ZnO nanostructures by Atomic Layer Deposition method

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Abstract. Nanotechnology is perceived as one of the innovatory disciplines of the XXI century science and the main direction of the economic and technological progress in the nearest years. Nowadays exist many ways of creating nanostructures and the Atomic Layer Deposition (ALD) method is one of them. This method, being a self-limiting growth process, can homogeneously cover the surfaces having very irregular shapes in the distinction from other methods. It is also possible a penetration of nanopores in the porous matrices. In this paper we introduce the innovatory use of the ALD method to receive the nanostructures of zinc oxide, where the execution of quantum dots will be presented. The unusual passivation of the surface of ZnTe nanowires received by the MBE method will also be shown. Finally we introduce some surprising types of substrates used to the low dimensional structures’ creation and a potential application of the received ZnO nanostructures.

1. Introduction

Nanotechnology is a revolutionary branch of science operating in the range of billion parts of the meter, and it lays out completely new investigative directions in the mechanics, chemistry, biology, physics, electronics and computer science. Low dimensional nanoscale materials have recently drawn much attention due to their interesting physical and potential nanodevice applications [1-4].

There are many ways of creating nanostructures (e.g Molecular Bean Epitaxy (MBE)). One of them is the Atomic Layer Deposition (ALD) technique, which is a self-limiting growth process widely used for many different applications [5-6]. During the ALD process the target samples are exposed to precursor molecules from the gas phase allowing the precursor to build a layer (in the ideal case a monolayer) on the substrate. Each cycle of precursor’s dose is separated by purging the growth chamber with neutral gas. These cycles can be repeated until the desired layer thickness is obtained. Due to the sequentiality of the process precursors react only at the substrate’s surface so we can use even very reactive ones.

Last years, zinc oxide (ZnO) has been extensively studied as a prospective material for electronics (sensors) and optoelectronics. Zinc oxide is a wurtzite-type II-VI semiconducting compound with a wide, direct band-gap (3.37 eV at room temperature (RT)) and has an exciton binding energy of 60 meV (so more than twice larger than thermal energy at RT). For this reason ZnO is a semiconductor with a variety of possible practical applications, notably in the area of ultraviolet
(UV)/visible emitting devices, gas sensors, solar cells, piezoelectric transducers, transparent electronics, spintronics and Light Emitting Devices (LEDs).

2. ZnO nanostructures
Nanostructures of oxide materials may have interesting electrical properties and thus a potential application in microelectronics. However, only a few techniques are predestinated for making oxide low dimensional nanostructures and hence the literature is limited. The use of various substrates and ALD offers a versatile method to make low dimensional nanostructures.

2.1. ZnO nanorods
As the substrate for our ZnO nanorods deposition process we used Au-coated GaAs (100). In this case the Au layer had thickness of about 15Å. Before the deposition the substrates were annealed at 560ºC for 25 minutes in a horizontal tube furnace. After the furnace was cooled down, the substrates were taken out and transferred to an ALD chamber. Subsequently the ZnO coating procedure was applied using the F-120 reactor. The pulse lengths were 1.1 s for dimethylozinc (DMZn) (with 1.1 s for purging the reactant), 2.75 s for H$_2$O (with 4.4 s for purging the reactant). The process was conducted at 190ºC. As a result we obtained ZnO nanorods as presented in Figure 1 - 4.

![AFM image of ZnO/Au/GaAs layer](Figure 1)

![SEM image of ZnO/Au/GaAs layer](Figure 2)

![SEM image of ZnO/Au/GaAs layer](Figure 3)

![SEM image of ZnO/Au/GaAs layer](Figure 4)
2.2. ZnO nanodots

ZnO nanodots formation was carried out on Si (100) substrates coated with a 15Å thick Au layer. The 25 minutes long pre-deposition annealing was done at 490ºC inside the F-120 reactor. After the annealing process the temperature was decreased to 380ºC at which the ZnO deposition was conducted. The pulse lengths were 1.1 s for DMZn (with 1.1 s for purging the reactant), 2.75 s for H₂O (with 4.4 s for purging the reactant). The deposition results (including AFM and SEM images) are presented in Figures 5-8 below.

