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Features of InP on Si nanowire growth

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The possibility of InP nanowhiskers growth from the saturated phosphorus and indium vapors with V/III ratio of 8−10 in a quasi-closed volume on (111) oriented silicon substrates with a natural oxide layer 2−2.5 nm has been demonstrated. The growth of InP nanowhiskers from Au-In-P catalytic droplets formed during the initial period is reported. Optical studies confirmed the formation of InP nanostructures upon the Si surface. The nanostructures exhibit a high doping level presumably with tin atoms.

Keywords: InP nanowires, growth from vapor phase, III-V on Si.

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1. Introduction

The challenges of manufacturing optoelectronic devices integrated with silicon technology are of particular interest. One of the directions in this field is related to the growth of A_3-phosphide nanostructures on silicon substrate [1–3]. The traditional technologies for the growth of such structures are based on catalytic growth by the vapor-liquid-solid (VLS) [4–6] mechanism and include the use of nanoscale catalyst droplets previously deposited on the silicon surface. When growing nanostructures on silicon, it is necessary to pay special attention to the initial stage of growth of nanostructures, since there is always an oxide layer on the silicon surface, which can significantly affect not only the initial stage of growth, but also the entire process of their formation regardless of the method of obtaining. As a rule, the „native" oxide is removed by various methods just before the growth process. These can be methods of liquid and/or plasma etching, high-temperature annealing of substrates, which are compatible directly with growth processes. Another approach is also possible, when an oxide with predetermined properties and thickness is formed on the surface, which further interacts with catalytic droplets, providing the growth of nanowires (NWs) [7,8].

The lack of complete data on the phase diagram of Au-In-P-Si requires additional experimental data on the interaction of Au catalytic droplets with indium, phosphorus and silicon surface containing a natural oxide layer. The processes of formation of initial and further growth of NWs on such surfaces remain poorly studied.

The aim of this work is to investigate the catalytic growth of InP NWs by the vapor-liquid-solid mechanism from a source of saturated indium and phosphorus vapor on a gold-activated silicon surface with a natural oxide layer in a quasi-closed volume. Considerable attention has been paid to simplify the initial preparation stage of synthesis of nanostructures. The time-temperature of growth, morphology, structure of the obtained InP NNCs, and their optical properties were also investigated.

2. Experiment

In our work, we used the method of NW growth in indium-phosphorus vapors developed previously to grow lateral InGaAsP NWs on GaAs substrates [9]. Colloidal gold droplets with a diameter of 60 ± 5 nm were deposited on the surface of Si(111) substrates containing SiO_2 2−2.5 nm thick layer of natural oxide. The nanostructures were synthesized in a flowing hydrogen atmosphere. The source of indium and phosphorus vapors was a saturated Sn-InP melt solution placed directly in the chamber.

In our case, the nanodispersed (catalytic) gold-indium-phosphorus particles were formed during te temperature rise. The initial period of temperature rise at which the catalytic droplets were formed was 20 min, after which the temperature in the growth chamber was stabilized at 560 ± 5°C for 20−60 min.The vapor ratio of phosphorus and indium was determined by the process temperature and the phase diagram of the Sn-InP system and was in the range of 8−10.

The morphological characteristics of the samples were examined using a Supra25 C.Zeiss scanning-electron microscope equipped with Ultim and Symmetry Oxford Instruments Inc. microanalysis and backscattered electron diffraction attachments. The results of the X-ray spectra were analyzed using AZTec software.

