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Growth mechanism of SiGe alloy nanowires synthesized in H-mode cylindrical cavity resonator

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ABSTRACT

In the present paper an attempt has been made to understand the growth mechanism of SiGe alloy nanowires synthesized in H-mode cylindrical microwave cavity resonator at 900 °C in a short time of nearly 5 min. The role of ambience, microwave H-field, duration of interaction with microwaves and germanium concentration in the starting precursor have been investigated. It is believed that H-field of microwaves efficiently interacts with the starting precursor powder in air ambience and results in superheating/supersaturation, which gives rise to the formation of innumerable critical sized nuclei via heterogeneous nucleation, leading to one dimensional growth of cylindrical nanowires.

1. Introduction

Nanowires of $Si_{1-x}Ge_x$ alloy semiconductor have recently gained importance due to their potential applications in electronic and optoelectronic devices capable of operating at low-power and high speed. Although the attempts to grow epitaxial and superlattices of SiGe on Si substrates were made as early as in the sixties and seventies. The first device application based on SiGe/Si heterostructures appeared around 1985 that is soon after sophisticated epitaxial growth technique, such as molecular beam epitaxy was available [1]. Several methods have later been employed for the synthesis of nanowires. These include: vapour–liquid–solid (VLS) technique [2], laser ablation [3], solution growth [4] and multimode microwave processing [5], etc. In VLS technique, first reported in 1960, metal particles were used as catalyst and the whisker growth was observed at a eutectic temperature of the starting mixture [2]. It is reported that epitaxially [111]-oriented, $Si_{1-x}Ge_x$ alloy NWs can be grown by VLS technique with Au-free sidewalls and it is possible to control alloy content and growth direction by varying process parameters [6]. Later, the nanowires were grown from solid catalysts below the eutectic temperature [7] by employing vapour–solid–solid (VSS) technique. In 1998, Zhang et al. [8] grew silicon nanowires by laser ablating a mixture of silicon and silicon dioxide in the presence of iron (catalyst). Interestingly, they found that the nanowires were grown with an oxide sheath sans the catalyst particle at the tip of nanowires, and invoked Oxide Assisted Growth (OAG) mechanism [9] to explain the growth of nanowires. Various reports have followed in support of this growth mechanism of nanowires [10–13]. Cheng et al. [14] have, however, explained the growth of Si nanowires owing to the presence of an electric field, arising due to decomposition of SiO into oppositely charged SiO_2 and Si.

In our previous report [15,16], we had described the synthesis of large quantity of SiGe alloy nanowires of uniform diameter and of length 10 μm by single mode (nominally pure microwave H-field) in air ambient at 900 °C in less than 5 min. The microwave processing has many advantages over other growth techniques including substantial enhancement in reaction and diffusion kinetics, volumetric heating and its environment friendliness [16–18]. It has inherent capability to render different microstructures, which needs to be understood to explore the capability of this emerging technique for further innovative applications. The efficient heating of the diamagnetic semiconducting powder in nominally pure H-field has been discussed in our previous report [19]. In the present work, we have directed our studies to understand the growth-mechanism of SiGe alloy nanowires in microwave (MW) H-field. This is carried out by investigating the role of various growth parameters including ambience of growth, processing duration, and germanium concentration in starting precursor.

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2. Experimental details

A single mode cylindrical cavity resonator, in which entire energy is confined to a desired mode (TE_{011}) and in a smaller volume, has been chosen for synthesis of SiGe alloy nanowires of different composition (x = 0.05, 0.15, 0.25). Nearly pure H-field at MW frequency of 2.45 GHz is present at the location of work piece inside the cylindrical cavity resonator. Schematic of field distribution inside the cavity is shown elsewhere [20]. The stoichiometric amounts of silicon and germanium powders were thoroughly mixed in a ball mill, and the resulting mixture was then pelletized. The pellets were exposed to MW radiation for different duration and at a suitable microwave power to achieve a temperature of 900 °C. Two different ambient i.e. argon and air were employed during processing. The MW processed SiGe samples are labelled as XSGt, where "X" denote the atomic weight % of germanium and "*t*" denotes the processing duration (in min), e.g. 15SG5 corresponds to 15 at wt% Ge in SiGe (SG) alloy and processed for 5 min. The details of processing parameters and nomenclature of microwave processed SiGe alloy samples are summarized in Table 1. The temperature acquired by the compact was measured using an optical pyrometer (Raytek, model RAYMA2SCSF). Scanning electron micrographs (SEM) were recorded by employing electron microscope (Zeiss EVO 50). An analytical high resolution transmission electron microscope (Tecnai G20-Stwin) operated at 200 kV was used to acquire TEM images. The phase analysis of the starting mixture and of MW processed pellets was carried out by employing X-ray diffractometer (Philips X'Pert PRO).

3. Results and discussion

Fig. 1 shows X-ray diffractograms (XRD) of the starting mixture and 25SG5 sample. The XRD of starting mixture understandably shows the prominent reflections corresponding to both the constituents Si and Ge. The XRD pattern of the grown nanowire (25SG5 sample) is in conformity with the diamond lattice structure, and reveals the alloying of Si with Ge in the nanowires. These SiGe alloy nanowires are found to be blue light emitter as already reported (20). The SiGe alloy nanowires are formed for other compositions as well [15].

