Photoelectric Property Improvement of 1.0-eV GaInNAs and Applications in Lattice-Matched Five-Junction Solar Cells

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GaInNAs with bandgap 1.0 eV is a promising material for multi-junction solar cell applications. However, the poor quality of GaInNAs grown by metalorganic chemical vapor deposition hinders its device performance. Here to reap the benefits of 1.0-eV sub-cell, we focus on the optimization of annealing temperature and growth ambient of GaInNAs. The GaInNAs sub-cell exhibits a concentration reduction of shallow level defects when it is annealed at 700 °C for 20 min. As compared with the growth case using a hydrogen ambient, the N incorporation efficiency of GaInNAs can be enhanced during the growth in an N_2 ambient. Furthermore, background carbon concentration is observed to reduce in the as-grown GaInNAs epilayer. A GaInNAs sub-cell with 82% peak external quantum efficiency is obtained in a dual-junction GaInNAs/Ge solar cell. Finally, a monolithic AlGaInP/AlGaInAs/GaInAs/GaInNAs/Ge five-junction solar cell is grown for space application. The fabricated device shows a conversion efficiency of 31.09% and a short-circuit current density of 11.81 mA/cm^2 under 1 sun AM 0 illumination.

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The conversion efficiencies of conventional GaInP/Ga(In)As/Ge triple-junction (3J) solar cells have reached 30% under AM 0 spectrum and 40% under 500–1000 sun AM 1.5D.[1–3] However, it is difficult to further improve the efficiency due to the limited bandgap (E_g) combination. To obtain higher efficiencies, solar cell structures with four-junctions (4J) and five-junctions (5J) have been put forward.[4] Researchers from Fraunhofer and Soitec reported wafer bonded GaInP/GaAs/GaInAsP/GaInAs 4J solar cells with an efficiency (E_{ff}) of 46% under 508 sun.[5] By using directly bonded GaInP/GaAs/GaInNAs/Ge structure, a 43.9% efficiency (under 1000 sun) solar cell was developed by the Semprius company.[6] Researchers from Spectrolab obtained a wafer bonded 5J solar cell with an efficiency of 35.1% and a short current density of 12.03 mA/cm^2 under 1 sun AM 0.[7] However, these 4J and 5J solar cells need to grow sub-cells on different substrates separately and require additional wafer bonding processes. These additional works have raised many problems such as the interface state and yield reduction. More importantly, the inherent lattice mismatch of sub-cells will cause stress mismatch, which will deteriorate the cell performance and reliability under harsh environments.

Lattice-matched multi-junction solar cells can avoid the above problems. Using 1.0-eV GaInNAs, we designed a 5J solar cell with the structure of AlGaInP/AlGaInAs/GaInAs/GaInNAs/Ge (Fig. 1) for space application. The E_g combination is 2.1/1.7/1.4/1.0/0.67 eV. A similar design was put forward by King *et al.*[4] However, there have hardly been any practical experiments on this structure. King *et al.* grew a lattice-matched 4J solar cell (AlGaInP/AlGaInAs/GaInAs/Ge) with an efficiency of 36.9% under 500 sun.[8] They also demonstrated a monolithic 4J solar cell ($GaInP_{(disorder)}$/$GaInP_{(order)}$/GaAs/GaInNAs) with an efficiency of 19.55% under AM 0.[9] Dimroth *et al.* reported a monolithic AlGaInP/GaInP/AlGaInAs/GaInAs/Ge 5J solar cell with an open-circuit voltage (V_{oc}) up to 4.826 V, but the efficiency (15.83%) was limited by the short-circuit current density (J_{sc}, 5.4 mA/cm^2).[10] For our 5J design, preparations of high efficiency AlGaInP and AlGaInAs sub-cells have been reported by other researchers in our group.[11,12] Thereby, the GaInNAs sub-cell became the limiting junction and its poor quality hindered the I–V performance of the 5J solar cell. In this study, we mainly explore some potential factors to limit the materials properties and their corresponding device performance of the 1.0-eV GaInNAs sub-cell.

