Fabrication method of the patterned mask for controllable growth of low-dimensional semiconductor nanostructures

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Abstract. One of the important problems on the way to development of highly efficient optoelectronic devices such as silicon-based light-emitting diodes, hybrid solar cells as well as semiconductor lasers based on quantum dots is to obtain nanostructures with high crystalline perfection and small size dispersion. In this paper, we studied the method of the growth mask fabrication using photolithography through a close-packed array of microspherical lenses to obtain monodisperse nanostructures on a silicon growth substrate for the subsequent epitaxy of ordered GaP nanowires (NWs) array with a controllable morphology. Theoretical modeling of UV wave propagation demonstrated the possibility of the light focusing under a microspherical lenses array in the photoresist. With the method use the growth masks made of silicon oxide on Si (111) substrates were fabricated. Molecular-beam epitaxy was used to synthesize GaP NW ordered arrays.

1. Introduction

Epitaxial growth of A3B5 materials on Si substrates is the problem of current interest. Solution of this problem will allow development of highly efficient and cheap LEDs, elements for solar energy and other optoelectronic devices [1]. Today the functional A3B5 structures for optonanoelectronics can be realized with the use of InGaN material system with a buffer layer on sapphire substrates. The buffer layer in this case reaches about 70% of the entire structure volume which leads to additional costs in the device manufacturing [2, 3]. The advantages of III-V materials grown on Si involve low cost and proven production and post-processing technologies of silicon substrates. However, there are several problems associated with a large lattice mismatch between most of III-V and Si, the polarity of III-V materials and the difference in their physical properties and crystal structures. These problems lead to poor electronic characteristics of the heterostructures while difference in lattice parameters and thermal expansion coefficients between the substrate and the layers leads to the mechanical damage of epitaxial layers [4]. The method of NWs epitaxial growth is a promising method for solving these problems since the area of the NW/ Si heterointerface is rather small while their surface area is large. Therefore NWs growth on Si substrates helps to reduce the number of defects and does not require the use of a buffer layer [5]. That is why these nanostructures are believed to be very promising in such applications as light-emitting diodes or optoelectronic devices.

The most common technique for NW arrays growth is the vapor-liquid-solid (VLS) method [6]. The main drawback of this method is the synthesized structures size dispersion. The dispersion is
determined by the initial size distribution of the catalyst droplets formed from a thin metal layer deposited on the growth substrate prior to the NWs growth. Another drawback of the technique is the unwanted doping of the NW with atoms of the catalyst reducing electronic properties of the nanostructures. The approach allowing to solve these problems is fabrication of an ordered nanometer-sized holes pattern with a given morphology for further growth of the nanowire arrays or quantum dots. Fabrication of a large-scale growth mask technologically is a challenging task. To this end, most commonly used technique for fabrication of the patterned substrates involves use of expensive electron-beam lithography method. The time spent on one lithographic process in the latter case is proportional to the area of the sample which makes this method inapplicable for mass production. The photolithography over micro- / nano-spherical lenses allows fast fabrication of large close-packed arrays of nanostructures and their surface density variation [7]. In this paper we present the results on development of the micro-spherical lenses enhanced photolithography method, including deposition of a chemically active layer on a silicon wafer surface and selective etching of this layer. The results on the semiconductor material growth over the fabricated pattern for verification of the selective area growth capability of the method are presented.

2. Pre-processing

The photolithography through micro- and nanosphere lenses (SiO2, polystyrene (PS)) method improves resolution of the conventional photolithography which is limited by the diffraction limit and enhances fabrication capability compare to conventional methods [7, 8]. An ordered array of microspherical lenses applied to the resist surface focuses the radiation in the resist when exposed as a result sub-micron-sized elements are formed on the substrate. This approach provides incident wave focusing by microspherical lenses into a photoresist layer and it is highly efficient for obtaining ordered micro- / nanostructure arrays. In our work this method is used for fabrication of a growth mask for selective area epitaxial growth. The mask material deposition technique depends on the choice of the mask material and could be either vacuum thermal deposition or plasma-chemical deposition. After liquid or plasma chemical etching of the obtained structure on the silicon substrate surface we obtain nanoscale pits in the mask material.