Optical properties were investigated by photoluminescence and Raman scattering spectroscopy at 67 K in a flow-

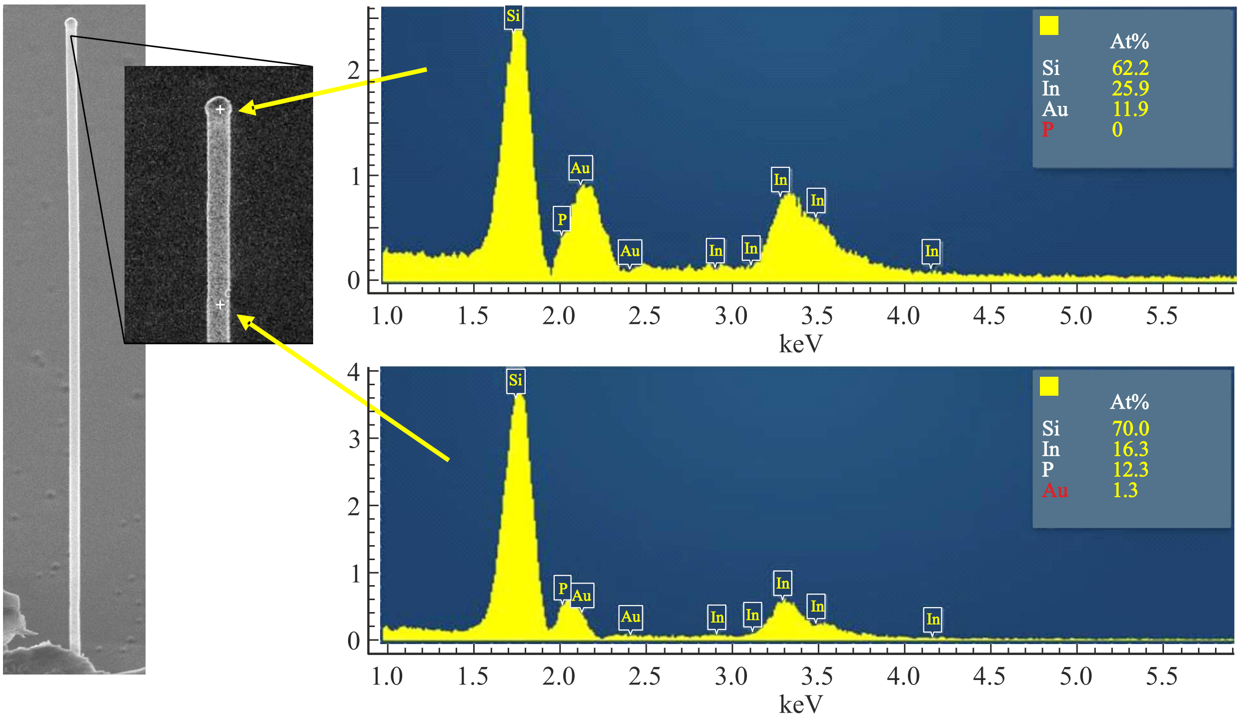

Figure 1. SEM image of InP NNCs, on Si(111) surface under optimal growth conditions (560°C, 60 min).

