the J_{SC} represented by the broken red and black lines in Figure 2. Both solar cells show a shunt-like characteristic under illumination. But because this characteristic does not appear in the dark for the reference cell or is much weaker for the cell with the reduced V/III it is not a shunt. In fact, one can see the field-aided collection decreasing with increasing forward bias as the depletion layer width is reduced by the

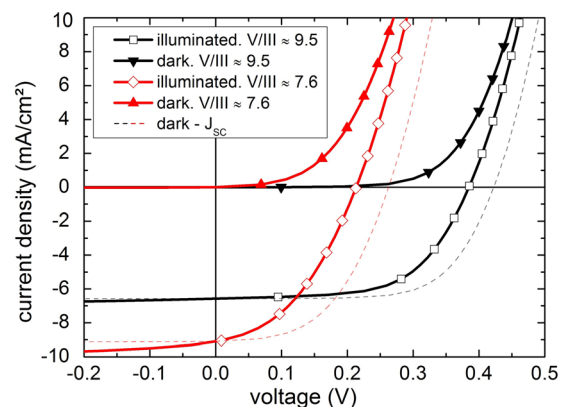FIG. 2. Illuminated (empty rectangles) and dark (filled triangles) I-V measurements of GaInNAs solar cells grown with a V/III ≈ 9.5 (black) and 7.6 (red), respectively. The broken lines (black and red) represent the dark measurements shifted by the J_{SC}. The cell with the higher (lower) V/III reaches a V_{OC} of 0.39 V (0.21 V), whereas the J_{SC} of the cell with the higher (lower) V/III is 6.6 mA/cm^2 (9.1 mA/cm^2).

applied bias. The photo current of the solar cell with reduced V/III shows a more pronounced dependency on the forward bias as it does for the reference cell. It is declining much faster as it would be if the illuminated I-V curve were only a superposition of the dark I-V curve and the photo current. This behavior is a clear indication of the increased part of field-assisted collection due to an increased depletion layer width. On the other hand, the lifetime limited diffusion current seems to be decreased. The dependency of the GaInNAs solar cell power generation on the V/III ratio was also observed by other groups.[20] To analyze the influence of these defects on the N_{eff} in the GaInNAs solar cells in more detail, a series with very fine and continuous variations of the V/III ratios during the GaInNAs growth has been investigated. The graduations were realized by a built-in group-III flux gradient of our growth machine. The fluxes of the Ga/In effusion cells decrease from the center of the wafer to the edge with an approximately quadratic dependency checked by measurements of the GaInNAs layer thicknesses at various positions. But the As cracker (veeco MARK IV) and the RF plasma source both have a special architecture to ensure an almost uniform flux over the complete substrate. The uniformity of the As flux was checked by the BFM, which is moveable in one direction of the growth plane. The homogeneity of the N-plasma flux was checked by the incorporation of N atoms in GaNAs layers by evaluating the secondary ion mass spectrometry signal of GaNAs layers at different wafer positions. Because of that the V/III ratio is steadily increasing from the center of the wafer to the edge of it with an overall difference of about 6% to 8%. Utilizing this gradient, only two wafers with slightly different group-III flux had to be grown for getting an appropriate range of V/III ratios. For the solar cell fabrication, the material from each wafer was taken in a distinct manner to get the incrementation of V/III ratios, as can be seen in the legend of Figure 1(b). Note that depending on the wafer position every specific cell resembles a mean average of V/III ratios defining different error bars. Figure 1(b) shows the IQE spectra of the produced cells with V/III ratios ranging from ≈ 6.9 up to 8.1. All curves show the GaAs cap layer absorption below 900 nm and the absorption edge of the GaInNAs material around 1280 nm. There are big differences in the IQEs among all cells. The curve representing the cell with the highest V/III ≈ 8.1 (green) shows its maximum IQE in the short wavelength part around 900 nm. The IQE is steadily decreasing for lower energy photons down to the GaInNAs energy gap suggesting an n-GaAs on p-GaInNAs configuration (see Figure 1(a)). This can easily be understood by considering the absorption coefficient of the GaInNAs layer. The absorption coefficient is decreasing for photons with energies approaching the bandgap of the GaInNAs and because of that the biggest part of the generated charge carriers in the upper part of the GaInNAs layer comes from photons with energies just below the GaAs bandgap. So if the IQE is highest for photons having that energy one can follow that the charge carriers have only a short way to reach the pn-transition, which has to be at the top of the GaInNAs layer. This can only be the case if the GaInNAs layer is p-type. When the V/III ratio is lowered to ≈ 7.8 (magenta) and further down to ≈ 7.6 (orange), the IQE characteristic stays the same, but the absolute values are increased drastically with reaching almost unity collection efficiency in the short wavelength part.

