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Single-junction solar cells based on p-i-n GaAsSbN heterostructures grown by liquid 1 2 phase epitaxy 3 Malina Milanova^a, Vesselin Donchev^{b*}, Kieran Cheetham^c, Zhongming Cao^d, Ian Sandall^d, 4 Giacomo M. Piana^e, Oliver S. Hutter^f, Ken Durose^c, Asim Mumtaz^c 5 6 ^a Central Laboratory of Applied Physics, Bulgarian Academy of Sciences, 61, St. Petersburg 7 8 blvd., 4000 Plovdiv, Bulgaria 9 ^b Faculty of Physics, Sofia University, blvd. James Bourchier, 5, 1164 Sofia, Bulgaria 10 ^c Department of Physics, Stephenson Institute for Renewable Energy, University of Liverpool, L69 7ZF, U.K. 11 12 ^d Department of Electrical Engineering and Electronics, University of Liverpool, L69 3GJ, 13 U.K. 14 ^e Department of Physics and Astronomy, University of Southampton, University Road, Southampton SO17 1BJ, U.K. 15 ^f Department of Mathematics, Physics and Electrical Engineering, Northumbria University, 16 17 Newcastle upon Tyne NE1 8ST, UK. 18 19 ABSTRACT 20 In this paper we present single heterojunction p-i-n GaAsSbN/GaAs solar cells grown by low-

- 21 temperature liquid-phase epitaxy (LPE) this is of interest as a component of multi-junction
- 22 solar cell devices. The quaternary absorber layer was characterized by low excitation power
- 23 photoluminescence to give the temperature dependence of the band gap. This conformed to

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24	the Varshni function at low temperatures to within 10 meV, indicating relatively small alloy	
25	potential fluctuations. The absorption properties and the transport of the photogenerated	
26	carriers in the heterostructures was investigated using surface photovoltage method. A power	
27	conversion efficiency of 4.15 % (AM1.5, 1000 W.m ⁻²) was measured for p-i-n	
28	GaAsSbN/GaAs solar cells, which is comparable to the efficiency of MOCVD grown devices	
29	of this type. This is promising for the first report of LPE grown GaAsSbN/GaAs solar cells	
30	since the current record efficiency for the cells based on these compounds grown by MBE	
31	stands just at 6 %. The long-wavelength photosensitivity of the cells determined from external	
32	quantum efficiency and surface photovoltage measurements was shown to be extended to	
33	1040 nm.	
34		
35	Keywords	
36	GaAsSbN, liquid phase epitaxy, p-i-n heterostructures, solar cells, photovoltaic	
37		
38	1. Introduction	
39	There has been great interest in dilute nitride III-V-N materials during the last two	
40	decades, driven in part by their potential application in multijunction solar cells (Friedman et	
41	al., 1998; Geisz et al., 2018; Harris, 2005; Isoaho et al., 2019; Johnston et al., 2005; Kurtz et	
42	al., 2002; Miyashita et al., 2013, 2012; Ptak et al., 2009, 2005) which are expected to out-	
43	perform single junction devices. A conversion efficiency of 46.1 % has been reported for	
44	four-junction solar cells under concentrated light, using wafer bonding to combine 2 two-	
45	junction solar cells grown on InP and GaAs substrates (Dimroth et al., 2016). The efficiency	
46	record is currently held by NREL for a six-junction inverted metamorphic concentrator solar cell	
47	which achieved 47.1 % (Geisz et al., 2018). The bandgap combination of the subcells is a key	
48	factor for further improvements in the overall cell efficiency. Presently multi-junction solar	