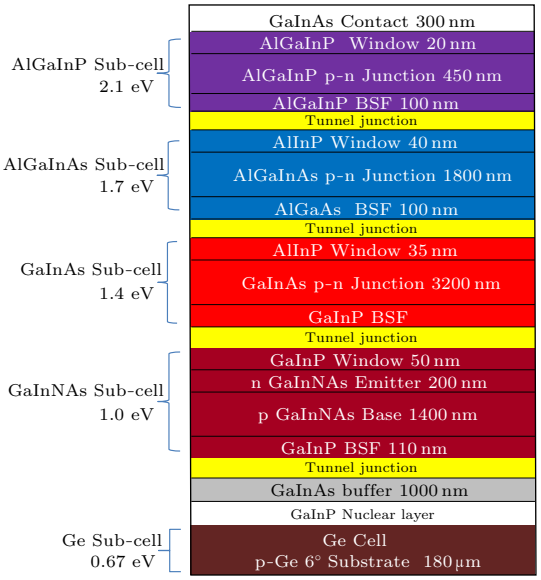

Fig. 1. Epitaxial structure for lattice matched AlGaInP/AlGaInAs/GaInAs/GaInNAs/Ge solar cell.

As a promising material working in the near-infrared range, diluted nitrides $Ga_{(1-x)}In_xN_yAs_{(1-y)}$

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have high flexibility in tuning their lattice constants and E_g. By adjusting the contents of In and N, the bandgap of $Ga_{(1-x)}In_xN_yAs_{(1-y)}$ varies from 0.9–1.4 eV, while lattice matched to a Ge substrate. According to our calculation based on the E_g formulation and Vegard's Law, when (x, y) is set to (0.078, 0.026), it is possible to grow 1.0-eV GaInNAs lattice matched to a Ge substrate. In practice, however, it is hard to grow high quality 1.0–1.1 eV GaInNAs materials and solar cells by metalorganic chemical vapor deposition (MOCVD).[13,14] Incorporation of N significantly increases the density of defect centers in GaInNAs, resulting in a short carrier diffusion length and low external quantum efficiency (EQE).[14,15] Meanwhile, high densities of background impurities make the material quality even worse.[16,17] As for the solar cell application, the peak EQE of the GaInNAs sub-cell grown in MOCVD by Wu *et al.* was 35%.[18] By using TEGa as the Ga source, Dimroth *et al.* reported a GaInNAs solar cell with a peak EQE of 70% at 600 nm and an average EQE of 46% in the expected working range (880–1200 nm).[19]

In this Letter, we study the 1.0-eV GaInNAs materials and solar cells, to obtain a J_{sc} over 11 mA/cm^2 in the 880–1200 nm range for applications in 5J solar cells. To obtain the GaInNAs sub-cell with a high EQE, a series of GaInNAs bulk layers and GaInNAs/Ge dual-junction (2J) solar cells (Fig. 2) were initially grown by MOCVD, and the annealing temperature for GaInNAs was optimized. To obtain higher N incorporation efficiency and better material quality, the influence of the growth ambient was also studied. Finally, the 5J solar cell shown in Fig. 1 was grown.

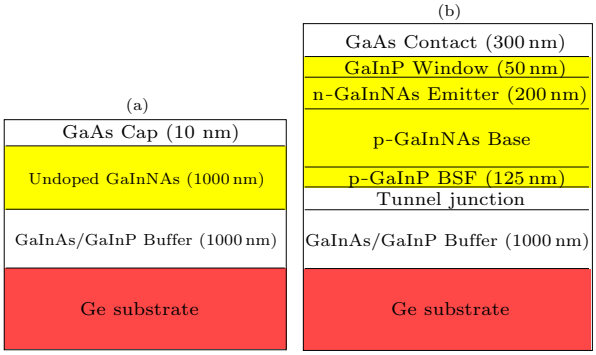

Fig. 2. Illustrations of (a) the GaInNAs bulk layer and (b) the GaInNAs/Ge 2J solar cell.