GaP was chosen as a material for selective areagrowth via molecular beam epitaxy. Si (111) wafer was used as a substrate since GaP has a low lattice mismatch with Si. Epitaxially grown GaP NWs can be obtained in the wurtzite phase providing direct-band [9] and can be used as a active elements for LEDs. On the other hand, ordered cubic GaP NWs grown on Si can function as a wide-band window and an antireflection coating of solar cells [10, 11].

It is known that growth of A3B5 group materials is suppressed on silicon oxide [12, 13, 14]. Consequently, we choose SiO, as the material for the mask fabrication. By the method of plasma chemical deposition (PECVD) 20 nm silica layer was deposited on the substrate at a temperature of 350°C. To create holes in the fabricated layer it is necessary to form a resistive mask. We selected optimal parameters for focusing of the light with a wavelength of 365 nm by microspheres into the photoresist layer and exposition of the photoresist.

The thickness of the photoresist was determined via numerical modeling and corresponded to the optimal propagation of the incident electromagnetic plane wave into the photoresist layer as shown in figure 1 (a, b). By changing the exposure parameters (for example, the exposure dose) we are able to change the diameter of the formed nano-holes obtained after the resist development. We also note that use of different diameters microspheres allows us to vary the period of the nanostructure array formed in the photoresist.
Figure 1 (a, b). The modeling results image of radiation absorption by photoresist using ordered array of SiO$_2$ microspheres deposited on photoresist coated Si substrate with SiO$_2$ layer (a). The modeling image of radiation power flow in photoresist using ordered array of SiO$_2$ microspheres (b).

Figure 2 (a) shows SEM image of an ordered array of SiO$_2$ microspherical lenses applied to the resist surface which were subsequently exposed under LED with wavelength of 365 nm. After the photolithography process etching of silicon oxide in SF$_6$ and removal of the residual resist the regular round holes of a fixed submicron size were formed in the SiO$_2$ layer as shown in figure 2 (b).

Further, the mask fabricated in SiO$_2$ was used as a growth pattern for epitaxy of GaP nanostructures. In molecular-beam epitaxy growth chamber degassing of the substrate occurred at 700°C measured with pyrometer and growth of GaP was carried out at a temperature of 620°C. In order to initialize the VLS mechanism 0.3 ML thick Ga layer was deposited providing formation of Ga droplets. The ratio of the equivalent partial pressures of the molecular beam (BEP) was 1/8 (GaP/P) measured with a thermal ionization vacuumeter placed on the beam path.

Figure 2 (c, d) shows SEM image of the synthesized GaP NWs. In the upper right-hand corner of figure 2 (d) the Fourier image of the obtained GaP NWs top view SEM image is shown. The hexagonal beams of Fourier image show that the nanostructures are arranged in a hexagon. It can be noted that at sprawl of GaP growth material over the mask takes place which can lead to closure of GaP nanostructures. This problem can be avoided via adjustment of the growth parameters. We also observed that the growth of GaP NW did not occur in every hole of the mask which certainly requires further optimization of the epitaxial growth parameters. Improvement of GaP NWs synthesis method will allow to fabricate ordered arrays of self-catalyzed nanostructures of a given morphology for realization of functional devices.
Figure 2 (a, b, c, d). Simulation SEM image of the ordered array of SiO$_2$ microspheres deposited over photoresist on Si substrate (a), nanostructures made of photoresist after development (b), ordered array of hollows in SiO$_2$ layer after lift-off (c), ordered array of epitaxial GaP nanowires and its Fourier image (FFT) showing the periodicity in nanostructure dislocations (rays of a hexahedron on inset) (d).

3. Conclusion
Combining the photolithography over micro-/nano-spherical lenses method with the technologies of plasma-chemical deposition from the gas phase materials and plasma-chemical etching enabled us to create arrays of ordered nanohollows in a SiO$_2$ layer on silicon substrates. Using numerical simulation the optimal thickness of the photoresist layer was obtained which corresponds to the focusing of the incident electromagnetic plane wave into the photoresist layer. An ordered array of nanostructures with a diameter of about 300 nm was obtained. Using molecular-beam epitaxy technique we synthesized ordered arrays of GaP NW on a silicon substrate.

Development of the substrate patterning method for synthesis of ordered semiconductor NWs with a given geometry is an actual problem due to high potential of their application as functional elements of nanophotonics and nanoelectronics.

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