The role of various process parameters (presence of MW in the cavity, ambience, composition of the starting precursor) and processing duration on growth of alloy nanowires have been investigated and these are described in the following sub-sections.

3.1. Role of microwave field

In a conventional multimode microwave applicator, there are over hundred modes but all are mixed and one cannot study the effect of individual fields on the processing of a material. Therefore, a single mode cavity with much more controlled field distribution and with ability to produce high fields is chosen to understand the alloy nanowire growth mechanism. Depending on the dimensions of resonator, the field distribution inside the cavity can be manipulated and E- and H-fields of electromagnetic wave can be isolated, which makes it easier to probe the effect of separated field on the growth dynamics.

Table 1
Details of microwave processed SiGe alloy samples.

Sample name	Composition	Processing temperature (°C)	Processing time (min)
5SG5	$Si_{0.95}Ge_{0.05}$	900	5
5SG2	$Si_{0.95}Ge_{0.05}$	900	2
15SG2	$Si_{0.85}Ge_{0.15}$	900	2
15SG5	$Si_{0.85}Ge_{0.15}$	900	5
15SG10	$Si_{0.85}Ge_{0.15}$	900	10
15SG15	$Si_{0.85}Ge_{0.15}$	900	15
25SG2	$Si_{0.75}Ge_{0.25}$	900	2
25SG5	$Si_{0.75}Ge_{0.25}$	900	5

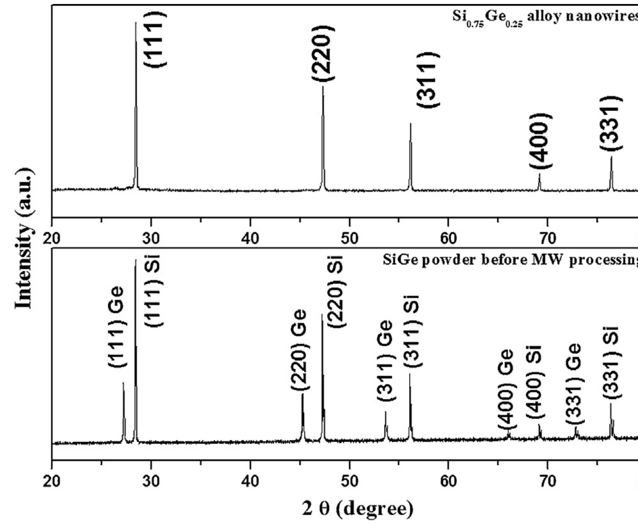

Fig. 1. The X-ray diffractograms of starting mixture and 25SG5 sample.

It is noted that the processing of powder compact in conventional furnace at a temperature of 900 °C had not resulted in any growth of nanowires (Fig. 2). Interestingly, processing of the same compact in a single mode (H-field) MW applicator resulted in a good yield of nanowires at the same temperature. Thus, it is imperative to discuss the role of microwave H-field on the growth of nanowires. Rybakov et al. [21] have revealed that mass transport in crystalline solids gets enhanced due to presence of ponder motive forces acting on charges carriers. Ponder motive force is a nonlinear force, which acts on charged particle placed in an inhomogeneous high frequency electromagnetic field. In the presence of ponder motive force, charge particle oscillates as well as drifts towards less intense field. The origin of inhomogeneous high frequency electromagnetic field inside SiGe powder compact in presence of MW H-filed is discussed elsewhere [19]. In our case, it is proposed that the charged tip will experience ponder motive force in an inhomogeneous high frequency electromagnetic field. The tip of a growing nanowire is charged is confirmed by Cheng et al. [14] from their field emission data while explaining the growth of silicon nanowires in the presence of SiO molecules. Consequently, the ponder motive forces will drive the charged entities towards weak field area, and hence will

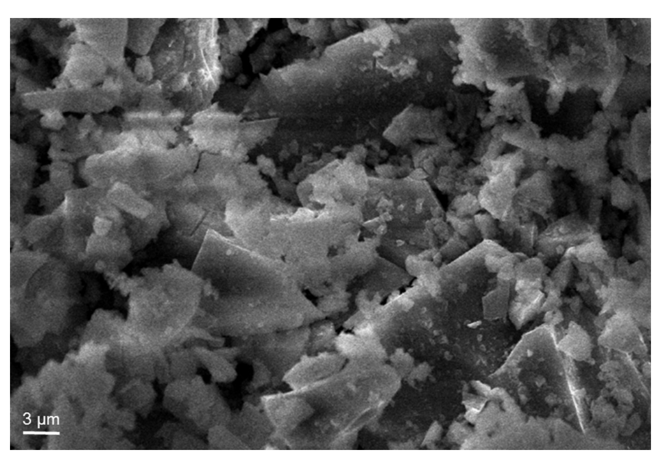

Fig. 2. Scanning electron micrograph of starting powder processed in conventional furnace at 900 °C.

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