49	cell performance is limited by the performance of the subcells which need to be chosen for
50	their bandgaps and also need to be grown with appropriate crystal quality. Dilute nitride alloys
51	such as InGaAsN or GaAsSbN can provide adjustable bandgaps between 1.2 and 0.8 eV
52	while remaining lattice-matched to GaAs or Ge substrates. Hence the development of these
53	materials is of great significance for high-efficiency multijunction solar cells, where they can
54	be used to collect the low-energy photons. However, the device performance has not reached
55	expectations, due to the low radiative efficiencies and low minority carrier diffusion lengths
56	(Johnston et al., 2005; Kurtz et al., 2002). The issue of poor minority carrier diffusion length
57	has been partially tackled by increasing the depletion region width by the use of undoped
58	layers to increase the current (Miyashita et al., 2012; Ptak et al., 2005). However, the trap-
59	assisted recombination dark current increases with the width of the depletion region, which
60	leads to the lowering of the open-circuit voltage.
61	It is therefore essential to improve the properties of dilute nitride compounds. There has
62	been significant progress in the development of InGaAsN materials. InGaAsN solar cells
63	grown by metalorganic chemical vapour deposition (MOCVD). A device based on a double-
64	heterostructure single-junction (and using an anti-reflection coating) has achieved 13.2 $\%$
65	efficiency as reported by Kim et al. (Kim et al., 2015). The Solar Junction Corporation
66	reported the highest efficiency monolithic triple-junction solar cells of 43.5 % under
67	concentrated light for using InGaAsN instead of Ge as the lowest subcell (Wiemer et al.,
68	2011).
60	Another dilute nitride material suitable for solar cell applications as an alternative to

Another dilute nitride material suitable for solar cell applications as an alternative to InGaAsN is GaAsSbN. It offers the possibility for independent tuning of the conduction and valence bands. While the bandgap of dilute nitrides is primarily reduced by lowering the conduction band minimum, the bandgap of antimonides is reduced by raising the valence band maximum energy. Both of these mechanisms are explained through the band anti-

74	crossing model. The incorporation of both Sb and N atoms into the crystal lattice enables
75	lattice matching with GaAs or Ge. In addition, their incorporation also causes a large
76	concentration of localized states which results in changed electronic and optical properties,
77	and lower device performance, due to reduced carrier collection. Despite the beneficial
78	features of this material it has not been as widely studied as InGaAsN, although interest in
79	GaAsSbN has risen over the last few years (Bian et al., 2004; Gonzalo et al., 2019; T. W. Kim
80	et al., 2014; Kim, Tae Wan et al., 2014; Lin et al., 2013; Milanova et al., 2019; Tan et al.,
81	2011; Thomas et al., 2015; Yurong et al., 2017). Recent solar cells based on GaAsSbN have
82	demonstrated efficiencies of 4 % for a nonoptimized single-junction solar cell structure,
83	without anti-reflection coating grown by MOCVD (Kim, Tae Wan et al., 2014) and 6 % for
84	molecular beam epitaxy (MBE) grown structures (Thomas et al., 2015).
85	In this paper, we present the results of single-heterojunction p-i-n GaAsSbN solar cells
86	grown by low-cost liquid phase epitaxy (LPE) method. To the best of our knowledge, no other
87	groups have reported on LPE grown GaAsSbN/GaAs heterostructures. Temperature-
88	dependent photoluminescence (PL) spectra at a low excitation power of 0.5 mW have been
89	used to identify the in-gap localized states, which increase the dark current of the cells. In the
90	first device trials for LPE GaAsSbN/GaAs devices, efficiencies of 4.15 % were achieved
91	under AM1.5 conditions on areas of 3.5 x 3.5 mm ² .
92	

93 2. Experimental Methods

94 The schematic structure of the single-junction solar cell investigated in this study is shown in

- 95 Fig. 1. It employs a *p-i-n* structure based on compensated GaAsSbN layers grown via LPE.
- 96 The epitaxial structures were grown in a horizontal LPE reactor using the "piston boat"
- 97 technique. The starting materials were Ga and Sb metal-solvents of 6N purity, and
- 98 polycrystalline GaAs and GaN powder used as sources for As and N, respectively. The

