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MBE growth of GaAs nanowires with a silicon rich particle on the top

N.V. Sibirev [1], I.V. Ilkiv [2], E.V. Ubyivovk [1], I.P. Soshnikov [3], I.V. Shtrom [1] ✉, R.R. Reznik [1], V.V. Brukhanova [1], G.E. Cirlin [2]

[1] St. Petersburg State University, St. Petersburg, Russia;
[2] Alferov University, St. Petersburg, Russia;
[3] Ioffe Institute, St. Petersburg, Russia
✉ igorstrohm@mail.ru

Abstract. The paper discusses the low-temperature growth of gallium arsenide (GaAs) nanowires on a silicon substrate initiated by a thin layer of lead. Typically, the growth of III-V semiconductor nanowires occurs via a vapor-liquid-solid mechanism with a droplet at the tip of the nanowire. The particles on the nanowire's tip act as physical catalysts, reducing the nucleation barrier. In case of GaAs nanowire, the droplet at the tip typically consists of Ga and a foreign catalyst. However, at a low growth temperature of 350 °C, a different situation was observed. The particle at the nanowire tip was found to contain a high concentration of arsenic. This suggests that the mechanism of nanowire formation is different from the classic vapor-liquid-solid process. The particle at the tip turned out to be a mixture of silicon and arsenic, rather than lead and gallium, indicating that the growth process followed a vapor-solid-solid mechanism.

Keywords: nanowires, lead initiated growth, silicon catalyzed growth, Vapor-Solid-Solid mechanism, molecular beam epitaxy

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Рост нитевидных нанокристаллов GaAs с частицей, богатой кремнием на вершине

Н.В. Сибирев [1], И.В. Ильких [2], Е.В. Убыйвовк [1], И.П. Сошников [3], И.В. Штром [1] ✉, Р.Р. Резник [1], В.В. Брюханова [1], Г.Э. Цырлин [2]

[1] Санкт-Петербургский государственный университет, Санкт-Петербург, Россия;
[2] Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия;
[3] Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия
✉ igorstrohm@mail.ru

Аннотация. В работе обсуждается низкотемпературный рост нитевидных нанокристаллов арсенида галлия на кремнии с использованием свинца. Обычно формирование A3B5 нитевидных нанокристаллов происходит по механизму пар-жидкость-кристалл. Их рост проводят с использованием катализатора, хорошо растворяющего только элемент III группы. В данной работе в качестве инициатора роста использовался свинец, который так же хорошо растворяет элемент V группы — мышьяк. Оказалось, что при низкой температуре роста 350 °C, механизм формирования нитевидных нанокристаллов сильно отличается от классического. Частица-катализатор на вершине оказалась не свинцовым, а кремниевым арсенидом. Это позволяет утверждать, что рост нитевидных нанокристаллов проходил по механизму пар-кристалл-кристалл.

Ключевые слова: нитевидных нанокристаллы, инициируемый свинцом рост, рост с кремниевым катализатором, механизм пар-кристалл-кристалл, молекулярно-пучковая эпитаксия

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Introduction

The growth of arsenides and phosphides nanowires (NWs) by the Vapor-Liquid-Solid (VLS) mechanism almost always occurs using a catalyst that dissolves group III element well [1], but poorly dissolves group V element. The most commonly growers use precious metals such as gold [1, 2], rarely silver [1] or copper [3], or group III elements (gallium, indium) [1, 2]. These materials dissolve the element of the third group well, but arsenic or phosphorus poorly, which complicates the possibility of obtaining *n*-type doping of NWs [2, 4]. Another disadvantage is the blurring of the heterojunction in InGaAs/GaAs or AlGaAs/AlAs [3–5].

These problems already have some technological solutions. However, it is proposed to consider an alternative solution for the growth of A3B5 NWs with a drop rich in element group V (nitrogen group), rather than metal. Only two such catalysts are mentioned in the literature: tin [6, 7] and lead [5]. NWs already grown with such catalyst, but tin is quite easily integrated into arsenides and phosphides. Even more in paper [6] shown that droplet composition is Sn-As.