Figure 5 AFM image of ZnO/Au/Si layer

Figure 6 AFM image of ZnO/Au/Si layer

Figure 7 SEM image of ZnO/Au/Si layer

Figure 8 SEM image of ZnO/Au/Si layer
3. ZnTe nanowires coating ZnO
Creation of ZnO nanorods was carried out on ZnTe nanowires grown on GaAs substrate by the MBE technique. The scheme of uncoated ZnTe nanowire is shown in Figure 9a, and Figure 10 shows SEM image of ZnTe – MBE nanowires. These ZnTe nanowires were subsequently put into the Savannah-100 reactor growth chamber. The precursors’ doses were 40 ms for diethylzinc (DEZn) (with 8 s for purging the reactant), 15 ms for H\textsubscript{2}O (with 20 s for purging the reactant). The schematic view presenting a passivation effect of the ZnO/ZnTe/GaAs nanowire can be seen in Figure 9a-b. The coating process was conducted at 100°C in 400 growth cycles.

![Figure 9 A schematic view of ZnTe nanowire before (a) and after (b) ZnO coating process](image1)

Figure 9 A schematic view of ZnTe nanowire before (a) and after (b) ZnO coating process

![Figure 10 SEM image of clean ZnTe nanowires before ZnO coating process](image2)

Figure 10 SEM image of clean ZnTe nanowires before ZnO coating process

![Figure 11 SEM images of ZnO coated ZnTe nanowires](image3)

Figure 11 SEM images of ZnO coated ZnTe nanowires

As a result of the ALD process we obtained uniformly coated nanowires as is presented in Figure 11. This shows an advantage of the ALD process over the MBE one for such kind of applications. It was not possible to obtain ZnO coated ZnTe wires using the MBE-type process as in this case ZnO caps were created on the top of the wires.
4. Fiber as templates
There are many various types of nanofibers that can be successfully used as templates for nanocomposites. Our choice was to use a polymeric fiber made of poliamide 6.6 as a basal material for the experiment described in this paragraph. The magnified view of stocking before deposition is presented in Figure 12.

![Figure 12 SEM images of polymeric fibers before deposition](image12)

This experiment was divided into two parts. In the first one we tried to directly deposit ZnO on the organic fibers. The precursors’ doses were in this case 1.1 s for DMZn (with 1.1 s given for purging the reactant), 2.75 s for H$_2$O (with 4.4 s given for purging the reactant). The coating process involving 800 cycles was carried out at 130°C. Corresponding results are shown in Figure 13.

In the second part of our experiment we coated the fibers material with a thin layer (about 20Å) of Au before beginning of the deposition process. The growth conditions were nearly the same as in the case described above, but the process involved 700 cycles only. Adequate results are presented in Figure 14.

![Figure 13 SEM images of polymeric fibers coated with ZnO](image13)

![Figure 14 SEM images of polymeric fiber coated with ZnO/Au](image14)
All the presented illustrations and Figure 15 below prove that in both cases we obtained the uniform coating of the fibers material with the ZnO layer.

![Figure 15 Photoluminescence (PL) of samples: ZnO/polymeric fiber, ZnO/Au/polymeric fiber and clear fiber](image)

However, some defected areas of unknown origin appear on the ZnO surface.

5. Conclusions
The Atomic Layer Deposition technique is a versatile tool for nanotechnology since it enables the growth of nanometer scale films on substrates of any shape and size. Its versatility has been proved in many nanomaterials, such as quantum dots, nanofiber and nanowires. The literature on ALD in nanotechnology is still rather limited but it expands fast.

In the present work we demonstrate the use of ALD for the growth of several types of nanostructures – nanowires, nanodots and nanocoatings. In particular, the important advantage of the ALD (excellent conformality) enables coating of nanowires and nanofibers with thin (a few nanometers) films of ZnO. Such a core-shell system has higher potential for various applications.

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