All the solar cells in this study were grown by a Veeco K475 MOCVD system. GaInNAs layers were grown at 520℃ at a growth rate of 1.5 μmh^{-1}. Dimethylhydrazine (DMHy), trimethylgallium (TMGa), and trimethylindium (TMIn) were used as the N, Ga, and In sources, respectively. Arsine (AsH_3) and phosphine (PH_3) worked as group V sources. The size for all solar cells was 12 cm^2. AuGeNi/Au and Au/Ag/Au were used as n and p contacts, respectively. SiO_2/TiO_2 was selected for the anti-reflective coating. All solar cells used p-type Ge (100) substrates with a misorientation of 6 ℃ toward [111]. The I–V test was conducted under an AM 0 simulator (Spectrolab X25).

To measure E_g and the lattice constant of 1.0-eV GaInNAs, a 1000 nm GaInNAs bulk layer (Fig. 2(a)) was grown and tested by x-ray diffraction (XRD) and photoluminescence (PL). As shown in Fig. 3, the GaInNAs layer has an angle difference of −60 arcsec from the Ge substrate. Its lattice constant is calculated to be 5.660 Å, 99.978% matched to the Ge substrate. The peak PL is located at 1212 nm, and E_g is calculated to be 1.02 eV. Electrochemical capacitance voltage (ECV) testing shows that the GaInNAs layer has a background p-type doping with a concentration around 1.2×10^{17} cm^{-3}.

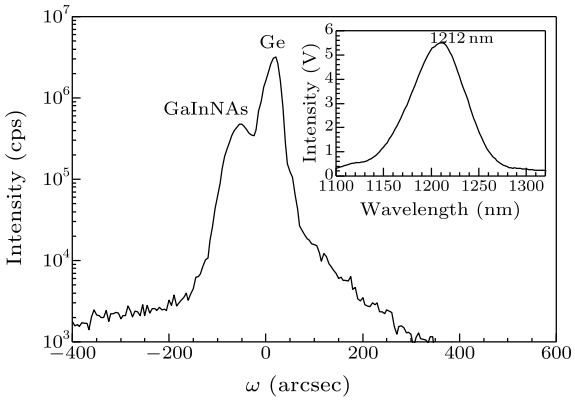

Fig. 3. XRD and PL measurement results of the GaInNAs bulk layer grown on a Ge substrate.

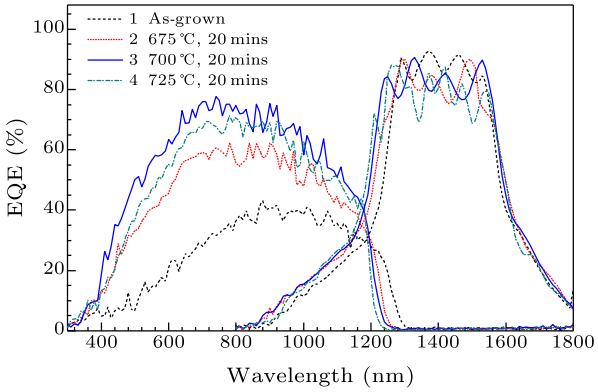

Fig. 4. EQE curves of 2J solar cells under different annealing conditions.

As listed in Table 1, three sets of *in-situ* annealing conditions were used for the optimization of GaInNAs/Ge 2J solar cells. The mole flow ratios of DMHy/AsH_3 and AsH_3/TMGa were set to 12.3 and 3.91, respectively. Figure 4 shows obvious increases in EQE for all of the three annealed samples compared to the as-grown one. The result can be explained by the dissolution of chain-like nitrogen-ordering in the [001] direction of GaInNAs under the high annealing temperature.[20,21] The chain-like nitrogen ordering can bring a high density of shallow hole traps, which will deteriorate the minority carrier diffusion length.[22] Thermal annealing allows N to diffuse to In-rich local environments in the GaInNAs film.[14] Thus most of the shallow level defects can be reduced.[23] When the annealing temperature is increased from 675 ℃ (Fig. 4, sample 2) to 700 ℃ (Fig. 4, sample 3), a higher EQE is obtained. However, the EQE drops

