Ultra High Vacuum Chemical Vapor Deposition Techniques for Economic Growth of Silicon Nanowires

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Abstract: Ultra High Vacuum Chemical Vapor Deposition (UHVCVD) reactor has been used to grow silicon nanowires via innovative economical approaches using chemical active materials as catalysts such as aluminum. Scanning Electron Microscopy has been used to study the success of the growth for further investigations and advanced applications such as solar cells. Solar manufacturers are looking for approaches to improve yield and cell efficiency and lower manufacturing costs overall. One of the main goals of this project is to tear down the various parameters involved in the current photovoltaic panels and improve it in one or more directions (properties, performance, costs). The current study is addressing the solar market with special concern of the efficiency goal. The mechanical flexibility of plastic materials is of high demands for all photovoltaic applications onto curved surfaces for architectural integration. Polycarbonate AND/OR poly methyl methacrylate encapsulation of photovoltaic modules and usage to fabricate advanced silicon nanowires solar cells can be emerging technologies delivering excellent performance and durability at a competitive cost. Although solar panels with glass protective facing still account for the majority of the installations of photovoltaic modules, however, it is expected that the adaptation of these new technologies will rapidly gain market share. The growth of silicon nanowires using chemical vapor deposition to fabricate advanced solar cells can be done via two innovative approaches. Alternative techniques for lithographic formation of the mask can provide advantages for low-cost processing, especially where a simple repeating pattern is required.

Keywords: Silicon, Nanowires, Ultra High Vacuum Chemical Vapour Deposition, Photovoltaic, Scanning Electron Microscopy

1. Introduction

Polycarbonate (PC) AND/OR poly methyl methacrylate (PMMA) commonly used in eye protection, as well as in other projectile-resistant viewing and lighting applications that would normally indicate the use of glass, but require much higher impact-resistance. Moreover, there are applications, such as solar modules, which require higher impact-resistance along with good mechanical properties such as high tensile, shear strength, high modulus of elasticity, and easy to fabricate & machine. These properties, plus good low frequency and high voltage insulating characteristics, make PC and PMMA carrier materials for electrical and electronic components [1-3]. It

has been established that the properties of the commercial PC can be altered by various techniques [2], in regards to change its wettability, adhesion, and surface mechanical properties. At extreme weather conditions of high temperatures, sand, strong wind, rain, and sometimes hail PMMA can be considered as a good candidate replacing PC, with high clarity over longer periods of time. PMMA is relatively hard, lightweight material, however, its impact strength is significantly lower than PC. It has a density of 1.17–1.20 g/cm³, which is less than half that of glass. [1] PMMA light transmittance is approximately 92% of visible light under standard conditions at 3 mm

material thickness, and light reflection from its planar surface is in the range of less than 5% due to its refractive index 1.4905 at wavelength of 589.3 nm [3]. Most importantly, PMMA has low water vapor absorption capacity makes it very suitable for electrical engineering purposes [4]. These properties of PMMA make it suitable for products intended for long open-air operation, such as PV cells and modules. Moreover, PMMA can exist in different forms including sheets and micro- down to nanospheres. Where PC or PMMA planar sheets can be used to encapsulate PV panels, and the microspheres represent an innovative approach in solar cells advanced fabrication technique, as the current study is presenting.

A promising recently emerged field for future low cost, decent efficiency solar cell devices is the use of vapor-liquid-solid (VLS) grown silicon nanowires (Si-NWs). Bottom-up approach of Si-NWs growth via VLS mechanism has a key advantage for device applications, since it is possible to template the position of the NWs by controlling the placement of the initial metal seed or catalyst particle. This templating then allows integration of NWs with other parts of the structure, as required for many of these applications [5-8]. It has been proposed by Khayyat et al. 2013 [6] that the technique of microsphere lithography to produce regular hexagonal arrays of Al-seeded nanowires, and the fabrication process continues to fabricate solar cells [7 & 8]. It has been reported that PMMA nanospheres were used to increase the surface area of functional surfaces and other desired properties [10-12]. One of the key goals of the current article is to create new application markets for acrylic such as applications for PC AND/OR PMMA in solar engineering and other alternate energy technologies.

