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(Ga,In)P nanowires grown without intentional catalyst

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ABSTRACT

We have grown (Ga,In)P nanowires through the MOCVD method without a intentional catalyst. The organometallic precursor triethylgallium ($(C_2H_5)_3Ga$), used as Ga source, is transported by the N_2 gas carrier to the reactor chamber where reacts with the InP vapor pressure producing the nanowires. Two different reactor pressures (70 and 740 Torr) were used leading to nanowires with different In contents. The nanowires are straight or wool-like and exhibit a twinned structure. They emit an intense orange to red color visible even to the naked eyes. Interface tunneling process at $Ga_{1-x}In_xP/Ga_{1-y}In_yP$ interfaces ($x \neq y$) is proposed to explain this efficient light emission mechanism.

1. Introduction

Metalorganic chemical vapor-phase deposition (MOCVD) is currently one of the most common techniques used to grow nanostructures for research and industrial applications, which includes heterostructures like GaP/GaInP nanowires, optoelectronic devices, solar cells, lasers, and sensors [1–5]. Other growth methods like molecular beam epitaxy have also been largely used [6].

The $Ga_{1-x}In_xP$((Ga, In)P) is a ternary semiconductor III–V with a direct energy band-gap that can reach 2.2 eV at room temperature [7]. It has been shown that the (Ga,In)P exhibits a direct–indirect band gap crossover which depends on the In fraction [7–10]. It is a material largely used in optical applications such as light-emitting devices, solar cells and heterojunction structures [11,8,12]. The inherently fluorescence of the (Ga,In)P makes it a promising tool for biological applications [13].

The MOCVD is a common technique to grow (Ga,In)P nanowires, it is usually a seed assisted growth process [8,11,14,15]. The traditional MOCVD method uses organometallic compounds as precursor source of the elements. In this work, however, besides the organometallic a InP powder was also used as source. We report a new method to grow (Ga,In)P nanowires on Si substrate, which does not use pre-prepared catalysts. Our nanowire growth technique is a MOCVD/CVD vapor transport method based on the transport of the organometallic triethylgallium ($(C_2H_5)_3Ga$ or TEGa) in the gas phase which is carried by N_2 gas to the Si substrate. The TEGa reacts with the InP vapor pressure from the powder providing the (Ga,In)P nanowire growth [16,17]. The nanowires were characterized through scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and photoluminescence (PL).

A novel issue is proposed to explain the light emission of the (Ga,In)P wires. Since the wires have a twinned structure, the model is based on the (e^-, h^+) recombination at $Ga_{1-x}In_xP/Ga_{1-y}In_yP$ ($x \neq y$) interfaces along the wire providing an intense red to orange light emission. These interfaces can be interesting for two photon excitation experiments because the (e^-, h^+) recombination is interface localized. Due to the different mobility between (e^-, h^+) reaching the interface, such structure could be appropriated to lasing, since interface population inversion can be easily obtained.

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2. Experimental method

The (Ga,In)P nanowires were grown in a home made MOCVD setup equipped with TEGa ($\simeq 1$ sccm) as Ga precursor source [4]. The growth temperature ($550-750^{\circ}C$) and the reactor pressure (70–740 Torr) were the main parameters used in the nanowire growth process, mainly to set the Ga or In content in the (Ga,In)P alloy. For the results reported here, the growth temperature is 700 °C and the reactor pressure is 70 or 740 Torr.

A Si substrate is placed in a horizontal quartz reactor and heated with infrared (IR) lamps (IR-Research INC). Onto the substrate or nearby, a InP powder is placed. Above 350°C, the InP evaporates and the In and P are present at the growth site as elemental species, with P being mostly P, P_2 or P_4. N_2 (20 sccm) gas carrier flows into the TEGa cylinder at $-15^{\circ}C$ to produce the organometallic precursor vapor. The N_2 flows across the reactor is 5 slm. The TEGa/N_2 flow reaches the substrate and reacts with the (In,P) vapor powder. The growth process lasts from 10 to 30 min. The nanowire growth takes place around the InP powder, as expected, but also at the edges of the substrate and even on nearby substrates, where initially did not contain the (In,P) powder. It occurs because within the experimental conditions the CVD vapor thermal diffusion of In and P atoms is about a few centimeters [16,18]. Fig. 1 shows a sketch of nanowire growth patterns observed at different places of the substrate, including the lateral faces.

Fig. 2 shows SEM images of the obtained structures, branched nanowires (Fig. 2a), wool-like rolls (Fig. 2b), and straight nanowires placed at the lateral faces of the substrate (Fig. 2c). The length and diameter of the nanowires vary from 10 to 100 μm and from 20 to 300 nm, respectively. For the sample preparation to MET and EDS/MET analyses the substrate with nanowires is immersed in isopropilic alcohol in ultrasonic bath for 20 min. The formed solution containing the nanowires is then dropped on a MET grid.