when the temperature is further increased to 725 ℃ (Fig. 4, sample 4). According to the work of Kurtz *et al.*, with a lower annealing temperature, the upper part of the GaInNAs base layer can show n-type behavior, which is helpful in the carrier collection because of the field-aided collection effect.[24] However, an exorbitant annealing temperature over 700 ℃ can remove hydrogen from GaInNAs, leading to activation of the carbon accepter and transformation of the n-type behavior region to p-type.[14,24] Although the material quality and minority carrier properties of GaInNAs can still be improved at a higher temperature, the photocurrent will be reduced without the field-aided collection. Hence, the annealing condition for subsequent experiments is set to 700 ℃ for 20 min.

Table 1. Settings and I–V test results for annealing experiments. Here J_{sc} of GaInNAs and J_{sc} of Ge are the short circuit current densities under AM 0 calculated from EQE data.

Cell number	Annealing Conditions	J_{sc} of GaInNAs (mA/cm^2)	J_{sc} of Ge (mA/cm^2)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	E_{ff} (%)
1	As-grown	16.12	16.78	16.56	652	61.24	4.87
2	675 °C, 20 min	26.88	16.92	16.87	709	69.50	6.15
3	700 °C, 20 min	33.62	17.50	17.64	728	71.41	6.80
4	725 °C, 20 min	30.12	17.13	17.38	741	71.92	6.84

Table 2. Settings and I–V test results for GaInNAs thickness and growth ambient experiments.

Cell number	Thickness of GaInNAs base layer	Growth ambient	J_{sc} of GaInNAs (mA/cm^2)	J_{sc} of Ge (mA/cm^2)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	E_{ff} (%)
3	1000	H_2	33.62	17.50	17.64	728	71.41	6.80
5	1400	H_2	35.49	17.57	17.77	713	68.41	6.38
6	1400	N_2	37.63	16.90	17.18	749	74.92	7.13

From the I–V result (Table 1), V_{oc} and filling factor (FF) increase with the growth of annealing temperature, proving the improvement in material quality. As illustrated in Table 1, J_{sc} of GaInNAs exceeds J_{sc} of Ge after annealing. Thereby, the values of J_{sc} of 2J cells are limited by J_{sc} of Ge sub-cells, making J_{sc} and conversion efficiency less useful for the analysis of GaInNAs.

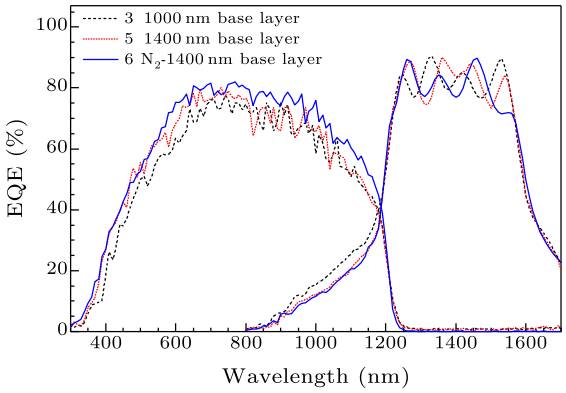

Fig. 5. EQE curves of 2J solar cells with different base layer thicknesses and growth ambient.

As illustrated in Fig. 4, there are cross-border absorptions of Ge sub-cells in the range of 900–1200 nm. This means that the GaInNAs base layers are not thick enough to absorb all the photons in this region. Thereby, a GaInNAs/Ge 2J solar cell with a thicker base layer (1400 nm) was grown. As given in Fig. 5 (sample 5), the EQE is about 5% higher in the 300—800 nm region. However, in the targeted 880—1200 nm range for GaInNAs absorption, there is no obvious EQE enhancement. From the I–V result in Table 2, V_{oc} and FF of the 2J cell with a thicker GaInNAs base layer become lower. Since the energy of photons in the 880–1200 nm range have energy levels in 1.0–1.4 eV, they are more affected by the deep level traps, which usually have energy levels of 0.48 eV and are hardly reduced by the annealing process.[23] With the increase of GaInNAs thickness, the density of deep level defects increases in the upper part of the GaInNAs layer and hinders the carrier collections. The values of V_{oc} and FF are affected as well.

