Journal of Crystal Growth 311 (2009) 1855–1858

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Chemical beam epitaxy of highly ordered network of tilted InP nanowires on silicon

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ARTICLE INFO

Available online 7 December 2008

PACS:
81.15.Hi
62.23.Hj
81.30.−t

Keywords:
A1. Eutectics
A3. Chemical beam epitaxy
B1. Nanowires

ABSTRACT

In this work, the growth of undoped InP nanowires on silicon(111) using gold as the metal seed particle was undertaken by chemical beam epitaxy. Prior to the growth process an ordered array of gold nano dots is integrated on the surface of a silicon substrate using self-assembled (hexagonal compact array) polystyrene nanospheres as the Au evaporation template. The size of the gold nanodots ranged from 20 to 150 nm. The InP nanowires were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL). The InP nanowires were found to grow tilted in the ⟨100⟩ direction and exhibited slightly broadened low-temperature photoluminescence emissions.

1. Introduction

Nanowires have shown great potential in the fields of nanoelectronics and photonics. Their unique geometry paves way to utilize them as both active devices and also as interconnects due to ballistic transport ability [1]. Extensive research in nanowires has lead successfully to implement them in various fields such as field effect transistors [2], bipolar junction transistors [3], lasers [4], biological and chemical sensors [5] and solar cells [6]. Epitaxial growth of bulk semiconductor materials with a slightest of lattice mismatch will lead to defective hetero-junctions due to the formation of misfit dislocations and grain boundaries. Nanowires are high-quality crystal structures in the dimensions of nanoscale range. This reduction in size paves way to fabricate hetero-structures of materials with different lattice parameters [7,8] without defects. Integrating an ordered array of III–V semiconductor nanowires with superior optoelectronic properties over the commercially well-established silicon will lead to fabrication of novel devices with new and improved functionality. This has lead the semiconductor industry to predict that these 1D structures will play a major role in developing smaller device with newer applications in the near future [9].

Vertical arrays of semiconductor nanowires have also been suggested to overcome fundamental efficiency limitations of single junction solar cells [10]. There are several methods of fabricating nanowires. The widely accepted mode of growth is the “bottom up” approach that follows the vapor liquid solid (VLS) growth mechanism. This gives a unique opportunity for on-chip integration of non-silicon based photonic materials on the already popular silicon nano-electronics. There is significant interest in the integration of III–V materials with silicon technology in the optoelectronic field. The success of the heteroepitaxial association of III–Vs (i.e. InP or GaAs) with silicon has been thus far limited by lattice mismatch and thermo-elastic strain issues. Since the heterostructures grown are of the geometry and size as of nanowires, they can relax laterally to minimize or eliminate the strain caused due to the lattice mismatch and maintain good epitaxial relationship [11].

The VLS growth mechanism was introduced in 1964 by Wagner and Ellis [12] to explain the growth of large whiskers of micrometer scale. Later in 1973 Givargizov and Chernov [13] proposed an empirical model for the VLS growth mechanism for whiskers grown using CVD. Extensive research was done on III–V semiconductor nanowire growth and morphology by Hiruma et al. [14–16]. Several growth techniques have been used to employ the VLS mechanism including metal-organic vapor phase epitaxy (MOCVD) [17,18], laser-ablation [19], molecular beam epitaxy (MBE) [20] and chemical beam epitaxy (CBE) [21]. A metal nanoparticle acts as a catalyst to form a liquid alloy which is a combination of the metal and the growth species leading to

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doi:10.1016/j.jcrysgro.2008.12.008

crystallization at the liquid solid interface. Various approaches have been used to obtain metal growth sites in nanoscale levels, such as mask templates of porous alumina [22,23], aerosol technique [24] electron beam lithography (EBL) [25] and nanosphere lithography (NSL) [26] or natural lithography [27,28].

In this paper, we investigate the morphology and evolution of InP nanowires grown on Si (111) substrates. Gold seed particles are evaporated on silicon using nanosphere lithography which acts as growth centers and the nanowires are grown by CBE. The nanowire growth direction, crystalline and optical qualities are discussed and examined by using scanning electron microscope (SEM), X-ray diffraction (XRD) and photoluminescence (PL).

2. Experimental details

Si(111) substrates (As-doped, resistivity of $<0.005\,\Omega\,\mathrm{cm}$ and P-doped, resistivity of 1–$20\,\Omega\,\mathrm{cm}$, respectively) were cut in to $2\times2\,\mathrm{cm}^2$ pieces and used in all experiments. Nanosphere lithography was used in order to form gold nanoparticle growth sites for the VLS mechanism. Monodisperse polystyrene nanosphers in a 10% water suspension were further diluted with methanol containing 0.25% Triton X-100. The corresponding suspensions were then spin coated onto the wafers according to the technique described by Hulteen and Van Duyne [26]. In order to make the surface of the silicon hydrophilic the substrates were cleaned by RCA I process, that is, a treatment with a 1:1:5 solution of NH_4OH (25%), H_2O_2 (30%) and water at 80 °C for 15 min just before usage. The pattern formed on the silicon surface can be controlled by manipulating the nanosphere concentration and the spin speed. This will lead to monolayer or bilayers of nanosphere pattern as shown by Fuhrmann et al. [29]. It should be mentioned that the periodic arrangement of the polystyrene spheres might be locally disturbed. The most serious defects are grain boundaries. These patterned spheres can be used as masks over the silicon surface over which a 10–20-nm-thick layer of gold is deposited at a rate of 0.1 nm/s in an evaporation system (B 30.2, HVT Dresden) with chamber pressure of 5×10^{-6} mbar. After gold evaporation the polystyrene nanospheres are removed from the substrate by (i) CH_2Cl_2 in an ultrasonic bath for 2 min and (ii) by a subsequent rinsing in acetone, ethanol, and water. This will leave a nanoscale pattern of gold on the silicon surface with size ranging from 20 to 150 nm. Synthesis of masks on hydrophobic surfaces can be done by using an elegantly simple mask transfer technique [30].

