Development of local catalytic centers positioning technology for carbon nanotubes growth

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Abstract. The paper presents the results of developing positioning catalytic centers technology for the local growth of carbon nanotubes using non-standard techniques of nanometer resolution lithography explosive. It is shown that using of ZnO as a sacrificial layer is promising for the formation of nanoscale catalytic centers, as well as actuality of using focused ion beam as a lithographic tool. An array of local catalytic centers with a diameter of 35 nm, completely repeating the given topology, suitable for the growth of carbon nanotubes is obtained. The obtained results can be used for developing technological processes formation of nano- and microelectronic structures, nano- and microsystems based on single or local CNTs arrays.

1. Introduction

Carbon nanotubes (CNTs) are promising material, which is associated with progress in the creation of a new element base for vacuum micro- and nanoelectronics [1-3]. Methods that make it possible to grow a single CNTs in places defined by the design of the device are the most interesting in device applications. [4, 5]. A solution of this problem is the using of lithographic techniques to create and position the CNT growth catalytic center (CC) with dimensions less than 50 nm. The most promising method with same resolution is electron-beam lithography. However, high cost, impossibility of providing high-temperature processes with the resist layers, complexity of equipment and low productivity are the main factors holding back this method of lithography. Development of local catalytic centers positioning technology for carbon nanotubes growth without described problems, is an actual task.

A promising method that allows to modify the surface of a substrate with a nanometer resolution is the method of focused ion beams (FIB) [6]. However, direct ion-beam etching of the catalytic Ni film leads to appearance of radiation defects and partial doping of the catalyst by ions of source (Ga+).

The aim of the work is developing of local catalytic centers positioning technology for carbon nanotubes growth, excluding direct interaction between FIB and the catalytic layer.

2. Experiments and methods

Si (100) was used as substrates. ZnO sacrificial layer (Fig. 1) sputtering was performed by pulsed laser deposition (PLD) system Peconer 100 (Neocera, USA) from a ZnO target (Kurt J. Lesker Co). The deposition thickness was 60 nm. Positioning of catalytic centers on the substrate was performed by local etching of array of "points" by FIB method by the gallium liquid metal ion source on Nova...
Nanolab 600 (FEI, Netherlands). The beam current was 0.1 pA, the accelerating voltage - 30 kV. At each "point" of the array, the dwell time of the beam was increased. On the FIB-profiled samples, Ni catalytic layer were formed by magnetron sputtering (in Ar atmosphere, pressure 0.5 Pa) on the Auto500 (BOC Edwards, UK) from the Ni target 99.995% (Kurt J. Lesker Co) at 150 °C temperature. Ni thickness was 15 nm. For selective etching of ZnO and formation of CNT growth local CCs, the samples were chemically etched in 40% aqueous ammonia solution for 10 sec at a temperature of 24 °C. CNT growth was provide by plasma chemical vapor deposition (PECVD) in an atmosphere of acetylene (C2H2) and ammonia (NH3) on samples with local CC by using multifunctional nanotechnology complex NANOFAB (NT-MDT, Russia). The growth temperature was 680 °C, the growth time was 15 min, the acetylene and ammonia flows are 70 and 210 cm³/min, respectively. Analysis of the samples was provided by using atomic force (AFM) and scanning electron microscopy (SEM) on the Ntegra scanning probe microscope system (NT-MDT, Russia) and Nova Nanolab 600, respectively.

![Image](image1.png)

(a) (b)

Figure 1. SEM (a) and AFM (b) images of ZnO layer.

3. Results and discussion

Analysis of obtained SEM and AFM data has shown that the PLD method allows the create of sacrificial material films with the necessary physico-chemical and morphological properties. Precise control of the of thickness, roughness, structure, adhesion and chemical composition parameters of the formed sacrificial layer, allows to create of thin films of material with the required parameters necessary for further technological operations. It is found that obtained ZnO films have a nanocrystalline structure, the grain size was 12 ± 3 nm, surface roughness 8 ± 1 nm.

AFM and SEM samples research after FIB-etching have shown (Figure 2, a) that increasing of beam dwell time results to increment a depth and diameter of etching. From the SEM images obtained (Figure 2, b), it is seen that NH₄OH exposure, induce a selective dissolution of the ZnO film and removal of the ZnO/Ni structure occurs, as a result on the substrate are formed of catalytic Ni regions with a given geometry. Thus, this operation allowed to remove the metal located on the sacrificial layer and save the catalytic centers on the substrate in the FIB-profiled areas.
Figure 2. SEM image of the structure: ZnO/Si after FIB etching (a); Ni/ZnO/Si after selective etching in NH₄OH (b).

The use of an etchant of non-aggressive composition allows us to apply the developed technique for creating devices for nanoelectronics in the formation of catalytic regions on multilayer structures with a complex topology that are critical to the effects of chemically aggressive solutions. At the same time, the developed technology makes it possible to form a CC with a diameter of ~35 nm (Figure 3, a). However, the FIB method imposes high demands on thickness uniformity, as well as the need to refine the ion-beam etching modes of the sacrificial layer, without affecting the substrate material.

A similar experiment with Ni deposition by the PLD method did not make it possible to obtain local catalytic centers. This can be attributed to the fact that the Ni particles (atoms, ions, clusters) deposited by the PLD method have a higher energy compared to the magnetron sputtering, which leads to their penetration into the substrate structure with increasing Ni layer adhesion, violating the further formation of catalytic centers during annealing films in CNTs synthesis process. In this case, films formed by the magnetron sputtering have adhesion, which satisfies the catalytic centers formation conditions.

Later, CNT was grown on the formed local catalytic centers by the PECVD. The analysis of the SEM images of the samples after growth (Figure 3, b, c) showed that the formation of nanotubes occurs in predetermined areas formed at the topology formation stage by FIB.

Figure 3. SEM image of a single catalytic center (a); a single CNT (b); an array of local CNTs (c).

It has been established that with the increase in the diameter of catalytic areas over 250 nm, the formation of 2 and more CNTs is observed under the presented modes. Thus, the developed
technology can be used to create new promising elements of nanoelectronics, micro- and nanosystems [7].

4. Conclusion
As a result of this work, a technique for nanolithography, suitable for the formation of nanoscale catalytic centers and growth of CNTs on them, was developed.

It is shown that the PLD method allows to create films of the ZnO sacrificial layer with the necessary physicochemical and morphological properties. Precise control of the thickness, roughness, structure and adhesion parameters of the formed sacrificial layer allows to create of the thin films material suitable for creation of the single CNTs and arrays based on them. Although that the FIP method imposes high demands on uniformity of thickness, as well as the necessary to refine the sacrificial layer ion-beam etching modes, shown the perspective of using FIB-technology for creating catalytic areas and CC with a diameter from 30 nm suitable for the single CNTs growth. In this case, the use of ZnO as sacrificial layer has a part of advantages associated with the possibility of carrying out high-temperature technological processes, due to the temperature-resistant sacrificial layer; a large set of selective etchants; ensuring the necessary adhesion of the sacrificial layer material (low adhesion) and functional material (high adhesion) to the substrate. Also the developed technology allows to avoid the operations connected with resist soft baking, development and hard baking.

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