The relative mechanical flexibility of thin plastic materials is of high demands for various technological applications including PV cells and modules. This allows the integration of this curved light weight module surfaces with architectural sites. Polycarbonate AND/OR poly methyl methacrylate encapsulation of photovoltaic modules and usage to fabricate advanced silicon nanowires solar cells can be emerging technologies delivering excellent performance and durability at a competitive cost. Although solar panels with glass protective facing still account for the majority of the installations of photovoltaic modules, however, it is expected that the adaptation of these new technologies will rapidly gain market share. The growth of silicon nanowires using Ultra High Vacuum Chemical Vapor Deposition UHVCVD to fabricate advanced solar cells can be done via two innovative approaches. Alternative techniques for the control growth of Si-NWs using the conventional photo or e-beam lithography in addition to the innovative micro- or nano-spheres can provide advantages for low-cost processing, especially where a regular repeating pattern is required [9-12].

2. Experimental [5, 6]

Si-NWs in the current investigation were grown in a home-built (UHVCVD) tool operated under extremely Low-Pressure conditions (LPCVD). A thermal Al evaporator and a monitor of quartz crystal are installed in the load lock chamber. The load lock chamber has a base pressure of 1×10^{-7} Torr, and the UHVCVD growth chamber has a base pressure of 4×10^{-9} Torr at room temperature and 2×10^{-8} Torr at 600°C. Si-NWs, as previously observed [5], grow preferentially perpendicularly in the (111) direction so Si(111) substrates were primarily used. The detailed growth conditions along with the pre-growth steps were described in previous work [5-8].

It has been shown, according to Khayyat et al [5], that as the thickness of Al catalyst layer is increased (from 2 nm to 5 nm) the fidelity of the growth increases, then after reaching 5 nm Al thickness then the growth fidelity decreases quite significantly. Based on these measurements, it has been decided to choose 5 nm of Al thickness. When the desired Al thickness, 5 nm, had been deposited, the substrates were moved out of the Al flux and the Al source was cooled. The samples were then transferred into the hot growth chamber for a pre-growth anneal at 600°C, which is above the Al/Si bulk eutectic temperature of 577°C. This anneal was 20 min long under full pumping and was intended to allow the Al film to agglomerate into small islands on the surface and form liquid droplets. The furnace was then cooled to the desired growth temperature (usually 520°C) and pure silane (SiH_4) was introduced at a fixed flow, 20 sccm, using a mass flow controller (MFC). Examining the Si-NWs morphology were examined with an environmental scanning electron microscope (SEM) FEI Co., Eindhoven, The Netherlands, model XL 30.

3. Results and Discussion

The vapor-liquid-solid (VLS) process (see figure 1) is well suited to producing structures with precisely controlled dimensions. NW growth occurs at the locations of the seed particles; the diameter of the NW is proportional to the seed volume; and compositional changes can be achieved by modulating the source gas flow [5-7].

Aligned, epitaxial growth can be achieved if a single crystal substrate is used, while random growth directions are seen on amorphous substrates [8]. Several techniques for controlling the placement, density, and diameter of noble metal seeds have been reviewed by Fan *et al* [9]. Electron-beam lithography (EBL) based patterning techniques are widely used in research but are less well suited for manufacturing because of their cost and low throughput. There are several Si-NWs growth techniques have been undertaken in this study, as follows;

Figure 1. At the edge of the collector-crystal interface where all three phases meet the nucleation probability is high.

3.1. Conventional Si-NWs Templating Catalysed with Au and Al

Conventional photolithography in conjunction with a SiO_2 mask has been shown to be practical for achieving templated NW growth with high yield for noble metals like gold (Au). Figure 2 shows Si-NWs growth catalysed with Au, where the position of those NWs is achieved with the photolithography. It has been well established to catalyse Si-NWs with Au, for

simplicity and a low oxidation rate. However, Au is a deep level trap if we consider those grown NWs for device applications. Semiconductors industries use aluminum (Al) as a dopant to create p-type materials, and it can be used as a catalyst for Si-NWs growth. However, Al is an active element which undergo oxidation very rapidly which suppress the NWs growth.

Figure 2. Si-NWs growth catalyzed with 15 nm thick Au on Patterned Si Wafer.

Growing Si-NWs catalysed with Al avoids the fundamental problem of low lifetime due to deep level traps caused by the

incorporation of noble metals such as Au into the Si [10-12]; furthermore, Al provides lightly p-doped Si NWs [11], without adversely affecting the nanowire growth morphologies, as occurs with doping strategies using only B_2H_6 .

