Journal of Physics: Conference Series **741** (2016) 012044 doi:10.1088/1742-6596/741/1/012044

Synthesis of GaN nanowires on Si (111) substrates by molecular beam epitaxy

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Abstract. In this work we study growth of semiconductor GaN nanowires (NWs) on Si(111) substrates by means of molecular beam epitaxy. We demonstrate that the substrate temperature affects both the surface density and growth rate of the synthesized NWs. It was determined that at a fixed flux of nitrogen equal to 1.3 cm^3/min the maximum growth rate of NWs is ~ 38 nm/h at a substrate temperature — 800 ^oC. It was also found that the growth rate of NWs on the substrates treated with the oxide removal procedure is half the growth rate on substrates covered with oxide, while their surface density is twice higher in the first case. In addition we have studied influence of Ga flux on NWs formation.

1. Introduction

For the last few decades low dimensional semiconductor nanostructures such as nanowires, quantum dots, nanoneedles, thin films and monoatomic layers attract a lot of attention because of their unique electronic properties which are believed to give birth for the future generation of opto- and nanoelectronic devices [1-3]. Due to high aspect ratio and large surface area nanowires can be grown epitaxially on highly mismatched substrates (e.g. GaN or GaAs on Si) possessing high crystal quality [4, 5] at the same time. Because of the latter property these structures are considered one of the most promising for the integration of A3B5 optical semiconductors on Si [6, 7].

Semiconductor photovoltaics is one of the implementation field for low dimensional nanostructures such as nanowires [8-11]. First of all, nanowires grown on the face side of the solar cell are known to improve light absorption of the device [12], which especially important if we're considering Si-based cell, because Si itself possess high reflection coefficient close to 30% [13, 14]. Another important property of A3B5 nanowires on Si is their high crystal quality which leads to good carrier transport and make them great conducting channels for photo-generated carriers [6, 15]. As to choice of GaN as a material for nanowires we have to mention its large band gap which makes it ideal semiconductor for the window of the solar cell. Together these features open up broad prospects for their use in photovoltaics, in particular solar cells.

In theoretical work [16] it was shown that the efficiency of the basic solar cell (quite simple in fabrication) with one junction based on GaN NWs can reach 20%. It's been demonstrated theoretically

that achievement of the peak efficiency requires optimization of the structure doping levels and its morphology namely surface density, diameter and length. In this work we investigated experimentally the influence of growth parameters on the growth rate and morphology of the synthesized GaN nanowires array on Si (111) substrate by plasma-assisted molecular beam epitaxy technique.

2. NWs synthesis

Before loading n-doped ($5*10^{19}cm^{-3}$) Si (111) substrates into the MBE system they were treated Shiraki cleaning procedure. After preparation every substrate passed degassing procedure and was transferred to the growth chamber, where was annealed at temperatures above 850 ^{o}C. The oxide removal was controlled using reflection high-energy electron diffraction (RHEED). The substrate temperature was then lowered to 650 ^{o}C and a thin layer of AlN was deposited following the procedure: 1) deposition of 3 nm Al layer, 2) interruption of deposition for 1min, 3) nitrogen deposition for 1.5 minutes at a flux of 1.3 cm^3/min. Formation of AlN layer was also controlled via RHEED. Deposition of AlN in our case played two roles: firstly, it allows formation of GaN nanoislands which during the growth then transform into nanowires and, secondly, it passivates substrate surface which in turn leads to reduction of recombination-induced losses [17-20]. The substrate temperature was then increased to 800±20 ^{o}C and Ga and N were deposited simultaneously resulting in formation of NWs. Some of the samples were also doped with Si for the further device application. The experiments were carried out in Veeco GEN III MBE system. Riber plasma cell served as a source of atomic nitrogen.

3. Experimental results

In this work over 10 arrays of GaN NWs on Si (111) substrate were synthesized. In our experiments we have varied annealing temperature of a substrate, a substrate temperature during NWs growth, a Ga deposition flux and a doping Si flux. After the growth, samples were studied by means of scanning electron microscopy (SEM) (Figure 1) in order to obtain morphology of the synthesized array. Results of the experiments are given in the Table 1.

Table 1. Growth parameters and properties of the synthesized GaN NWs array. Here T_{sub} – substrate temperature, T_a – annealing temperature, F_{Ga} – Ga deposition flux, T_{Si} – Si doping effusion cell temperature, t_{gr} – growth time, V_{gr} – average NWs vertical growth rate, D – average NWs top diameter, d – average NW base diameter, σ – average NWs surface density.

sample	T_{sub} (^{o}C)	T_a (^{o}C)	F_{Ga} (Torr)	T_{Si} (^{o}C)	t_{gr} (h)	V_{gr} (nm/h)	D (nm)	d (nm)	σ (mkm^{-2})
1	800	850	$1.5\ 10^{-8}$	-	31	32.3	73	76	31
2	800	850	$1.5\ 10^{-8}$	1050	31.5	38.1	79	75	29
3	800	850	$1.5\ 10^{-8}$	1000	27	38.9	74	71	45
4	800	850	$1.5\ 10^{-8}$	1060	92.5	28.6	153	108	42
5	800	1000	$1.5\ 10^{-8}$	1050	34	20.6	67	61	86
6	800	970	$1.5\ 10^{-8}$	1000	31.6	15.5	62	67	85
7	820	1000	$1.5\ 10^{-8}$	-	18	7.8	32	30	20
8	810	1000	$1.5\ 10^{-8}$	1050	39	10.5	54	48	75
9	790	910	$1.5\ 10^{-8}$	1050	38	13.1	101	75	149
10	800	1000	$2.2\ 10^{-8}$	1000	30	8.8	58	61	159
11	800	1000	$1.5\ 10^{-8}$	1160	31	14.8	87	44	79

