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Fine-tuning of catalytic tin nanoparticles by the reverse micelle method for direct deposition of silicon nanowires by a plasma-enhanced chemical vapour technique

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ABSTRACT

The reverse micelle method was used for the reduction of a tin (Sn) salt solution to produce metallic Sn nanoparticles ranging from 85 nm to 140 nm in diameter. The reverse micellar system used in this process was hexane-butanol-cetyl trimethylammonium bromide (CTAB). The diameters of the Sn nanoparticles were proportional to the concentration of the aqueous Sn salt solution. Thus, the size of the Sn nanoparticles can easily be controlled, enabling a simple, reproducible mechanism for the growth of silicon nanowires (SiNWs) using plasma-enhanced chemical vapour deposition (PECVD). Both the Sn nanoparticles and silicon nanowires were characterised using field-emission scanning electron microscopy (FE-SEM). Further characterisations of the SiNW's were made using transmission electron microscopy (TEM), atomic force microscopy (AFM) and Raman spectroscopy. In addition, dynamic light scattering (DLS) was used to investigate particle size distributions. This procedure demonstrates an economical route for manufacturing reproducible silicon nanowires using fine-tuned Sn nanoparticles for possible solar cell applications.

1. Introduction

The search for sustainable renewable energy sources that can form part of a comprehensive approach to solving the world's current energy needs has recently been focused on the use of photovoltaic (PV) solar cells. Currently, the PV solar cells in common use are based on silicon (Si) materials and have been employed since the early 1950s [1]. However, recent investigations have focused on improving the conversion efficiency of the electrical energy produced per unit of solar radiation for these devices [2]. The properties of crystalline Si have been extensively studied and exploited by the semiconductor industry for the manufacture of PV solar cells for many years [3]. But, because of the significant cost and low availability of solar-grade PV crystalline-Si based solar cells; cheaper amorphous silicon-based cells are generally used. This is despite amorphous Si having a lower efficiency and suffering from photo-degradation effects [4].

The general shortage of solar-grade Si coupled with the high cost of manufacturing PV cells has demanded a more efficient use of Si in solar cells. To address this problem thinner Si wafers (4 μm) have been designed by the solar PV industry [5]. This technological trend towards thinner wafers will continue, but the manufacturing techniques required for these thin wafers are challenging [6]. Muller et al. recently reported on the trend to fabricate silicon-photovoltaic (Si-PV) cells with even thinner layers of silicon and discussed the possibility of using nanometer thick devices in advanced PV cells [7].

In recent years, developments in nanotechnology have produced new materials with novel properties that can be used to produce superior PV cells. One-dimensional nanomaterials, such as Si, have demonstrated unique physical and chemical properties. These properties include size-confinement effects [8], strong infrared absorption [9] and a high sensitivity to conductance [10]. For example, this high sensitivity to conductance has greatly enhanced the application of nano Si as a bio-sensing device [11]. These distinctive properties of one-dimensional materials (when compared to their bulk counterparts) makes them commercially valuable for novel applications. One area of current interest is the application of Si nanostructures for the manufacture of solar cells. Leiber's group recently investigated and demonstrated the application of SiNWs for the manufacture of nanowire electronics and photonic devices was feasible. Furthermore, their unique properties were diagnosed to be superior, in comparison to the current amorphous and crystalline Si counterparts [12]. In addition, both Tian et al. and Wang et al. have confirmed the possible incorporation of SiNWs into nano-electronic power sources, PV devices and electronic applications [13,14]. And recently, Perraud et al. investigated a novel manufacturing process that incorporated SiNWs into a new solar cell

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configuration. Subsequent testing, resulted in a relatively low energy efficiency value of 1.9%, when the cell was illuminated by a 100 m W cm^{-2} light source. Further investigation of this low efficiency revealed that the gold (Au) catalyst used to produce the SiNWs had interfered with the device's characteristics [15].

In 1964, Wagner and Ellis were the first to explore and explain the metal catalytic growth of SiNWs using the vapour–liquid–solid (VLS) mechanism (Fig. 1) [16]. Recently, Lee et al. demonstrated an alternative SiNW growth model that followed a solid–solid growth mechanism that incorporated a titanium nitride substrate [17]. In the majority of cases, the catalytic metal used for the growth of SiNWs is Au. However, metals such as tin (Sn) [18], nickel (Ni) [19] and iron (Fe) [20] have also displayed similar catalytic effects.

