XPS analysis of metallic wetting layer in In/GaAs system obtained at different growth temperatures

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Abstract. In this paper we investigate the processes of nucleation and growth of In/GaAs(001) nanostructures by droplet epitaxy. We determined the temperature dependence of the wetting layer thickness. Using the X-ray photoelectron spectroscopy technique to examine samples with In/GaAs droplet nanostructures formed under different conditions we experimentally confirm an increase in the metallic wetting layer thickness with a decrease in the deposition temperature. Analysis of the data obtained shows that droplet nanostructures consist of In are without Ga impurity.

1. Introduction

The formation of nanoscale structures can be carried out by various methods, but one of the most promising is molecular beam epitaxy (MBE), the technology of which allows semiconductor structures, in particular, based on GaAs [1-10], to be obtained for the subsequent manufacture of nanophotonics devices, optoelectronics and nanoelectronics [11-16]. For a long time, the Stranski-Krastanov method was used to form structures with quantum dots (QDs), during which growth components of group III and V were deposited on the surface of the substrate simultaneously. However, this method limits the ability to control the parameters of nanostructures, which is associated with the impossibility of forming QDs in unstressed systems, the interdependence of size, shape and surface density of nanostructures, the technological complexity of controlling the thickness of the wetting layer, and the size and uniformity of QDs.

To further improve the functional parameters of devices based on semiconductor QDs, it is necessary to control the characteristics of nanostructures. Droplet epitaxy, due to the separate deposition of components, significantly expands the possibilities in the field of control and variation of the parameters of the obtained nanostructures. Previous complex studies of samples obtained by the method of droplet epitaxy show that changes in main control parameters can accurately vary the geometric characteristics of the droplets [17-28]. However, the role of the wetting layer formed in the process of droplet epitaxy still needs to be clarified as well as dynamics of its thickness during the growth. Because the wetting layer has a negative influence on the parameters of the nanostructures and devices based on them [29, 30], it is necessary to study the methods of accurate and reproducible control of the wetting layer thickness with the possibility of its complete removal.
2. Experimental procedure

For our experimental study, we grew a series of samples with In/GaAs(001) nanostructures using droplet epitaxy at various temperatures and deposition thicknesses. Growth temperature varied in the range of 100–300°C. The effective deposition thickness of In for each temperature corresponded to subcritical (without droplet formation) and supercritical (with droplet formation) values (Figure 1(a, b)). Then all obtained samples were investigated by the XPS technique.

![Figure 1(a, b)](image)

**Figure 1(a, b).** SEM images of droplet arrays after deposition of indium at various growth conditions: (a) $T = 100^\circ C$, $H = 3$ ML, (b) $T = 300^\circ C$, $H = 1.5$ ML.

3. Results and discussion

The results of experimental studies of samples with In/GaAs nanostructures by the XPS method, obtained by etching with a beam of Ar ions with an energy of 3 keV, are ambiguous (Figures 2, 3). Changes in the X-ray photoelectron spectra and the distribution of elements in depth, despite the high sensitivity of the method in surface studies, are insignificant from sample to sample and even for extreme points. Quantitative characteristics can be given only when comparing extreme points of the range and only for the initial stages of etching (0–60 s), and they correlate with the difference in the density of ensembles of In droplets, or rather, with the total effective area occupied by the droplets on the sample surface: there is a 4-fold increase in signal intensity when moving from a sample obtained at $300^\circ C$ (Figure 3) to a sample obtained at $150^\circ C$ (Figure 2).

![Figure 2(a, b)](image)

**Figure 2(a, b).** The content profiles of the various components of the In spectra obtained on the In/GaAs structure formed at $150 ^\circ C$ based on (a) In-line and (b) O-line.
The content profiles of the various components of the In spectra obtained on the In/GaAs structure formed at 300 °C based on (a) In-line and (b) O-line.

The thickness of the wetting layer using the selected method can only be estimated at a qualitative level. First, an analysis of the nature of the surface conductivity of the samples allows us to conclude that with a decrease in the growth temperature, the nature of conductivity changes from n-type impurity conductivity with localization of the Fermi level near the bottom of the conduction band (300 °C) to quasimetallic character (150 °C). This behavior is caused not only by an increase in the density of metal droplets at lower temperatures, but also by a 6-fold increase in the thickness of the wetting layer partially oxidized. The specificity of conductivity of high-temperature samples is due to the formation of an In wetting layer of submonolayer thickness on an As-stabilized surface (that is, in fact, the formation of an InAs monolayer terminated by In atoms) followed by disordering and the formation of a mixed oxide phase (In(Ga),As)\(_x\)O\(_y\).

Secondly, a comparative analysis of the dynamics of changes in the intensity ratios of the In, In\(_2\)O\(_3\), In\(_3\)O\(_y\) phases taken from the In3d5 (Figures 2a, 3a) and O1s (Figures 2b, 3b) spectral lines shows that, in low-temperature samples, the intensity of the transitional In\(_3\)O\(_y\) oxide phase begins to dominate relatively rapidly over the In\(_2\)O\(_3\) phase. At the same time, in high-temperature samples, the ratios of these intensities remain unchanged. In addition, on samples formed at low temperature, the metal component begins to predominate over the oxide much earlier (270 versus 510 s). This behavior may be due to the fact that as the etching and removal of the oxide layer from the surface of the ensemble of nanostructures, a metal sublayer is exposed (in the presence of a relatively thick, oxidized wetting layer), which leads to a change in the intensity ratios. At the same time, as the three-dimensional metal droplets are “turned”, the metal core and the oxide shell are exposed, which in the case of high-temperature samples (taking into account large droplet sizes) leads to a constant phase relationship for a very long time.

However, reducing the energy of the sputtering beam to 1 keV makes it possible to significantly increase the resolution of the method with respect to solving the problems posed within the framework of the work. Figure 4 shows the comparative profiles of changes in the intensity of the In3d5A line upon etching samples with In/GaAs nanostructures formed at 100°C, 3 ML (curve 1) and 300°C, 1.5 ML (curve 2).

From the presented data (Figure 4(a, b)) it is clear that the intensity of the In3d5A line on curve 1 (low-temperature sample without droplets) drops to zero much earlier than the lines on curve 2 (high-temperature sample with droplets) – by 360 s and 840 s, respectively. This may indicate a different thickness of the deposited material on the samples (a change of 2 times). At the same time, the lines differ from the different samples qualitatively: curve 1 decreases conventionally monotonously, while curve 2 has two distinct parts: a sharp decline (0 – 120 s) followed by a relatively gentle decrease to zero (120 – 840 s). The conventionally monotonous nature of the decrease in the intensity of the
In 3d5A spectral line in the first case indirectly indicates the relatively homogeneous structure of the In wetting layer. The complex nature of the intensity curve in the second case is due to the complex structure on the surface. It should be noted that the 3-fold difference in this case also correlates with the previously obtained experimental data.

![Figure 4(a, b). XPS spectra (a) from samples obtained at $T = 100^\circ C, H = 3$ ML and $T = 300^\circ C, H = 1.5$ ML and change of In 3d5A line intensity during etching of sample surfaces (b).](image)

4. Conclusions

Thus, the results of X-ray photoelectron spectroscopy of In/GaAs samples formed under different conditions confirm an increase in the wetting layer thickness with a decrease in the formation temperature of the systems. A quantitative analysis of the data obtained shows that droplet nanostructures consist of In, without Ga impurity, which suggests that in the range of temperatures and deposition modes under consideration the etching of the substrate with a metal droplet can be neglected.

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