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Supersaturation state effect in diffusion induced Ge nanowires growth at high temperatures

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ABSTRACT

We report on supersaturation state effect in diffusion-induced vapor-liquid-solid growth of Ge nanowires at high temperature. Our experimental investigation establishes that at $T \geq 550$ °C the growth is hindered while the growth limitation is not resulted from a high value of the desorption rate. We demonstrate that the suppressed growth is a result of the droplets large chemical potential that inhibit the supersaturation state. This results either in a strong growth limitation due to a significant droplets enlargement or to a growth cessation.

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The enhanced mobility in Ge compared with silicon and its compatibility with CMOS technology can be used to improve the electronic and optical properties in many applications such as photovoltaics [1], electronics [2] and sensors [3]. The vapor liquid solid (VLS) method, introduced by Wagner et al. [4] is one of the most studied and highly controllable process among those developed for semiconductor nanowires (NW) synthesis. The implementation of the VLS growth by physical evaporation techniques, such as molecular beam epitaxy (MBE), occurs via a diffusion induced (DI) mechanism, since the metal droplet does not act as a catalyst but as a seed where diffusing Ge adatoms will be adsorbed, passing in the liquid solution [5].

In the DI-VLS model, the diameter of the wire is strongly dependent on the initial diameter of metal droplet that facilitates the growth by nucleation in a supersaturated metal-semiconductor eutectic liquid [4]. It has been demonstrated that vertical growth rate of the wires is dependent on the reciprocal of the droplet radius, r, while, r is considered to be nearly constant during the growth [5]. However, recent studies have confirmed the droplet diffusion and ripening during the growth that result in a diameter transition of the wire either by reduction or increase in the droplet diameter [6]. While this diffusion does not prevent the wire growth, unless the droplet is completely diffused away, it can strongly modifies the growth rate of a single wire.

Recent experimental studies have also shown that the growth can be hindered at relatively high temperatures (≥ 500 °C) compared to the eutectic temperatures (361 °C for Ge) [7,8]. Though, it has been qualitatively suggested that this effect is a result of a high desorption rate of adatoms from the Au droplet [7,8], a clear understanding of the mechanisms involved in growth at high temperatures is still lacking. Hence, a systematic and detailed study to clarify the mechanisms behind the effects of high temperatures seems necessary.

In the present work, we investigate the growth behavior of the Au mediated Ge nanowires by MBE at high temperatures. The structural and morphological properties of the Ge NWs are discussed in the framework of a phenomenological model based on the DI-VLS theory. Our results evidence a growth hindrance at $T \geq 550$ °C while our analysis rules out a substantial desorption rate effect below $T \leq 650$ °C. Hence a complimentary mechanism is suggested to explain the growth hindrance in studied temperature range.

The Ge NWs were prepared in an Ultra High Vacuum MBE chamber with base pressure of 3×10^{-11} Torr, using a Ge Knudsen cell. Ge(111) wafers were ultrasonically cleaned in methanol and trichloroethylene, followed by removal of the native oxide using sulfuric acid. Afterwards, they were dipped in $H_2O_2 : NH_3OH : H_2O$ for re-oxidation. Previous to the Au deposition, wafers were annealed at 400 °C for 30 min, in the MBE chamber, to remove the

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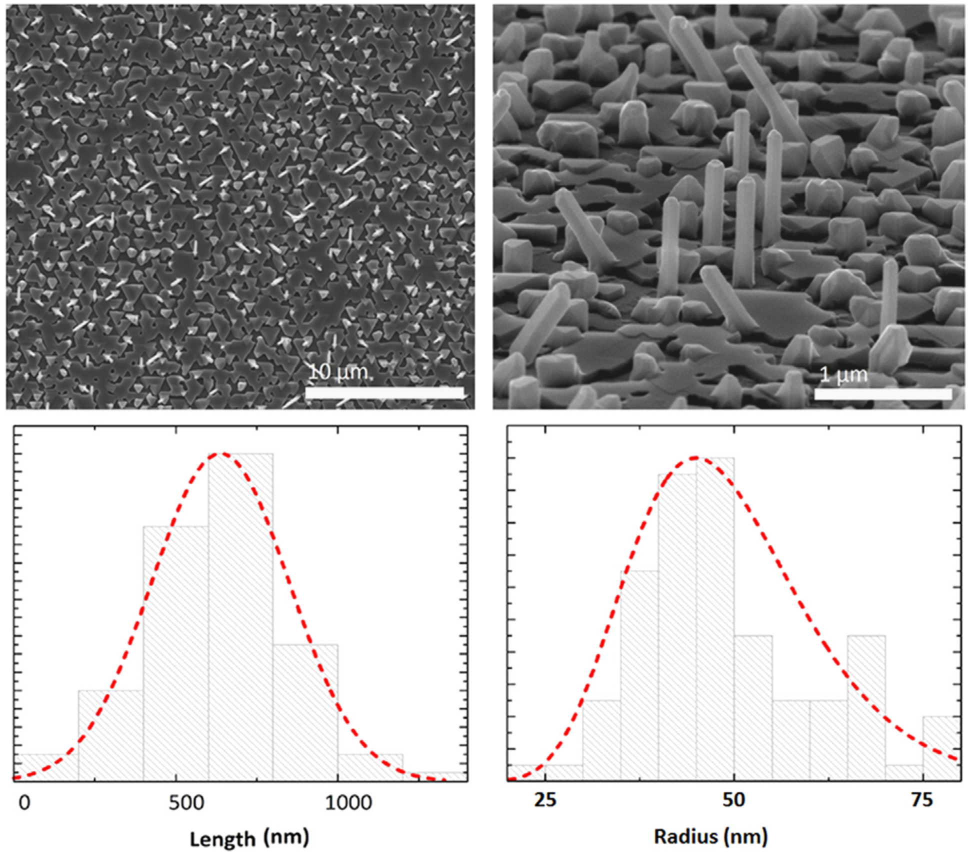