99	elements choosen as dopants were Te for n-type doping and Mg for p-type doping. The	
100	epitaxial structure was grown in the temperature interval 640-546 °C at a cooling rate	
101	0.8° C/min. Dilute nitride i-GaAsSbN layer was grown from a 7°C supercooled mixed Ga + 5	
102	at. % Sb solution in the temperature range 558 -550 $^\circ$ C. The GaAs capping and AlGaAs	
103	"window" layers were grown in the temperature intervals 550-548 $^{\circ}\mathrm{C}$ and 548 -546 $^{\circ}\mathrm{C},$	
104	respectively. The Sb content in the $GaAs_{1-x-y}Sb_xN_y$ layers was measured at several points on a	
105	cross-section by energy-dispersive X-ray spectroscopy (EDX). The average value of x was	
106	determined to be 6.7 % and it is confirmed by X-ray photoelectron spectroscopy (XPS)	
107	measurements. The presence of 0.1% nitrogen in the studied samples was determined by XPS	
108	measurements using excitation with Mg K α radiation. The lattice mismatch between the LPE	
109	grown GaAsSbN layers and the GaAs substrate is about 0.48 %, as was determined from X-	
110	ray diffraction (004)) curves. The details of the structural characterization based on the XRD	
111	results are presented in Ref. (Milanova et al., 2019)	

Commented [A1]: The doping concentration in written correctly in the revised figure



Fig. 1. Schematic structure of a single-junction *p-i-n* solar cell based on compensated
GaAsSbN heterostructure grown by LPE.

119	Samples were processed into $3.5 \times 3.5 \text{ mm}^2$ photovoltaic mesa diodes comprising of a 3
120	mm diameter optical window using standard mask lithography. Firstly, a common back n-
121	contact was formed via thermal evaporation of an InGe/Au layer, which was subsequently
122	annealed at 400°C for 1 minute. Following this, top Ohmic contacts were defined via
123	lithography consisting of 10 μ m wide stripes, separated by 90 μ m, across the optical window
124	to ensure homogenous current injection. The contacts were deposited via thermal evaporation,
125	which consisted of Au/Zn/Au layers, and subsequently followed by a 380°C anneal for 1
126	minute. Prior to the contact deposition the top Al _{0.8} Ga _{0.2} As layer was selectively etched using
127	hydrogen peroxide and citric acid solution. The mesas were then etched using phosphoric
128	acid, hydrogen peroxide and de-ionized water etchant. They were etched to a sufficient depth
129	to ensure electrical isolation between adjacent devices.
130	Temperature dependent PL spectra were measured in the temperature range between 10
131	and 150 K in order to investigate the optical properties of the grown structures. The
132	excitation was obtained with a laser light having an energy density of 100 $\rm nJ/cm^2~(80~MHz$
133	repetition rate and 550 μW laser power) and wavelength of 680 nm provided by
134	supercontinuum white laser (Fianium WhiteLase) monochromated with a tunable bandpass
135	transmission filter (Fianium SuperChrome). The light spot diameter on the sample surface
136	was 130 $\mu m.$ The sample was mounted in a closed-loop He cryostat and its temperature was
137	controlled through an Oxford Instruments ITC503 unit. The PL was collected and recorded by
138	a fibre-coupled spectrometer (BWSpec Glacier X). Surface photovoltage (SPV) spectroscopy
139	in metal-insulator-semiconductor (MIS) operation mode was undertaken. This technique was

- 140 applied to study the optical absorption of the structures using the set-up and the measurement
- 141 procedure as described elsewhere (Donchev, 2019).
- 142 J-V measurements were undertaken using a calibrated TS Space Systems solar
- 143 simulator with an AM1.5 spectrum at 1000 Wm⁻². The external quantum efficiency (EQE)
- 144 measurements were performed using a Bentham PVE 300 system in the dark, i.e. without
- 145 white light bias. A total of 8 different solar cell variants were produced, each sample having
- 146 approximately 9 complete cells.
- 147

148 **3. Results and Discussion:**

- 149 3.1 Photoluminescence Characterization
- 150 The temperature-dependent PL spectra of a solar cell epitaxial structure in the range 11
- 151 K 300 K measured under low excitation intensity (~0.5 W/cm²) are depicted in Fig. 2. The
- 152 peak with high intensity comes from the p+ GaAs layer and the weak peak red-shifted to
- 153 GaAs comes from GaAsSbN layer of the structure.





155 Fig. 2. Temperature dependent PL spectra of a GaAsSbN/GaAs solar cell structure in the

156 range 15-300 K with step intervals of 10 K.