Such an improvement can only be attributed to a decreased N_{eff} in the GaInNAs layer with a strong effect on the field-aided collection. Following that trend for the next curves with a V/III ≈ 7.5 (blue), 7.3 (lime-green), and 7.1 (red), the IQE and especially the short wavelength response is decreasing. Finally, the IQE spectrum of the cell with a V/III ≈ 6.9 (black) has its maximum in the long wavelength region around 1125 nm, whereas the response for shorter wavelength is suppressed. This condition suggests an n-GaInNAs on p-GaAs configuration, with the result that charge carriers generated by long wavelength photons with large penetration depths have a relatively short way to the pn-transition, which in this case is located at the bottom of the GaInNAs layer. This condition does only apply if the GaInNAs layer is n-type. However, the IQE is only sensitive to $N_{eff} = (N_a(active)-N_d(active))$. Generally, there are three possible interpretations of our results. First of all, additional to the p-type defects (N_a may stay constant or even raise) new compensating n-type defects (increasing N_d) could be formed. This interpretation is supported by the finding that as soon as the p-type N_{eff} starts to decrease the V_{OC} also starts to decrease significantly (cf. Figure 2). Moreover, this finding makes the second option unlikely which is, that only the p-type defects (N_a decreasing) are reduced, eventually revealing n-type defects (N_d constant). However, the third possibility has to be taken into account. It may also occur that some of the p-type defects change to n-type (N_a decreasing in the same magnitude as N_d is increasing) as the V/III ratio is decreased with deteriorating effect on the V_{OC}. Considering our results, one can see a transition of N_{eff} from p-type (V/III > 7.6) to n-type (V/III < 7.6). Near the transition region (V/III ≈ 7.6), one can expect a very low N_{eff} producing wide depletion layers.

We performed electrochemical current-voltage (ECV) profiling of the GaInNAs layer of the reference cell (V/III ≈ 9.5). The p-type doping of this cell was measured to be in the range of $1-2 \times 10^{16}$ 1/cm^{-3}. ECV-profiling of the solar cells with the reduced V/III ratios resulted in non-interpretable results due to the formation of non-uniform etch pits when electrolytically etching the sample during measurement. We attribute this behavior to crystal defects formed due to the low V/III ratio.

