MBE formation of self-catalyzed GaAs nanowires using ZnO nanosized films

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Abstract. We studied the influence of nanoscale ZnO films deposited onto GaAs (001) on the process of GaAs epitaxial growth. We took into consideration the most important control parameters of molecular beam epitaxy, such as substrate temperature, As\textsubscript{4}/Ga effective flux ratio and growth rate and different thicknesses of ZnO films. We found that a ZnO film deposited on GaAs surface acts as a native GaAs oxide when the thickness of the film is being decreased, and can be removed thermally at a temperature of 620-630°C. We showed that it is possible to use nanoscale ZnO films with thickness \~{}5 nm in order to create horizontal GaAs nanowires grown by a self-catalytic mechanism.

1. Introduction

One-dimensional nanostructures, including semiconductor nanowires, are considered to be one of the most promising candidates for the role of active elements of device structures to be used in nanoelectronics, photonics, sensor technology and MEMS/NEMS \cite{1-4}. Having unique structural, transport, optical and electrical characteristics, they can be used both to improve existing systems and to create new types of devices \cite{5-7}. Self-catalytic nanowires formed by a vapor-liquid-crystal mechanism seem to be the most appropriate means to achieve the abovementioned purposes \cite{8, 9}. The process of autocatalytic nanowire growth, as opposed to the case of heterocatalytic growth, is characterized by the fact that catalyst droplets are formed directly in the growth process, which requires the creation of specific surface conditions to initiate the formation of droplets of one of the components \cite{10-16}. To make sure this happens, thin (a few to tens of nanometers) layers of heterogeneous material are formed on the surface, which gives rise to the liquid phase. In most cases, a thin SiO\textsubscript{x} film acts as such a sublayer \cite{17, 18}. However, the presence of a SiO\textsubscript{x} sublayer on the surface and its partial destruction which takes place during the growth process may negatively affect the electrical characteristics of the nanowires obtained \cite{19}.

In the present work, our aim was to study the possibility of nanosized ZnO films use as sublayers initiating the formation of self-catalytic GaAs nanowires during molecular beam epitaxy (MBE), which is necessary to investigate the impact that ZnO films have on GaAs epitaxial growth processes.
2. Experiment

We studied the influence of nanoscale ZnO films on GaAs epitaxial growth processes using an MBE system SemiTEq STE35 which was equipped with a solid-state sources of the elements of the group III and valved As source. We used “epi-ready” GaAs (001) wafers as substrates. After removed GaAs native oxide in the MBE growth chamber we transferred the samples to a pulsed laser deposition (PLD) system Neocera Pioneer 180 where we deposited amorphous ZnO films. To avoid possible interaction between ZnO surface and sputtered GaAs, the PLD process was carried out at a substrate temperature of 50°C. The pressure of the residual atmosphere was $1 \times 10^{-3}$ Pa, the laser power was 260 mJ, the laser pulse frequency was 10 Hz and ZnO (Kurt J. Lesker) was used as a target. The ZnO films had thicknesses of 5 and 20 nm at 3000 and 10 000 pulses, respectively. Then we placed the samples back into the MBE growth chamber where GaAs epitaxial growth was carried out from molecular fluxes of Ga and As$_4$. The effective deposition thickness for all the samples was 100 nm.

We varied the deposition rate $V$ from 1 to 1.5 ML/s, the effective ratio of Ga and As fluxes ($J_{As/Ga}$) ranged from 1 to 4 and the substrate temperature $T$ during the growth ranged from 500 to 650°C. We controlled the process by recording the patterns of reflected high-energy electron diffraction (RHEED). Prior to the beginning of GaAs growth, we made a preliminary deposition of gallium (about 5-10 ML) and then opened the source of arsenic. After completed GaAs deposition, we closed the sources of Ga and As$_4$ simultaneously and cooled the sample rapidly in order to avoid any redistribution of the material on the surface. Then we studied the samples by means of scanning electron (SEM) and atomic force (AFM) microscopy using the FEI Nova Nanolab 600 and NT-MDT Ntegra systems, respectively [20–24].

3. Results and discussion

When we preheated the samples ZnO(20 nm)/GaAs(001) in a vacuum ($1 \times 10^{-7}$ Pa), there was no change in the RHEED pattern across the entire growth temperature range and the diffuse background we registered proved that there was ZnO on the surface of the amorphous film. Therefore, GaAs was being deposited over the ZnO layer. At the same time, at low temperatures (below 550°C) we observed the formation of a GaAs films with polycrystalline structure. For instance, at $T = 500°C$ we observed the formation of an array of GaAs crystallites on the ZnO surface (Figure 1a). The crystallites were characterized by a density of $4 \times 10^9$ cm$^{-2}$, lateral dimensions of 100-250 nm and a height of 40-100 nm. An increase in the growth temperature to 580°C resulted in a fusion of the generated GaAs crystallites into a GaAs film with a rough surface, which was caused by an increase in the surface mobility of adatoms.