158	Fig. 3 presents the normalized PL peaks of the GaAsSbN layer in the structure
159	measured in the range (11 – 150 K). The PL peak energy evolution presents an anomalous,
160	nearly S-shaped temperature behaviour. It is seen that there is a blue shift of the PL emission
161	energy as the temperature is increased from 10 to about 60-70 K. With further increase of the
162	temperature (beyond 70 K) the PL peak exhibits a red shift. This type of behaviour is a well-
163	known characteristic of carrier localization effects associated with band-tail states (Gao et al.,
164	2016; Lai et al., 2006; Lourenço et al., 2007) which are known to depend on the degree of
165	disorder of the compound. In the quaternary GaAsSbN compounds the incorporation of N and

166	Sb into the crystal lattice locally modifies the conduction and valence bands respectively, thus
167	creating localized states and potential fluctuations. The blue-shift of the emission at low
168	temperatures indicates that as the temperature increases the excitons gain sufficient thermal
169	energy to transfer to higher-energy localized levels, thus increasing the emission energy. As
170	the temperature increases further (above 70 K) the higher energy localized states are gradually
171	saturated, the excitons become almost delocalized and the PL peak energy decreases as a
172	function of temperature due to reduction in the bandgap.



Fig. 3. Normalized PL spectra of GaAsSbN in a *p-i-n* solar cell structure measured from 11K (top) to 150 K (bottom) with step intervals of 10 K under excitation power of 0.5 W/cm².

174

Fig. 4 illustrates the variations of the PL peak energies as a function of temperature for the p^+ -GaAs and the GaAsSbN layer in the structure. The PL peak energy for GaAs decreases monotonically with increasing temperature. Its temperature dependence is well fitted with Varshni's relation $E_g(T) = E_0 - aT^2/(T+b)$ using the parameters typical for GaAs (Blakemore, 1982), namely $E_0 = 1.519$ eV for the bandgap at T = 0 K, and $a = 5.4 \times 10^{-4}$ eV.K⁻¹, and b =204 K as fitting parameters.



Fig. 4. Temperature dependence of the PL peak energy of GaAs (squares) and GaAsSbN
(circles) in a *p-i-n* solar cell structure. Lines represent Varshni fits to the data.

186	The GaAsSbN peak exhibits the non-typical S-curve (blue-red) behaviour. The first red-
187	shift is missing (see Fig.4), while the blue shift is only around 10 meV. This indicates that the
188	potential fluctuations in these samples are relatively small and even at low temperature the
189	excitons receive enough thermal energy to escape from the localized states and transfer to
190	higher-energy localized states in the band-tail closer to the conduction band. The fit to the
191	data above 60 K was obtained using Varshni's relation with the following fitting parameters:
192	$E_0 = 1.348 \text{ eV}, a = 6.41 \times 10^{-4} \text{ eV}.\text{K}^{-1} \text{ and } b = 600 \text{ K}.$ The blue shift of the PL peak energy
193	observed in this work is compared to the blue shift measured in MBE grown GaAsSbN/GaAs
194	single quantum wells after annealing. It is nearly the same as the values reported in (Li et al.,
195	2005) for <i>in-situ</i> annealed samples, while in other works (Lourenço et al., 2007; Nunna et al.,
196	2007) larger values were observed. In our previous work (Milanova et al., 2020) the
197	temperature-dependent PL spectra of the <i>p-i-n</i> structures were measured under higher
198	excitation intensity (5 W/cm ²) and no blue shift of the PL peak position was observed at low
199	temperatures. In the whole temperature range $20 - 300$ K, the PL peak energy showed a

- 200 monotonous decrease with increasing temperature and this behaviour was well fitted by an
- 201 empirical Varshni relation (Milanova et al., 2020).
- 202 Fig. 5 shows the temperature dependence of the PL full widths at half maximum
- 203 (FWHM) for p^+ GaAs and GaAsSbN layers. The FWHM values increase monotonically with
- 204 temperature from 7.3 meV at 11 K to 15.2 meV at 150 K for GaAs layer. The FWHM for
- 205 GaAsSbN is 11.7 meV at 11 K and increases slightly from 14.5 meV to 18 meV in the
- 206 temperature range 20 60 K where the emission is dominated by localized excitons. FWHM
- 207 values increase more rapidly with increasing temperature above 60 K where the emission is
- 208 dominated by delocalized excitons.
- 209