As discussed above, the material quality of GaInNAs is still the main challenge of this study. Previous studies reveal that high DMHy flux has a great influence on the material quality and deep level defects of GaInNAs.[25] It is important to promote the incorporation efficiency of N to reduce the DMHy flux. According to our analysis in the following, the growth ambient may influence the incorporation of N in GaInNAs. However, there are hardly any studies on this issue.

According to the pyrolysis of DMHy, two important products including $NH_2^\bullet$ and HCN can be helpful for the N incorporation in GaInNAs. The black dot $^\bullet$ here represents a free radical of NH_2 with unpaired electron. $NH_2^\bullet$ can be produced by reaction (1) and HCN can be produced by reactions (2)–(5).[26] However, HCN is also considered as an important source of carbon impurities in GaInNAs,[25]

$$(CH_3)_2NNH_2 \rightarrow (CH_3)_2N^\bullet + NH_2^\bullet, \quad (1)$$

$$(CH_3)_2NNH_2 + s \rightarrow (CH_3)_2NNH_2(ads), \quad (2)$$

$$(CH_3)_2NNH_2(ads) \rightarrow NH_3 + CH_3NCH_2, \quad (3)$$

$$CH_3NCH_2 \rightarrow CH_3NCH^\bullet + H^\bullet, \quad (4)$$

$$CH_3NCH^\bullet \rightarrow HCN + CH_3^\bullet. \quad (5)$$

In this work, condensed structure formulas are used for a better understanding of the chemical reaction. Moreover, in the above formulas, s stands for a vacant surface site.

In the above-mentioned experiments, GaInNAs layers were grown in the H_2 ambient. H_2 was purified in advance. In this ambient, reactions will occur

as follows:[26]

$$(CH_3)_2NNH_2(ads) \rightarrow 2CH_4 + N_2, \quad (6)$$

$$(CH_3)CH_2NNH_2^{\bullet} \rightarrow CH_4 + CH_3^{\bullet} + N_2, \quad (7)$$

$$NH_2^{\bullet} + H_2 \rightarrow NH_3 + H^{\bullet}. \quad (8)$$

In reactions (6) and (7), N atoms are converted into N_2, which has high thermostability and will not contribute to the N incorporation. Furthermore, reaction (8) can convert a $NH_2^{\bullet}$ into NH_3. The $NH_2^{\bullet}$ is the most important intermediate product for N incorporation, while NH_3 will not participate in this incorporation. However, in a N_2 ambient, the probability of reactions (6) and (7) can be reduced with a high pressure of N_2. Reaction (8) will also be inhibited in a N_2 ambient because of the deficiency of H_2.

Using the structure given in Fig. 2(a), the GaInNAs bulk layer was regrown in a purified N_2 ambient. The growth conditions are listed in Table 3. As shown in Fig. 6(a), there is a 91 nm (0.073 eV) redshift of the peak PL after being grown in the N_2 ambient, indicating a higher N content in the GaInNAs. The XRD result in Fig. 6(b) also shows a reduction in the lattice constant. Since the N atom has a smaller size compared to the As atom, the reduction in lattice constant implies a higher N content as well. Thereby, it can be obtained that the incorporation efficiency of N is enhanced in the N_2 ambient. By reducing the mole flow ratio of DMHy/AsH_3 to 9.6, we obtain the 1.0-eV GaInNAs layer again. Meanwhile, enhancement of its PL intensity (Fig. 6(a) sample 9) is observed as well, indicating that a better material quality is obtained.[21] The improvement in material quality can be explained by the reduction of the carbon concentration in GaInNAs. The ECV test of the GaInNAs layers shows that the p-type doping concentration reduces from 1.2×10^{17} cm^{-3} (H_2 ambient) to 7.4×10^{16} cm^{-3} (N_2 ambient), indicating the concentration reduction of carbon, which is considered as the p dopant in GaInNAs.[16,17] This can be explained by the reduction of $CH_3^{\bullet}$ and $CN^{\bullet}$ impurities in GaInNAs. The reduction of $CH_3^{\bullet}$ is a result of a lower DMHy flux, while the reduction of $CN^{\bullet}$ impurities in GaInNAs may be caused by the relatively higher incorporation efficiency of $NH_2^{\bullet}$ compared to that of HCN. This is because the increase in proportion of $NH_2^{\bullet}$ can be higher than that of HCN, as a result of the restraint of reaction (8) in the N_2 ambient.