Figure 3. Si-NWs catalyzed with Al on Si(111) substrate. (a) Rounded-tops NWs, shows at the top of the NWs, Al, (b) Flat-tops NWs, after removing the Al from the top of the NWs using HF.

3.2. Nanoscale Chemical Templating (NCT) Technique

The novel oxidation scheme of Nanoscale Chemical Templating involves several steps (see figure 4). First, creating an about 50 nm thick oxide layer on the top of Si(111) chip, by placing the sample in oxygen environment furnace for certain time according to a calibration chart. Then undertaking a photolithography process via a pre-designed mask and developing to get a pre-patterned SiO_2 . After that in situ Al deposition in the load lock of the UHVCVD to be transferred to the growth chamber of the UHVCVD for annealing. The Al droplet at the top of Si in the opening balls-up, while it oxides on the top of SiO_2 layer between opening. The last step of NWs growth is performed as routinely explained [7-11]. While the 6th step depicted in figure 4 describes building p-n junctions for PV application, after removing Al from the top of the NWs for PV applications. Figure 6 presents details SEM images of areas of several μm^2 , where SiO_2 layer appear where there is no growth of Si-NWs. Nanoscale Chemical Templating process has been optimized reaching growth fidelity of almost 94% of a single Si-NW/ opening (see figures 6 & 7).

Figure 4. Schematic representations of the various steps involved in the process of Nanoscale Chemical Templating (NCT).

Figure 5. Perpendicular growth of nanowires catalyzed with Al, on Si(111) substrate, using Nanoscale Chemical Templating (NCT) technique. (a) SEM micrograph of the side view of NCT growth shows a region where the growth occurs, and regions where there is no growth occurs as Al_xO_x exists (see the thin white layer). (b) SEM image of relatively a low magnification shows bright regions where NWs growth exists and dark regions where there is no NW growth. (c) a high magnification SEM image shows a single NW where the oxide layer was etched and a planar growth on the top of the oxide layer. (d) a SEM image shows the thickness of both the isolating oxide layer and the planar layer.

Figure 6. Low magnification SEM image show control growth Si-NWs using NCT, and regions where Si-NWs growth occur all around the controlled region. (scale bar 10 μm).

Figure 7. (a) SEM image shows of SiO_2 patterned Si(100) after annealing. (b) NWs growth perpendicularly of Si(100), where Al at the tops of the NWs, a single NW/ an opening, showing high growth yield at 800 Mtorr growth pressure.

Figures 5, 6 and 7 show SEM micrographs of NCT growth of Si-NWs. The figures display illustrations, cross section and planar SEM images of various stages of NCT, using the typical growth conditions described above. In many applications of patterned NWs, obtaining a single Si NW in each mask opening is critical. Therefore, the growth yield and fidelity of the templating process have been investigated

as a function of different processing parameters.

3.3. Nanoscale Chemical Templating (NCT) Using PC or PMMA Microsphere Lithography

Alternative techniques for lithographic formation of the mask can provide advantages for low-cost processing, especially where a simple repeating pattern is required [12–15]. We have evaluated the technique of microsphere lithography to produce regular hexagonal arrays of Al-seeded nanowires. Silica microspheres are commercially available with narrow size distributions, and when dispersed properly on a surface they form a close-packed array that defines gaps through which a material can be deposited. Substrates, $\sim 2 \text{ cm}^2$ cleaved from a p-type, (111), Si wafer, were cleaned using standard techniques which leave a thin oxide on the Si

surface. A drop of $1 \mu\text{m}$ diameter silica microspheres in solution taken directly from the commercially provided stock solution (various suppliers were used) was dispersed onto the substrate. Variable speed spin routines were used on a resist spinner to remove the liquid and disperse the particles [2]. After spinning on the microspheres, the substrates were processed using the sequence described above for the photolithography samples after the resist strip: cleaning with O_2 ash, etching with BOE, insertion into the load lock, then deposition of Al and growth of nanowires. Figures 8 and 9 illustrate the NCT scheme using microspheres. Regions of Al that will act as seeds form at the gaps between microspheres, while on top of the microspheres the Al layer reacts with the oxide and becomes inactive [16].

Figure 8. MS Using Polyesterene Sphere of $2 \mu\text{m}$ Diameter.