- 210
- 211

212 Fig. 5. Temperature dependence of the FWHM of the PL peak of GaAs (squares) and

- 213 GaAsSbN (circles) in a p-i-n solar cell structure.
- 214
- 215 3.2. Surface photovoltage characterization
- 216 SPV spectroscopy has seldom been used to study dilute nitride materials, e.g. the optical
- 217 absorption (Bansal et al., 2006) and the band offset (Galluppi et al., 2005) in InGaAsN/GaAs
- 218 single quantum wells and the E_{-} and E_{+} transitions in GaNAs layers (Kudrawiec et al.,

219	2014). However, no other groups have reported on SPV investigations of GaAsSbN dilute
220	nitride materials. We apply this method to study the optical absorption and photocarrier
221	transport in the investigated structures. It is well known that in MIS operation mode the SPV
222	amplitude spectrum emulates the optical absorption spectrum (Kronik and Shapira, 1999),
223	while the SPV phase spectrum carries information about the direction of the energy band
224	bending and therefore about the direction of the photocarrier movement (Donchev, 2019). The
225	SPV measurements were performed at room temperature with a light modulation frequency of
226	94 Hz. The scanning was from high to low wavelengths, keeping the photon flux constant at
227	each wavelength.



229 230

Fig. 6. Surface photovoltage amplitude (symbols) and phase (line) spectra of a *p-i-n* solar cell



233

Fig. 6 presents the SPV amplitude and phase spectra of a p-i-n single-junction solar cell structure based on compensated GaAsSbN. The amplitude spectrum reveals a step in the range of 1.24 - 1.38 eV and another one for energies above 1.38 eV. The former originates

237	from the absorption in the GaAsSbN layer and the latter from absorption in the GaAs layers.
238	We emphasize that the signals from GaAsSbN and GaAs are comparable in magnitude, which
239	attests for good quality of the dilute nitride layer. The absorption edge of GaAsSbN from SPV
240	was confirmed by a Tauc plot as being 1.26 eV. Considering its thickness (0.5 $\mu m)$ and Hall
241	carrier concentration ($\sim 10^{15}$ cm ⁻³ (Milanova et al., 2020)) the GaAsSbN layer is fully depleted
242	and the photogenerated electrons are swept towards the n-GaAs layer, while the holes -
243	toward the p^+ -GaAs layer thus giving rise to photovoltage. The direction of the carrier drift is
244	evidenced by the SPV phase values, which are close to zero degrees in agreement with the
245	upward energy bands bending (in the direction towards the surface) in the <i>p-i-n</i> structure
246	(Donchev, 2019).
247	
248	3.3 Photovoltaic characterization: J-V and EQE characteristics
249	A typical J-V curve for the GaAsSbN <i>p-i-n</i> solar cell measured at AM1.5 conditions is
250	presented in Fig. 7a. Fig. 7b shows the corresponding J-V curve measured in the dark.
251	Photovoltaic parameters measured on several devices in this work are given in Table 1. The
252	best solar cell shows an efficiency of 4.15 %, an open-circuit voltage V_{oc} = 0.44 V, short-
253	circuit current $J_{sc} = 17.31 \text{ mAcm}^{-2}$ and fill factor $FF = 54.5 \text{ \%}$. The series resistance is $R_{series} =$
254	5.73 Ω cm ² and shunt resistance is $R_{\text{shunt}} = 478 \ \Omega$ cm ² . This is comparable to the efficiency
255	reported for single-junction 1.25 eV GaAsSbN solar cells with 600 nm thickness of the
256	GaAsSbN base layer grown by MOCVD (Kim, Tae Wan et al., 2014). A higher efficiency of
257	about 6 % has been achieved for 1.15 eV MBE grown GaAsSbN solar cells (Thomas et al.,
258	2015). In both cases, a rapid thermal annealing (RTA) at 800°C of the solar cells was
259	performed, which significantly increased the open-circuit voltage values to $0.5 - 0.6$ V due to
260	the decrease in the density of the localized states. However, typical values of $V_{\rm oc}$ measured in
261	our cells based on as-grown LPE structures without RTA are in the range $0.40 - 0.44$ V.