The wire growth process is started by heating the substrate which leads to the diffusion and adsorption of Ga, In and P onto the substrate surface. The pyrolysis of the organometallic molecules produces the Ga metallic that is deposited onto the substrate also helping the growth process [4,5,19,20]. As In and P atoms are initially available in the chamber by the InP evaporation, we cannot discard their eventual participation in the wire nucleation process.

Increasing the partial pressure of the TEGa flow rate (1–3 sccm) the main result observed was the increasing of the nanowire growth rate and its density on the substrate surface. It means that the organometallic is one of the main candidates as the starting point of the nucleation site. However, we cannot discard the presence of In that starts its evaporation early and can be associated to Ga to help the wire nucleation site and growth. The results reported here using TEGa were previously obtained also for trimethylgallium (TMGa),

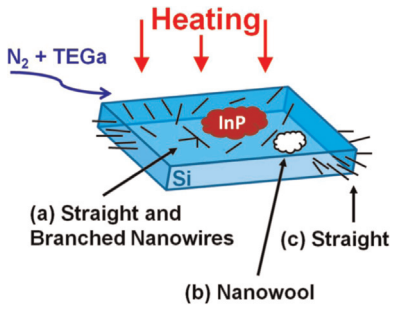

Fig. 1. Sketch of different growth patterns of (Ga,In)P nanowires. InP powder is placed on the Si substrate. Due to the heating, In and P evaporate from the powder, reacts with the TEGa (Ga source) giving rise to three kind of structures: (a) straight and branched, (b) wool-like and (c) straight.

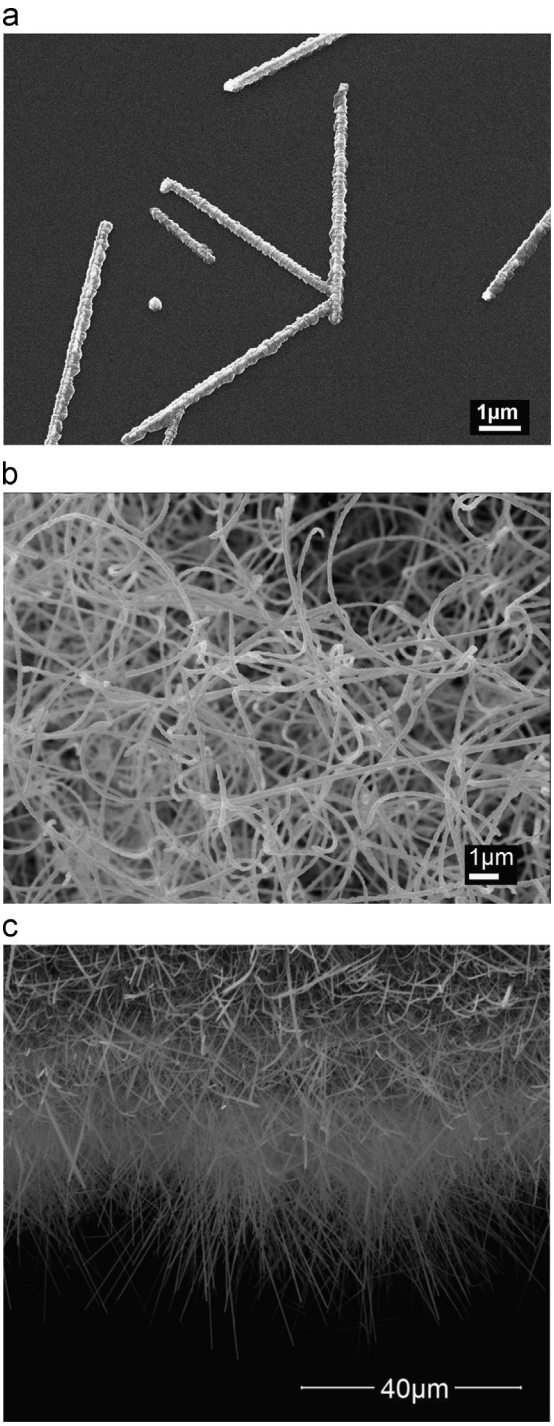

Fig. 2. SEM images of nanowires grown at different places of the Si substrate (see Fig. 1). (a) Straight and branched, (b) wool-like and (c) straight nanowires.

which roughly yields the same results showing that the C–Ga and C–C–Ga bonds do not affect the growth mechanism.

Through EDS/MET one observed single (Ga,In)P spheres with low P content, with the relative content of 10% of P, 21% of In and 69% of Ga, approximately (see Fig. 3a). Still rare but found at the wire tips are the GaIn spheres, as can be seen from Fig. 3b. In such spheres one measured 68% of In and 32% of Ga, approximately. In general, no catalyst was found at the wire tips. However, it is possible that an eventual "growing" wire tip was consumed either during the cooling after the TEGa was turned off or when the heating process was turned off.