Figure 1(c) shows averaged IQE values of all cells in the range from 900 nm to 1240 nm, reaching 83% at V/III ≈ 7.6 what is among the highest values for a 1.0 eV GaInNAs solar cell reported in the literature. It has to be noted that the V_{OC} of all cells are as low as 0.2 V with similar I-V characteristics as the red curve in Figure 2 and that the values might be lower when the cells are operated at a more realistic operation point (cf. Figure 2) away from I_{SC}. To study the effect of RTA on the N_{eff}, we have grown another solar cell and for processing selected four samples from the same radial position of the wafer, ensuring that all of the cells were grown under exactly the same growth conditions with a V/III ≈ 7.7. They were annealed differently using temperatures of 680 °C, 700 °C, 720 °C, and 740 °C. Figure 3(a) shows the IQE spectra of those cells. One can see that the shape of the curve representing the cell with the RTA temperature of 680 °C (black) shows no clear evidence of an n-GaAs on p-GaInNAs configuration because the sensitivity in the short wavelength part around 900 nm is suppressed. It seems that
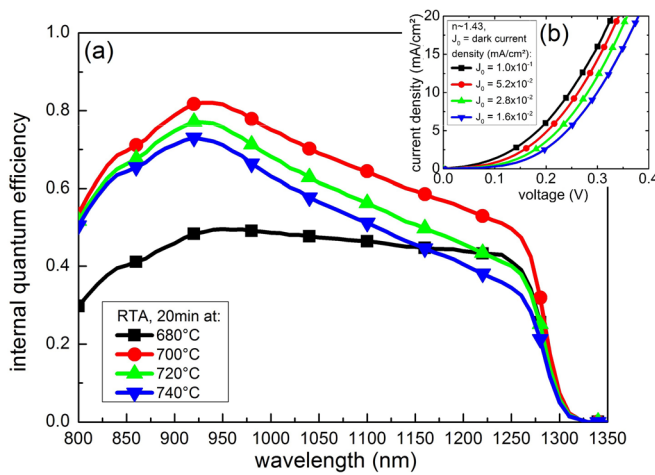
FIG. 3. (a) IQE spectra of four GaInNAs solar cells grown under identical conditions but annealed differently for 20 min at 680 °C (black), 700 °C (red), 720 °C (green), and 740 °C (blue). The shape of the GaInNAs after the lowest temperature annealing (black) looks like it can be expected from an n-GaInNAs layer. Increasing the annealing temperature switches the GaInNAs to p-type. (b) Dark I-V measurements of the four cells annealed differently. The dark current is decreasing almost one order of magnitude from 1.0×10^{-1} mA/cm² down to 1.6×10^{-2} mA/cm² as the RTA temperature is raised from 680 °C (black) to 740 °C (blue).

at least some part of the solar cell has an n-type GaInNAs layer. The IQE of the cell annealed at 700 °C (red) shows the highest IQE and its shape is as expected for an n-GaAs on p-GaInNAs configuration. The remaining cells after RTA at 720 °C (green) and 740 °C (blue) have similar shapes like the cell after exposure to 700 °C, but the overall IQE is decreasing with increasing temperature. Following our argumentation carried out to interpret Figure 1(b), it seems that the highest concentration of n-type N_{eff} is in the sample with the lowest annealing temperature. Increasing the temperature switches N_{eff} steadily to increasing p-type, with the already discussed influence on the depletion layer width and charge carrier collection. Figure 3(b) shows dark I-V measurements of the four cells together with their diode parameters. The cell with the highest concentration of n-type N_{eff} also has the highest J_0 of 1.0×10^{-1} mA/cm² ($n \sim 1.43$). Increasing the RTA temperature apparently helps to cure defects related to the p-type to n-type transition of N_{eff}, and J_0 is decreasing almost one order of magnitude down to 1.6×10^{-2} mA/cm² as the temperature is raised up to 740 °C. This finding clarifies that using this growth technique it seems not possible to produce a solar cell with high performance in the J_{SC} as well as in the V_{OC} because our results indicate that when the N_{eff} is decreasing the dark current is raised and vice versa.

In conclusion, we have grown dilute nitride, 1.0 eV GaInNAs, solar cells with a fine incremented spread of V/III ratios. We have shown p-type to n-type transition of the N_{eff} in the GaInNAs layer with reducing the V/III ratio during growth. We believe that a compensation effect of the existing p-type background doping due to the formation of n-type defects is most likely at this point. However, based on our experiments, we cannot exclude other influences resulting in a low N_{eff} as well. Near the transition region of the GaInNAs layer, we produced solar cells with high current generation

and IQEs up to 85% at 0.2 eV above the band gap indicating a large depletion layer width due to very low N_{eff} in the GaInNAs layer. However, it has to be noted that the low N_{eff} comes along with a significant increase in the J_0 leading to reduced V_{OC}s indicating the formation of non-radiant defect centers. Decreasing the J_0 through curing some of the defects by RTA is possible but in turn the N_{eff} is raising with strong effect on the current generation. Looking for ways to decrease the p-doping in the GaInNAs material and avoid the formation of additional defects seems a more promising way. Taking our results into account, one can expect a serious performance boost of the GaInNAs solar cell.

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