Fig. 7. J-V curves of a GaAsSbN *p-i-n* solar cell measured at AM1.5 conditions (a) and in the

264 dark (b).

265

266 Table. 1. PV parameters of several devices measured in this work

Sample	Efficiency	$V_{ m oc}\left[{ m V} ight]$	$I_{\rm sc} [{\rm mA/cm^2}]$	FF [%]	
	4.00	0.43	17.58	53	
E407	4.02	0.44	17.26	53	
	4.07	0.43	17.85	53	
	4.10	0.44	17.27	53.90	
E409	4.09	0.44	16.92	55.00	
	4.15	0.44	17.31	54.50	
	4.06	0.44	17.23	53.50	
	4.10	0.43	18.7	51	
E410	4.03	0.42	18.45	52	
	3.87	0.41	18.16	52	

267

268



- assuming that the charge transport is dominated mainly by diffusion of minority carriers.
- 271 However, even in the best cells, different recombination mechanisms are present which lower
- 272 the maximum open-circuit voltages below the theoretical limits. It is known that the

Commented [A2]: It does not look right that FF for E407 and E410 are not to 2 decimal points, as is shown for E409









An example of a corresponding EQE graph is given in Fig. 8. EQE values of around 50 % were measured in the wavelength range 550 - 850 nm, which suggests that the upper p^+ -

288	GaAs emitter layer is of good quality despite being grown on GaAsSbN. A significant
289	decrease of the EQE in the infrared part of the spectrum is due to the short minority carrier
290	diffusion length in the dilute nitride layer because of the efficient recombination via localized
291	defect levels. Nevertheless, the EQE extends to approximately 1040 nm (1.19 eV) with an
292	inflexion point at 1.26 eV in agreement with the SPV results for the bandgap of GaAsSbN. A
293	slight reduction in EQE is observed at approximately 900 nm (1.377 eV), which can be
294	associated with the onset of the optical transitions in GaAs in accordance with the SPV
295	spectrum. The short wavelength photosensitivity of the structure is determined by the
296	composition and thickness of the AlGaAs layer.
297	
298	4. Conclusions
299	Single junction solar cells based on a <i>p-i-n</i> GaAsSbN/GaAs structure grown via LPE
300	were developed and studied. Mesa diodes measuring 3.5 \times 3 .5 mm ² with circular optical
301	window 3 mm in diameter were fabricated using standard lithography and wet etch
302	processing. n- and p- type Ohmic contacts based on InGe/Au and Au/Zn/Au were deposited
303	via thermal evaporation on the back and the front surface of the cells. Temperature-dependent
304	PL measurements at low excitation power of 0.5 mW show a slight blue shift of the GaAsSbN
305	PL emission energy at low temperatures from 10 K to about 70 K, which led to the conclusion
306	that the potential fluctuations are relatively small. SPV measurements provide information on
307	the optical absorption and photocarrier transport in the investigated structures. The bandgap
308	energy at room temperature of GaAsSbN determined from the optical absorption edge is 1.26
309	eV. Nearly the same IR photosensitivity behaviour was revealed from EQE measurements.
310	J-V curves were measured under standard test conditions (25°C, one sun AM1.5). A
311	power conversation efficiency of 4.15 %, an open-circuit voltage of 0.44 V, short-circuit
312	current of 17.31 mA/cm ² and fill factor 54.5 $\%$ were obtained for the cells without anti-

313	reflection coatings and without the rapid thermal annealing that has achieved higher voltages
314	for MOVPE and MBE materials. This is very promising result for the first LPE grown
315	GaAsSbN/GaAs solar cells, especially given that these cells are non-optimized, and the record
316	GaAsSbN/GaAs solar cell currently stands at just 6 % efficiency. Further improvements in
317	materials quality and in device design are needed to ensure higher photovoltaic performance
318	of these cells.
319	
320	Declaration of competing interest
321	The authors declare that they have no known competing financial interests or personal
322	relationships that could have appeared to influence the work reported in this paper.
323	
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