Table 3. Parameter settings and test results of H_2 and N_2 experiments.

Number	Ambient	DMHy/AsH_3 mole ratio	Growth temperature (°C)	PL (nm)	Doping concentration (cm^{-3})
7	H_2	12.3	520	1212	1.2×10^{17}
8	N_2	12.3	520	1303	1.3×10^{17}
9	N_2	9.6	520	1207	7.4×10^{16}

Table 4. Calculated J_{sc}s of sub-cells in the 5J solar cell.

Sub-cell	AlGaInP	AlGaInAs	GaInAs	GaInNAs	Ge
J_{sc} (mA/cm^2)	12.13	12.20	11.81	12.40	16.93

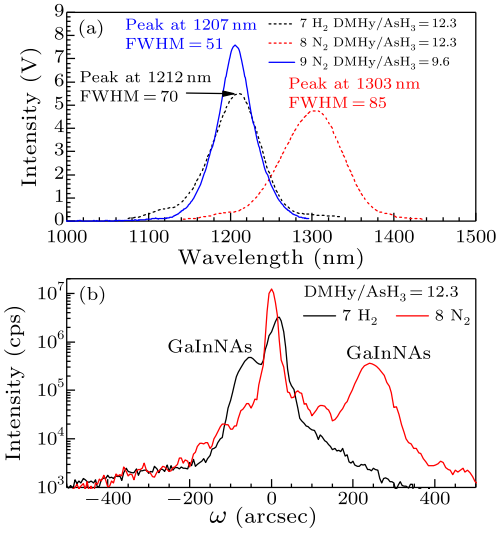

Fig. 6. PL comparison (a) and XRD comparison (b) between GaInNAs materials grown under H_2 and N_2 ambient.

In a N_2 ambient, the GaInNAs/Ge 2J cell with a 1400 nm base layer thickness was regrown, and the EQE of GaInNAs (Fig. 5, sample 6) is enhanced for 5–10% in the 880–1210 nm range. More importantly, as listed in Table 2 (sample 6), V_{oc} and FF are enhanced as well, representing a better material quality of GaInNAs. The calculated J_{sc} of GaInNAs in the 880–1210 nm range exceeds 12 mA/cm^2, meeting the requirement for 5J solar cell applications.

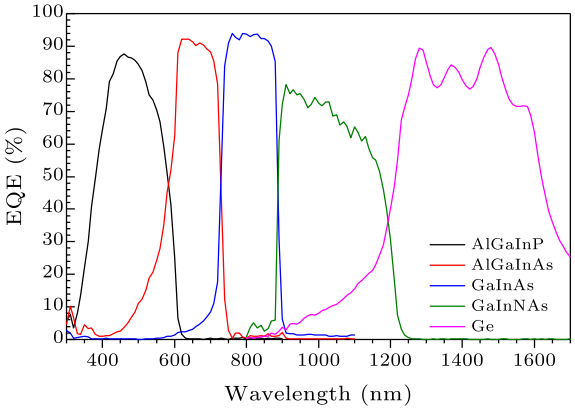

Fig. 7. EQE test result of the AlGaInP/AlGaInAs/GaInAs/GaInNAs/Ge 5J solar cell.