4. Discussion

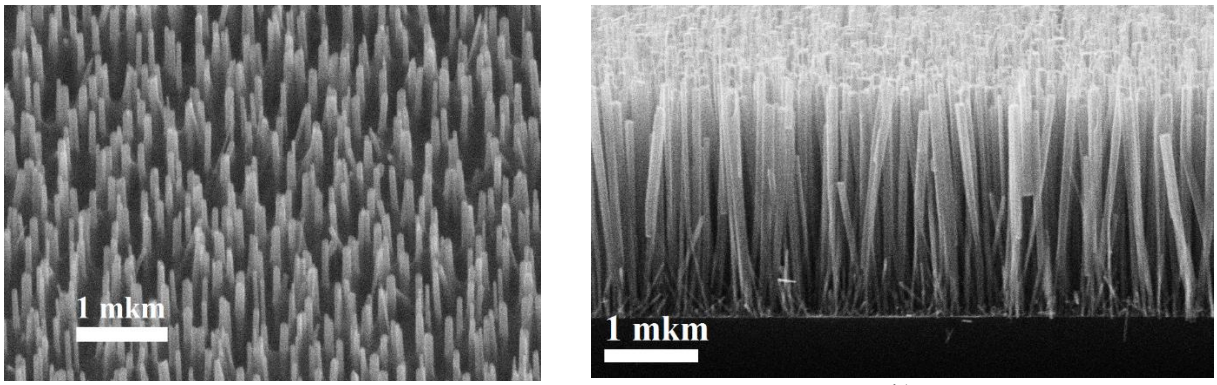
The first few samples were grown on the substrates that didn't pass the oxide removal procedure, as they were annealed at only 850°C. Surprisingly, it turned out that NWs growth rate is twice faster in that case comparing to the samples grown on substrates annealed at 910°C and above. In the latter case the oxide was removed from the substrate which was controlled via observation of changes in RHEED pattern. This effect is probably related to the difference in a mean migration length of the adatoms on these surfaces probably due to the lower sticking coefficient of Ga adatoms on oxide surface. It is expected that the longer adatom motion the faster NWs formation and lower the surface density.

We have also varied the substrate temperature in a small range of 790-820°C. It was found that optimum temperature corresponding to the fastest NWs formation was 800 °C. Lower temperatures correspond to lower growth rate and higher surface density, which is intuitively understandable as adsorption from vapour phase should increase and mean free path decrease. At higher substrate temperatures situation is different: the growth rate decreases again, but also density of the array greatly reduces, which should be caused by reduction of particle adsorption.

We didn't have an opportunity to carry out straight forward study of gallium flux influence on the NWs formation, though one sample was grown using higher flux than the others. It was demonstrated that elevation of the Ga flux leads to fall of the growth rate and rise of the surface density. Again, it should be caused by shift in mean free path related to higher adatom concentration this time.

Another observation concerning shape evolution of the NWs is that they suffer radial extension with time while their surface density doesn't change sufficiently. The latter fact mean that all the sites available for NWs formation (which as far as we know are Si or SiOx sites not covered with AlN) get settled simultaneously at the initial stage of growth. Though NWs do grow radially, no sufficient tapering was observed with one particular exception of growth with high-intensity Si doping flux.

Part of the samples were doped with Si for further device application. The samples were examined by photoluminescence spectroscopic techniques. According to the optical experimental data in the sample number 11 grown at highest intensity doping flux we were able to reach 5 10^{19} cm^{-3} of donor concentration.



a) b)

Figure 1. SEM images of the grown samples: a) sample 1, b) sample 4.

5. Summary

In this work the growth of GaN quasi-onedimensional structures on Si (111) substrate by MBE was studied. We investigated the influence of growth parameters and Si doping on morphology of the synthesized array. Firstly, we have obtained that NWs growth rate is two times faster, while NWs surface density is more than twice smaller on the substrates where an oxide layer wasn't removed by means of annealing, comparing to the substrates treated with oxide removal procedure. It was found that optimum substrate growth temperature corresponding to the fastest NWs formation is 800 °C.

Lower temperatures correspond to lower growth rate and higher surface density, at higher temperatures growth rate decreases, but also density of the array decreases. It was also demonstrated that elevation of the Ga flux leads to fall of the growth rate and rise of the surface density. We speculate that all the mentioned effects related to the change of adatoms mean free path resulting in modification of the growth kinetics.

Acknowledgments
This work was carried out with the support of the Russian Federation President grant (14.W01.15.7736-MK), the Russian Foundation for Basic Research (15-02-06839 A, 16-29-03113 ofi and 16-32-00560 mol_a), the leading universities of the Russian Federation (grant 074-U01). The work is partially supported by the Skolkovo Foundation (grant agreement for Russian educational and scientific organisation no.6 dd. 30.12.2015).

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