Unlike the previous case, when we heated ZnO(5 nm)/GaAs(001) heterostructures above 550°C, the RHEED system recorded a dot pattern with a very weak brightness appearing in the diffuse background. A similar pattern was observed in the case of GaAs native oxide film. Notably, a prolonged annealing (up to 30 min) at $T = 550-600°C$ did not cause any significant change neither in the brightness or in the structure of the diffraction pattern. An increase in temperature up to 600°C led to a gradual increase in the brightness of RHEED pattern, and at $T = 620-630°C$, the pattern was similar to the one we observed during the process of GaAs native oxide thermal desorption at 580°C, i.e. there was a sharp increase in the brightness of the diffraction pattern followed by a dot RHEED pattern related to GaAs (001) surface. This can be accounted for by the thermal removal of the ZnO thin film from the surface of GaAs.

Epitaxial growth of GaAs on the surface of a 5 nm thick ZnO film within the temperature range of $T = 620-640°C$ at $V = 1$ ML/s resulted into the formation of a GaAs layer with a rough surface. Reducing the temperature to 600°C led to a increase in the density of the pits from $4 \times 10^7$ cm$^{-2}$ up to $2.2 \times 10^8$ cm$^{-2}$ and a simultaneous decrease in their size from 300-600 nm to 100-200 nm.

Having increased the deposition rate up to 1.5 ML/s and reduced $J_{As/Ga}$ ratio to 1 within the same temperature range, we formed deep pits on the GaAs surface. The pits had a diameter of 200-300 nm, a depth of 150-200 nm and a significantly lower density of $2 \times 10^7$ cm$^{-2}$ (Figure 1b).
Figure 1. A SEM images of the surface of ZnO/GaAs (001) structure after the deposition of GaAs at $T = 500^\circ\text{C}$ and 20 nm thick ZnO film (a) and $T = 600^\circ\text{C}$ 5 nm thick ZnO film (b).

Having reduced the growth temperature further while maintaining the values of the other parameters within the temperature range of 570-590°C, we obtained horizontal non-oriented GaAs nanowires (Figure 2a). The density of the array of horizontal GaAs nanowires reached $1.2 \times 10^7 \text{ cm}^{-2}$. The nanowires had a length of 0.5-1 μm, a diameter of 250-500 nm and a height (above surface level) of 120-160 nm. The AFM analysis of the structures confirmed the liquid origin of the droplets on the tops of GaAs nanowires since switching to the contact scan mode led to the destruction of spherical formations on crystal tops prominent in the phase contrast picture and the formation of pits with a depth of 60 nm on their site (Figure 2b). The droplet material redistributed over the surface around the nanowires according to the current AFM technique.

Figure 2. Surface of ZnO/GaAs (001) structure after the deposition of GaAs at $T = 580^\circ\text{C}$: (a) SEM image, (b) AFM image in a contact mode.

The presence of liquid Ga droplets on crystals tops indicates a self-catalytic mechanism of crystal growth. Horizontal crystal growth may be predominant due to a small difference between the values of
the surface energy and/or specific conditions on the surface during the formation of the catalytic centers (droplets) and the subsequent crystal growth [25]. In addition, the effective thickness of the deposition can also have a significant impact on the final morphology of the crystal obtained by self-catalytic growth [26].

Our experimental results are similar to those presented in [27, 28]. In any case, the formation of any type of GaAs surface morphology including nanowires can be explained not only by kinetic effects on the surface but also by chemical interactions between ZnO film and GaAs substrate. The presence of such an interaction helps to explain the effect of ZnO film thickness on the morphology of the growing layer of GaAs as when the film is thick, the effective area of interaction between materials decreases and, consequently, there is a decrease in the intensity of chemical reactions at the interface. This also accounts for the observed effect of thermal desorption of thinner ZnO films. Its mechanism is similar to the mechanism of GaAs native oxide removal happening during MBE [29]. Notably, the activation of chemical processes leading to ZnO film degradation, according to RHEED, starts at a temperature of 550°C.

4. Conclusion
In summary, we studied the influence of nanoscale ZnO films deposited on GaAs surface on GaAs epitaxial growth processes taking into account the technological parameters of MBE. We found that there is a significant effect of ZnO film thickness, growth temperature, effective deposition rate and flux ratio on the resulting morphology. We obtained self-catalytic GaAs horizontal nanowires and defined the conditions of their formation. We also found that in addition to kinetic factors, the chemical interaction at ZnO/GaAs interface has a considerable influence on the morphology of GaAs epitaxial layer. Notably, the activation of chemical reactions starts at a temperature of 550°C, and a 5 nm thick ZnO film gets desorbed from the surface at temperatures of 620-630°C.

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