Finally, the AlGaInP/AlGaInAs/GaInAs/ GaInNAs/Ge (2.1/1.7/1.4/1.0/0.67 eV) 5J solar cell was grown by MOCVD on the basis of the GaInNAs/Ge 2J solar cell (Fig. 5, sample 6) with the layer structure given in Fig. 1. As shown in Fig. 7, the peak EQE of the GaInNAs sub-cell reached 77% at 900 nm. The average EQE for the GaInNAs sub-cell is 65% in the targeted 880—1200 nm range. Table 4 lists the calcu-

lated J_{sc} of all the sub-cells. The value of J_{sc} of the GaInNAs sub-cell is no longer the limiting junction, and J_{sc} of this 5J solar cell is 11.81 mA/cm^2 under 1 sun AM 0. Compared to J_{sc} (12.03 mA/cm^2) of the wafer bonded five-junction solar cell obtained by Chiu *et al.*,[7] there is a difference of 0.22 mA/cm^2.

Figure 8 shows the I–V result of the 5J solar cell under AM 0. The value of E_{ff} is 31.09% and FF is 81.4%. The values of V_{oc} and I_{sc} are 4.38 V and 141 mA, respectively. As compared in Table 5, E_{ff} of the 5J solar cell exceeds E_{ff} of a conventional GaInP/GaAs/Ge TJ solar cell. Compared to the 35.1% efficiency wafer bonded 5J solar cell,[7] there is still a 4% difference. However, the five-junction solar cells prepared in this study are monolithic and lattice matched. This structure is promising in large scale production and space application. We will further improve the efficiency of this structure. Here J_{sc} is still the critical factor in future works. If J_{sc} of the 5J solar cell can be increased to 13 mA/cm^2, E_{ff} will become higher than 34%.

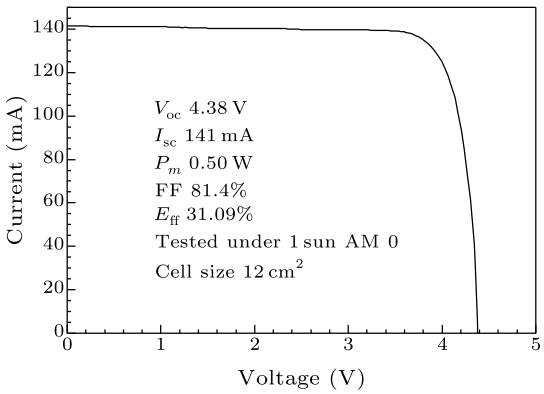

Fig. 8. The I–V curve and characteristics of the 5J solar cell.

Table 5. Comparison of I–V characteristics between 5J solar cells.

Source	Structure	E_g (eV)	Preparation	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	E_{ff} (%)
This study	AlGaInP/AlGaInAs /GaInAs/GaInNAs/Ge	2.1/1.7/1.4 /1.0/0.67	Monolithic growth	11.81	4.38	81.4	31.09
Chiu *et al.*[7]	AlGaInP/AlGaInAs /GaInAs-GaInAs/GaInAs	2.2/1.7/1.4 /1.05/0.73	Wafer bonding	12.03	4.78	83.5	35.11

In conclusion, we have studied the influence of *in-situ* annealing temperature and growth ambient on the materials properties and device performance of the 1.0-eV GaInNAs sub-cell. It is found that GaInNAs solar cells annealed at 700 ℃ for 20 min exhibit an enhanced performance. The N_2 ambient is proved to be useful for the efficient N incorporation, resulting in lower carbon concentration and higher EQE as well. The peak EQE value for the 1.0-eV GaInNAs sub-cell reaches 82% in a GaInNAs/Ge 2J solar cell. The efficiency of the monolithic AlGaInP/AlGaInAs/GaInAs/GaInNAs/Ge 5J solar cell is 31.09% under 1 sun AM 0 with a J_{sc} of 11.81 mA/cm^2. This study demonstrates a great potential of high efficiency monolithic 5J solar cells using GaInNAs as a sub-cell grown by MOCVD.

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