The substrate with patterns of gold nanoparticles was introduced into a RIBER ultrahigh vacuum CBE chamber. The native oxide on the silicon surface was not removed prior to growth. Trimethylindium (TMI) was used as group III precursor and phosphine was used as group V precursor. Phosphine was thermally cracked at 900 °C on entering the growth chamber to the highly reactive P_2 molecules which either incorporates at the position of impact i.e. at the gold particle or desorbs immediately from the surface and are pumped away. The group III precursors (TMI) are the stable molecules that react at the heated gold particle leading to supersaturation and the formation of the eutectic alloy which is mixture of InP and gold. The composition of the alloy is controlled by the temperature of the substrate. When the eutectic system is created, the driving force for wire growth is the supersaturation of the growth species in the molten seed. The growth species is fed continuously to maintain supersaturation and aid anisotropic growth of nanowires. The growth temperature was maintained at 420 °C for 20 min with a bulk InP growth rate of $0.2\,\mu\mathrm{m/h}$. A reference InP sample was loaded along with the sample and growth rate was measured using reflection high-energy diffraction gun.

3. Results and discussion

The substrates were characterized by using a scanning electron microscope (SEM-LEO 1525 Carlzeiss). A primitive honey-comb structure of gold nanoparticles, each having a pyramidal structure can be formed using the nanosphere lithography process. This structure can be formed by a single layer nanosphere mask using precise spin speed and nanosphere solution concentration. The Fig. 1 shows the honey-comb structure with the red circle indicating the position of the polystyrene spheres after they were removed. Annealing studies at 500 °C on the samples showed that the pyramidal shaped gold dots of size 120 nm transformed in to about 60-nm-sized hemispherical dots.

The gold patterned silicon substrates were introduced into the CBE chamber and VLS growth of InP wires was attempted. SEM analysis of the sample after growth indicate that the some of the InP wires grow surprisingly in the tilted $\langle 100\rangle$ direction contrary to the typical expected growth direction of $\langle 111\rangle$ [21]. During the growth of III–V nanowires there is a transition from zincblende to wurtzite as shown by Glas et al. [31]. This may be because the nucleation of the nanowire generally is controlled by the interface energies at the liquid–solid interface. Depending on this the phase is determined. There is also evidence for formation of staking fault during nanowire growth. These defects and change in phase could be reason for growth in $\langle 100\rangle$ direction rather than in the expected $\langle 111\rangle$ direction. Fig. 2 shows the top view of InP wires on silicon. The InP nanowires are of dimensions 100 nm in diameter and length ranging from 150 to 300 nm in the growth direction of nanowires. Here the honey-comb pattern is mostly maintained and there is an absence on a pyramidal base at the bottom of the wires [32].

To investigate the crystalline and optical quality of the InP wires X-ray diffraction (XRD) and photoluminescence (PL) studies were done. Fig. 3 shows the XRD patterns obtained from the InP nanowires on Si(111) in log scale. The full width half maxima (FWHM) of all the InP nanowire peaks ((111)—0.33°, (200)—0.21° and (220)—0.25°) compared with the FWHM of the Si(111) peak—0.15° shows a slight broadening of the peaks. This might be attributed to the presence of stress fluctuation or structural defects in the nanowires. Also the InP nanowire peaks are slightly shifted from the peak positions of bulk zinc blende

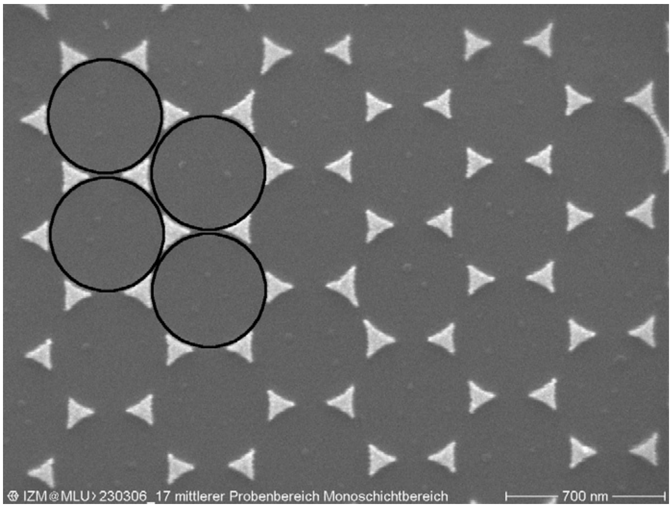

Fig. 1. SEM of self-assembled gold nanoparticles on Si(111) using polystyrene nanospheres (PSN) (marked in Black are the PSN positions after they were removed).