Development of methods for orderly growth of nanowires

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Abstract. Method of manufacturing substrates for self-catalyst/free-catalyst ordered growth of the nanowires has been developed. Experiments show the possibility of autocalytic growth of ordered GaAs NWs on the substrates produced during the research.

1. Introduction
Nanowires are crystalline structures the length of which considerably exceeds the diameter which is from 8 to 300 nm. Nowadays the interest in nanowires stems from the prospects of their use in many applications, such as: chemical and biological highly sensitive sensors \cite{1-4}, emission cathodes and cantilevers for STM / AFM, fuel cells and batteries \cite{5}, in optoelectronics and onolactone, in electromechanical devices (tensor sensors, microphones, piezoresistors, nanobodies).

The creation of device structures based on nanowires requires the development of methods and technologies for the synthesis of ordered semiconductor NWs and research of their features. We emphasize that approach developed by many researchers based on the creation of orderly catalytic growth centers of NWs \cite{6, 7, 8, 9} has a number of disadvantages, including the possibility of growth centers' shifting to their complete removal from the surface, branching of NWs, uncontrolled growth in other directions, uncontrolled alloying of catalyst by the material etc. Therefore, the work is dedicated to the research aimed at the development of autocalytic and catalyst free methods of growth of ordered arrays of NWs in materials A\textsuperscript{3}B\textsuperscript{5}.
2. The essence of the method.
The aim of the work is to determine the possibility of producing $A^3B^5$ structures with ordered free-catalyst or self-catalytic NWs through inhibitory layer with ordered windows of growth. The initial goal is the formation of holes in the inhibitory ordered SiO$_2$ layers by electron lithography.

Polished wafers Si (111) brand KDB-10 with SiO$_2$ layer about 50-100 nm thick previously synthesized by magnetron sputtering and/or thermal oxidation were used as the samples.

Electron resist layer 672 ARP (PMMA-polymethylmethacrylate K 950) was applied with centrifugation on the surface of the samples and after that dried for 15 minutes at $T = 90^\circ$C. Then the sample was exposed in the electron microscope Zeiss SUPRA 25 and subsequently developed in special solutions. The next step was etching with argon ion beam at energy of 0.5 keV to form lithographic windows in the SiO$_2$ layer and removal of residual polymer. At the final stage MBE growth of GaAs NWs was carried out using self-catalyst method [10, 11].

3. Results and discussion.
The sample surface after electron-beam lithography is presented in figure 1. The image shows three groups (2x10) of arrays produced with lithography at accelerating voltages of 10, 15 and 20 kV.

When the exposure time is less than the minimum response time of EBW, ticks appear instead of points due to the finite time of operation of the system control beam in the electron microscope (figure 2). This fact means that we are limited in the choice of the values of the beam current and exposure time below.

Figure 1. Review electron microscopic image in geometry top view of the sample surface after carrying out lithography.
Figure 2. Electron microscope image in geometry top view of the array of slots in the resist during the exposure time greater than the minimum response time ELS. Lithography was performed at an accelerating voltage of 20kV.

Figure 3 shows the dependence of the diameter of the "window" in resist on the distance between adjacent "windows" at different accelerating voltages. By increasing the step up to two microns the diameter of the element decreases. Such dependence of the size on the step can be explained by the influence of proximity effects when the step is less than 2 microns. Lithographic elements of all sizes, used to analyze the results, were measured in areas with a step of 2, 4 and 6 microns.

Figure 3. The dependence of the diameter of the "window" in the resist on the step between adjacent elements at accelerating voltages of 10, 15 and 20 kV and a dose of 600.

Dependence of the diameter of the "window" on the dose is shown in figure 4. At high doses (> 100 mC / cm²) a "burning" of the resist can be seen where the electron beam enters into the sample. It should be noted that in following experiments on the growth of the NWs observed the formation of holes where the resist had been burnt.
Figure 4. The dependence of the diameter of the "window" on the dose for a single layer of resist. Lithography was performed at accelerating voltages of 10, 15 and 20 kV and Electron microscope image in geometry top view of the array of slots in the resist, there is the burning of the resist. The exposure was conducted at an accelerating voltage of 20 kV and a beam current of ~1 nA.

The result ion etching is represented in figure 5. Analysis of the characteristic size of the bitmap window showed that the minimum stable diameter Windows in the SiO$_2$ layer is about 40 nm.

Figure 5. Electron microscope image in ISO array of "Windows" in the SiO$_2$ layer on the Si substrate after ion etching

There is SiO$_2$ flaking from the silicon surface in a number of cases after etching on the samples with SiO$_2$ layer was applied by magnetron sputtering (figure 6). This happens due to the lack of adhesion between SiO$_2$ layer and the silicon substrate during magnetron sputtering. No flaking of the inhibitory layer is observed on the samples with SiO$_2$ layer produced by oxidation of the substrate.
Preliminary experiments on the growth of GaAs NWs are carried out in this work. The Example of the sample with surface lithographic structure in the SiO$_2$ layer is shown in figure 7. NW is 1000 nm high and 30 nm in diameter. The growth of individual NWs with low density is observed off the field of lithographic picture, the arrangement of these NWs is disordered and random and apparently due to insufficient purity of the process.

4. Conclusions.
The Dependence of the lithographic windows size on the main parameters (energy, beam current, the exposure step between elements, the thickness of the resist layer and inhibitory layer, peculiarities of the application of the inhibitory layer, etc.) are studied in the work. It is shown that if the distance between the elements is less than 2 microns, it is necessary to consider the impact of proximity effects. At high doses ($>100$ mC/cm$^2$) "burning" of the resist can be seen where the electron beam enters the sample. The optimal conditions for the formation of lithographic windows with dimensions less than 50 nm are defined. The features of ion etching in the inhibitory SiO$_2$ layer are searched. The possibility of the formation of the windows with the characteristic sizes from 40 to 250 nm is demonstrated. The effect of inhibitory layer adhesion on the formation of lithographic substrates for growth is also researched.
The experiments show the possibility of autocatalytic growth of orderly GaAs NWs on the substrates produced during the research. The necessity of systematic research of growth conditions using the chosen method to get higher quality (homogeneous) arrays of NWs is evident.

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References

[1] Patolsky F, Zheng G and Lieber C M 2006 Nature Protocols 1 1711
[2] Mathews M, Jansen R, Rijnders G, Lodder J C, and Blank D H A 2009 Phys. Rev. B 80 064408
[3] Man-Fai Ng, Liping Zhou, Shuo-Wang Yang, Li Yun Sim, Tan Vincent B. C., and Ping Wu 2007 Phys. Rev. B 76 155435
[4] Markussen T, Rurali R, Brandbyge M and Jauho A-P 2006 Phys. Rev. B 74 245313
[5] Chan C K, Peng H, Liu G, McIlwrath K, Zhang X F, Huggins R A and Yi Cui 2008 Nature Nanotechnology 3 31-35
[6] Givargozov E I 2003 Nature 11 20
[7] Cheng G and Moskovits M 2002 Advanced Materials 14 1567
[8] Roest A L, Verheijen M A, Wunnicke O, Serafin S, Wondergem H and Bakkers E P A M 2006 Nanotechnology 17 271
[9] Persson A I, Fröberg L E, Samuelson L and Linke H 2009 Nanotechnology 20 225304
[10] Noborisaka J, Motohisa J and Fukui T 2005 Appl. Phys. Lett. 86 213102
[11] Soshnikov I P, Petrov V A, Proskuryakov U U, Kudryashov D A, Nashcheyokin A V, Cirlin G E, Treharne R, Durose K 2013 Semiconductors 47 865