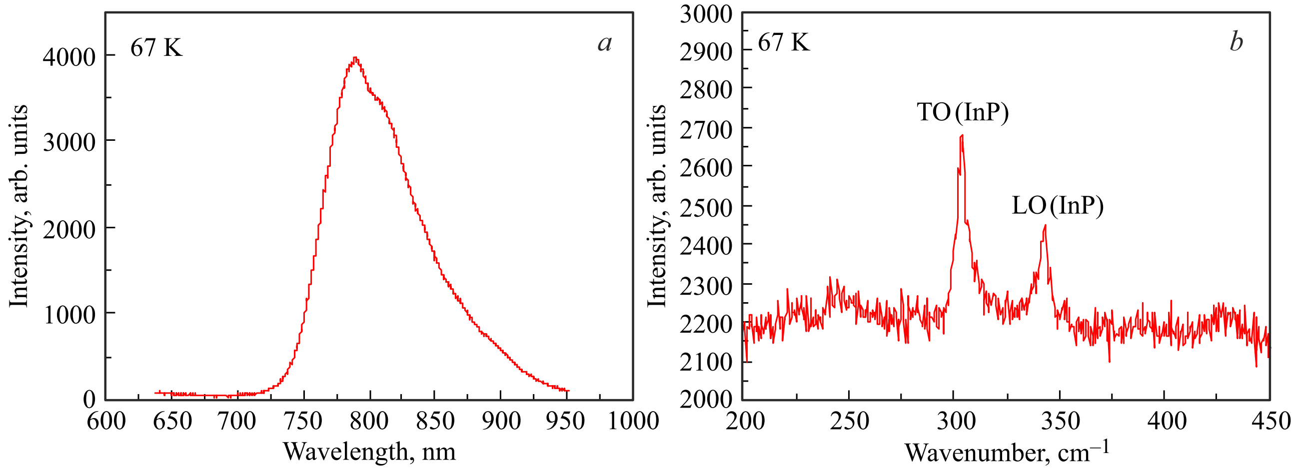

Figure 2. PL (a) and Raman scattering (b) spectra measured on a single NNC at $T = 67$ K.

type cryostat using a 532 nm CW laser. The PL spectra were investigated at excitation power density $\sim 2 \cdot 10^3$ W/cm^2. The unpolarized Raman scattering spectra were measured in backscattering geometry.

3. Results and discussion

Figure 1 shows the SEM image of InP NWs on Si(111) surface under optimal growth conditions (560°C, 60 min). In the case of catalytic droplet formation with the optimal composition of Au-In-P, vertical growth of InP NWs with a diameter of 75–120 nm and a height of 7–13 μm was observed. At the same time, „parasitic“ islands formed directly on the oxide surface were observed. When the system is stable, the NWs retain their shape and direction of growth. Analysis of the NW composition along its length showed that the catalytic droplet at the top of the NW does not contain phosphorus (Figure 1), which may provide indirect evidence for the fact that phosphorus mainly comes from the vapor phase.

Figure 2 shows characteristic PL and Raman scattering spectra measured in the sample point at $T = 67$ K (single NW). The emission band in the PL spectrum is broad and ranges from ~ 800 to 900 nm. Two bands corresponding to longitudinal and transverse vibrations of InP are present in the Raman scattering spectrum. The study of Raman spectra at reduced temperature allows us to exclude the contribution of forbidden acoustic vibrations of the Si substrate, and also allows us to measure Raman scattering and photoluminescence spectra from the same point. The presence in the spectrum of relatively narrow bands with frequencies ~ 303.7 and $\sim 342.8\,\text{cm}^{-1}$, corresponding to transverse and longitudinal vibrations of InP type, indicates the formation of InP compound. Unfortunately, the low temperature of the measurements leads to a decrease in the scattering intensity, making it difficult to identify the lattice type (WZ or ZB) [11,12]. The width of the PL spectrum, the position of the maximum shifted relative to the values of the band gap width (E_g) of the bulk InP crystal towards higher energies, and its asymmetric shape indicate that this NW is highly doped, and this behavior is described by the Burstein–Moss [13] effect. The tin used as the base of the vapor source can act as an impurity. A slight effect of tin atoms transfer from the Sn-In-P source was recorded by us earlier [14]. The best way to reduce the doping level would be to eliminate the use of tin and switch to an indium-based solution. Also, the method developed by us provides the realization of self-catalytic growth using indium droplets on the Si surface. The use of gold-free catalyst is considered promising for improving the properties of NWs.

4. Conclusion

Thus, for the first time, we have demonstrated the feasibility of a method for the growth of filamentary nanostructures on silicon substrates, which we have previously developed and successfully applied to grow compounds based on III-Vs. The essence of the method is that the presence of saturated indium and phosphorus vapors in the growth chamber under optimum temperature conditions allows the formation of catalytic Au-In-P droplets on the (111) oriented silicon surface with a natural oxide layer directly in the initial period of growth and provides further stable growth of NWs. Comprehensive photoluminescence and Raman scattering studies confirmed the formation of InP NWs. The high doping level of the obtained structures is presumably related to the use of saturated solution-melt Sn-In-P as a vapor source. Analysis of the obtained results showed that further optimization of the process using the In-InP source and rejection of the gold-based catalyst would allow the growth of weakly doped InP NWs.

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Conflict of interest

The authors declare that they have no conflict of interest.

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