In this paper, the growth of GaAs NWs with a lead (Pb) catalyst is discussed. Pb dissolves both Ga [8] and As [9] as well. Ga and Pb are immiscible liquids and easily separate into two distinct layers [8]. Pb with As forms an eutectic system [9].

Materials and Methods

Growth experiments were carried out in a Riber Compact 12 MBE system, equipped with effusion sources of gallium and arsenic. The growth of GaAs NWs proceeds on Si(111) substrates with a pre-deposited layer of lead. In more details growth method is described here [5].

In order to remove the defective oxide layer, the substrates were previously treated in a weak hydrofluoric acid solution. The deposition of a 10 nm thick lead film was carried out by electron beam evaporation on an Auto500 (Boc Edwards) system with oil-free pumping at a residual vacuum of at least 5×10^{-6} Torr and a sample table temperature of about 80 °C. The thickness of the deposited layer was controlled by an optical meter and fixed to 5 nm. The purity of lead was at least 99.99%.

After that, the substrates were transferred to a growth chamber. The substrate was heated to a rising temperature of 350 °C. Lead dissolves quite easily in silicon, so we avoided long annealing to prevent lead droplets from dissolving in the substrate. After stabilization of the substrate temperature, the gallium and arsenic deposition started and NWs growth began. The gallium flux during NW synthesis corresponded to the growth rate of the GaAs planar layer is 0.7 ML/sec. The flow of arsenic was ten times greater than the flow of gallium. The growth time was 10 minutes.

The morphology of the surface of the samples was studied using a Supra 25 scanning electron microscope (SEM) (C.Zeiss) equipped with the Ultim microanalysis console (Oxford Instruments inc.). Studies of the structural properties and composition of synthesized the NWs were performed using transmission electron methods (TEM) on a Zeiss Libra 200FE microscope equipped with an X-Max energy dispersive X-ray detector.

Results and discussion

The results of morphology studies did not bring any surprises, most of the NWs were needle-shaped, and some still had droplets on them, see Figure 1.

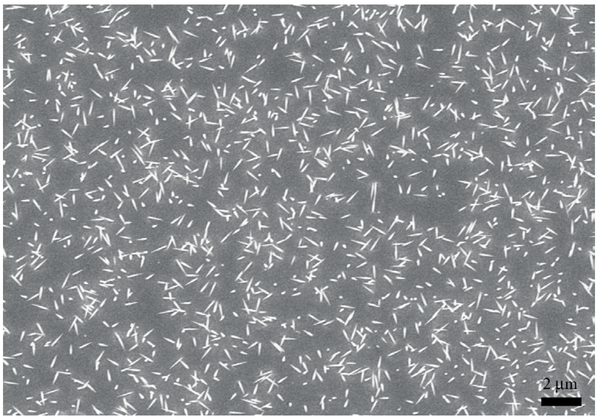

Fig.1. SEM image of GaAs NWs

It is natural to explain the NW shape by the gradual dissolution of lead in the NW body, as well as the superiority of arsenic flux over gallium. The length of the NW was approximately 1.5 microns, which corresponds well with usual idea of a 10-fold increase in the NW growth rate. The base radius is about 70 nm.

The study of the NW composition gives unexpected results. The lead level turned out to be extremely low and practically did not differ from the error of the energy dispersion detector (EDX). Only near the NW tips signal was greater than 2%. At the same time, the silicon content was significantly higher than that of lead. These data for five different NWs are shown in Figure 2.