Fig. 1. (Top): large scale HRSEM images of the wires grown at 430 °C (Left) and 500 °C (Right) at a constant evaporation rate of 0.02 nm/s. Both samples have similar morphology. Since both samples, at 430 °C and 500 °C, have similar morphology and comparable diameters of wires two different perspectives of the samples are shown, which allow us to identify the geometry and the orientations of Ge NWs. The apparent vertical wires (left panel) are due to the artifact caused by tilting the sample to improve the visibility. (Bottom): length and diameter distribution of the wires grown at 500 °C. At 430 °C, wires radius distribution is comparable to that at 500 °C while wires are longer (not shown). In both samples the Au droplets size is similar to the one prior to Ge evaporation.

overgrown oxide. Ge nanowires were grown using Au droplets formed at 600 °C. After nanoparticles formation with a narrow size distribution of $r=45$ nm [9], the samples were cooled down rapidly (430 – 650 °C) and exposed to an optimized Ge flux of 0.02 nm/s [10] for a constant duration of 60 min.

For structural analysis, we used scanning electron microscopy (SEM) and high resolution transmission microscopy (HRTEM). The droplet distribution and dimension were measured using a back scattering electron detector (BSD) and scanning transmission electron microscopy (STEM).

Ge NWs grown at both 430 °C and 500 °C (Fig. 1) are crystalline and defect free and are ⟨110⟩ and ⟨211⟩ oriented to form dominant {111} facets (having the minimum surface energy). They also are with small {110} facet to the sides [9]. Wires are tilted of 54.7° with respect to the substrate plane, in three different directions, in agreement with previous reports for Ge NWs [7]. Wires have irregular cross sections close to rhombohedral (hereafter referred to as diameter), as reported in a previous work [10]. It was also observed that droplets are always on a tilted {111} facet at the tip that occurs due facet surface energy minimization [10]. At 430 °C and 500 °C few wires with a diameter variation were detected (Fig. 2) that can be assigned to the surface diffusion of the Au droplets (Ostwald ripening) during the growth [11–13]. In some cases we have also detected the disposition of the Au droplet from the tip to the side of the wire (Fig. 2). The similar length of these wires compared to ones with atop droplets suggests that the droplet movement occurs after Ge NW growth and during the cooling process. If this movement were to occur during the growth, the wire should have been shorter in length or branched.

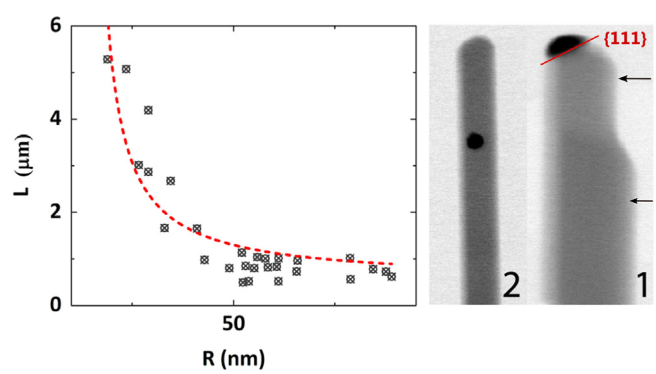

Fig. 2. (Left panel): Dependence of the Ge wires length on their radius (grown at 430 °C). The experimental data fits with the theoretical model of DI-VLS growth, reproduced by the red dashed line in the plot. Ge NWs grown at 500 °C also show the identical behavior (not reported). (Right panel): STEM images of two wires evidencing Au droplet (dark spot) diffusion. In (1) the Au diffusion (ripening) resulted in a change of the wire diameter and in (2) the droplet displacement to the sidewall of the wire without a size alteration. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

A statistical analysis on our sample synthesized at 430 °C and 500 °C shows that the size of Au droplets and its distribution are similar to those of the Au nanoparticles prior to the Ge evaporation with $r=45$–50 nm (see Fig. 1). This experimental evidence indicates that: (1) at 430 °C and 500 °C, the supersaturation in droplets is reached within the initial stage of the growth; (2) the droplets ripening during the growth must be low ($dr/dt \sim 0$) at both

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