To date, several techniques have been used to produce SiNWs. These include laser ablation [21], chemical vapour deposition (CVD) [22], thermal evaporation [20], electrolytic methods [23] and even growth from an organic solution [9]. For example, Gunawan and Guha were able to grow SiNWs using the VLS method and then demonstrate the improved performance of solar cells that were built from the resulting SiNWs [24]. Traditionally, Au is the catalytic metal used for growing SiNWs in a CVD process. This is because the eutectic temperature of the Au–Si alloy is relatively low (363 °C) [25]. The advantage of using an Sn–Si alloy comes firstly from its lower eutectic temperature of 232 °C [18] and secondly, from the lower contamination rate during the manufacture of the SiNWs [24].

Micro emulsions and reverse micellar solutions have been thoroughly investigated for the manufacture of nanomaterials [26–28]. Both techniques offer significant advantages, the first being that they are both fairly simple to produce in a general laboratory. The second lies in the fact that the experiments are robust and can be easily quantified. And thirdly, the reaction can be carried out at room temperature and pressure. Above all, the size-diversity of the final product can be controlled and can also be scaled-up. This is an important feature that can assist in the mass production of large quantities of nanostructured materials for a wide range of commercial applications. To date, the reverse micelle (RM) technique has been used in the manufacture of numerous devices and applications. Typical examples include carbon monoxide detection [29], purification [30], extraction systems [31], pharmaceutical [32] and electronic devices [33].

In the present work, we investigate the direct application of an Sn salt as a nanocatalytic metal precursor for the manufacture of SiNWs. In addition, we use the RM technique to fine-tune the size of the metallic Sn nanoparticles that will ultimately dictate the final size of the SiNWs and provide a more economical route for the manufacture of SiNWs. Fig. 2 presents a schematic representation of the fabrication process.

2. Materials and methods

2.1. Materials

Commercially available tin (II) chloride [$SnCl_2{\cdot}2H_2O$], *n*-butanol, *n*-Hexane, Cetyltrimethylammonium bromide (CTAB) [$CH_3(CH_2)_{15}N(CH_3)_3Br$], and sodium borohydride [$NaBH_4$] were purchased

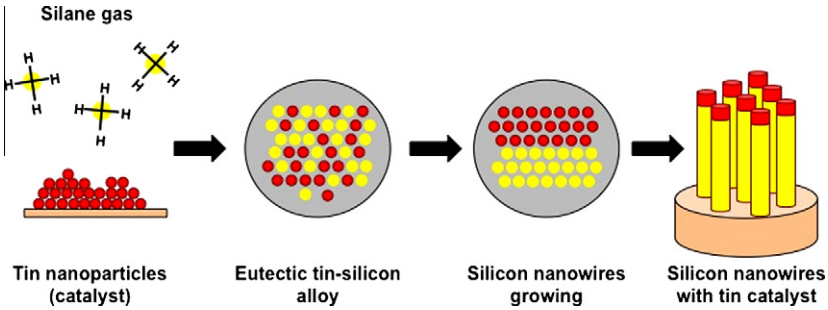

Fig. 1. Vapour–Liquid–Solid (VLS), mechanism for the 1-D growth of SiNWs.

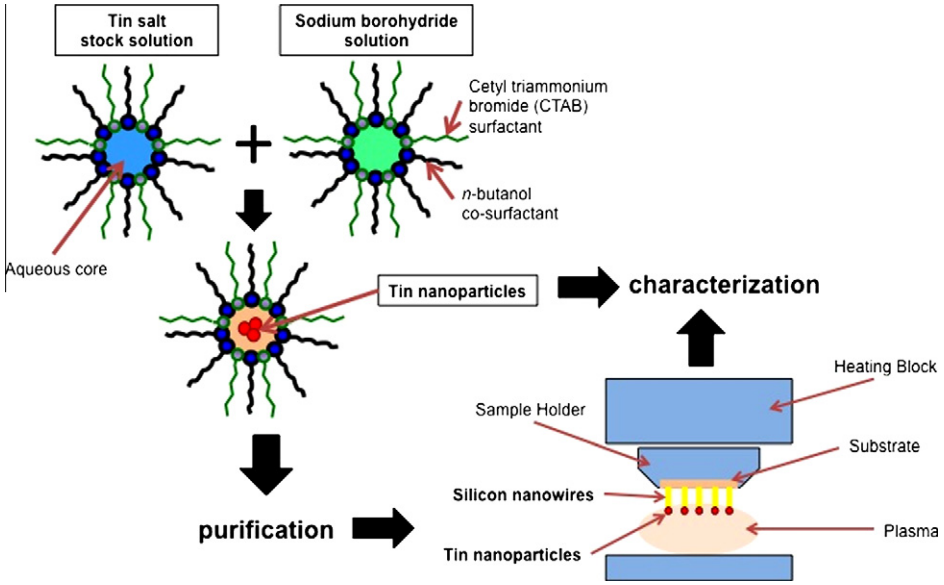

Fig. 2. Synthesis of Sn nanoparticles *via* RM and the subsequent fabrication of silicon nanowires using the PECVD process.