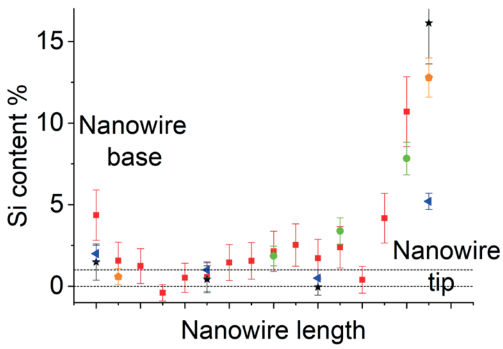

Fig. 2. The results of measuring the Si content along NW length. Different symbols (squares, stars, circles, triangles and pentagons) correspond to different NWs

The TEM image of the NW tip showed an elementary contrast. Several layers at the NW tips clearly differed in composition, see Figure 3. EDX clearly indicated that the particle on the nanowire tip contains a lot of silicon.

The solubility of silicon in lead at this growth temperature does not exceed 1%, that is, it cannot be silicon that got into the droplet at the initial stage. Autocatalytic growth of GaAs NWs at such a temperature is usually not observed, and the solubility of silicon in gallium is also not high, less than 1% [4, 10]. This means that during the growth of the NW, silicon was constantly coming from the substrate. Silicon was etched with lead from the wafer. The mechanism of Si etching is similar to the formation of black silicon (*b*-Si) via metal-assisted chemical etching [11]. Pb acted as a catalyst to etch the Si substrate surface. However, there is a difference between our process and the formation of *b*-Si. In our method, active Si atoms diffuse to the NW, whereas in the formation of *b*-Si, atoms are removed through gas or liquid flow.

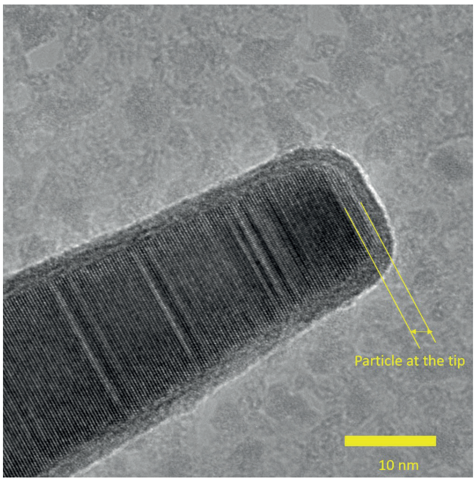

Fig. 3. TEM image of NW tip

No Pb was found at the top, but Si and As clearly observed. Most probably it means that particle on the tip is one of the polytypes of SiAs. The crystal structure of SiAs has really similar to GaAs(111)B facets [12]. Arsenic atoms form an elongated octahedron around a pair of silicon atoms. The distance between neighboring atoms varies in range 3.7–4.7Å. In the most stable configuration, the direction of the elongated axis alternates through three layers, in our case it's not necessary. The As octahedra can be rotated so that the lattice mismatch between the GaAs(111)B and SiAs facet is less than 2%.

Conclusion

The paper discusses the unusual growth of GaAs gallium arsenide NWs initiated by lead. The growth was carried out by the MBE method in a highly nonequilibrium regime on a Si substrate. High supersaturation was achieved by a low substrate temperature of 350 °C. At this temperature, the solubility of Si in Ga-Pb mixtures, or Pb-As solution is less than 1%. An unexpected formation of SiAs solid particle on the NW tip was observed. The NW growth rate with solid particle on the tip was of the same order as for convenient Vapor-Liquid-Solid method.

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THE AUTHORS

SIBIREV Nickolay V.
n.sibirev@mail.spbu.ru
ORCID: 0000-0002-7566-2522

ILKIV Igor V.
fiskerr@ymail.com
ORCID: 0000-0001-8968-3626

UBYIVOVK Evgenii V.
e.ubyivovk@mail.spbu.ru

SOSHNIKOV Iliya P.
ipsosh@beam.ioffe.ru

SHTROM Igor V.
igorstrohm@mail.ru

REZNIK Rodion R.
moment92@mail.ru
ORCID: 0000-0003-1420-7515

BRUKHANOVA Vera V.
brukhanova@mail.spbu.ru

CIRLIN George E.
george.cirlin@mail.ru

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