Figure 9. Microsphere of polystyrene and silica processing optimization.

We show the results of this process, where NWs can be seen growing between the gaps of the microsphere array. This process has not been optimized for yield [10, 11, 17].

3.4. Si-NWs Growth on Cheap Substrates Such as Al Foil

1. Nanowires can be grown on Cheap Substrates (Al foil, ...), as shown in figure 10.

Quick Growth

2. Apply “nanowires” as Light Trapping option for Solar Cells

Figure 10. Nanowires grow on Al foil, at 490°C / 500 mTorr SiH_4 / 30 min . (a) schematic representation, (b) SEM micrograph of Si-NWs growth.

3.5. Overview: Applications of Innovative Si-NWs Growth Using UHVCVD

Nanoscale Chemical Templating (NCT) technique, proposed by Khayyat [5], proposed the concept of controlling the position of the grown NWs catalysed with chemically active elements such as Al. The Ultra High Vacuum Chemical Vapor Deposition UHVCVD reactor usually does not include a metal of generally speaking a catalyst evaporator. So, seed materials have to be evaporated on the substrate in a stand-alone evaporator as routinely practised with gold (Au) catalyst. However, when we catalyse the nanowires growth with chemically active element such as aluminum (Al) so we have to install it in the tool of UHVCVD.

The proposed concept has been evaluated applying the technique of microsphere lithography to produce regular hexagonal arrays of Al-catalysed Si-NWs. Silica microspheres are commercially available with narrow size distributions, and when dispersed properly using a spinner on the Si substrate surface they form a close-packed array that forms gaps through which a material can be deposited. Si (111) of p-type substrates were cleaned using standard techniques [5-11] which leave a thin oxide on the Si surface. A drop of 1 μm diameter silica (SiO_2) microspheres in solution taken directly from the commercially provided stock solution was dispersed onto the substrate. Then the growth procedure has been adopted as explained earlier [5]. Figure 1 illustrates schematically the various steps of NCT process using microspheres. After spinning in the microspheres (step 1), where it followed by step 2, where then layer of 5 nm Al deposited on the surface covering the top surfaces of the microspheres and bare Si surface. Step 3 describes regions of Al that will act as seeds form at the gaps between microspheres, while on top of the microspheres the Al layer reacts with the oxide and becomes inactive [16, 17]. The final step of this process, step 4, shows the growth of Si-NWs after allowing SiH_4 to flow, providing the required medium of VLS system, to be followed by epitaxial perpendicular Si-NWs growth [17, 18, 20].

It has been reported that the overall market of solar photovoltaic installations is growing markedly with a rate exceeding 30% per annum [15, 19, 21]. The conventional glass PV modules with EVA double sheets at severe weather conditions might results in substantial glass damage and module power reduction. PV modules encapsulate in PC AND/OR PMMA sheets are aiming to overcome these difficulties, in addition to other related issue with the conventional panel. There are several advantages of this adopted technology as follows;

1. Weight: It is approximately weigh 5 times less than the double-glass one, which has also a positive impact on economy.
2. Mechanical resistance: it is virtually unbreakable.
3. Utility: flexible, can be drilled and cut easily.
4. PC reduces the possible damage of the solar cells caused during the placement of the second piece of

glass.

5. PC or PMMA modules do not require frames, which are used to protect the glass edges from impact during transport in the current PV modules.
6. PC or PMMA modules have almost no risk of module breakage.
7. Advanced solar cells of Si-NWs can be grown directly on PC substrates (to be studied in details).
8. Most importantly, it can be subsequently transferred to the current manufacturing line of solar panels factory.
9. PC or PMMA with improved properties can be provided from companies such as SABIC.
10. Using PMMA to fabricate Si-NWs PV cells is an innovative economical solution (to be studied in details).

4. Conclusions

The Ultra High Vacuum Chemical Vapor Deposition UHVCVD reactor, which was used in the previous studies, does not include an aluminum evaporator, so we have to install it in the tool separately. The study includes several growth approaches of Si-NWs, where main conclusive remarks can be stated as follows;

- 1- The structure and electronic characteristics of these Al-catalyzed silicon nanowires (Si -NWs) are highly relevant to many applications, for example, in photovoltaics.
- 2- Nanoscale Chemical Templating (NCT) method has been employed to achieve controlled spatial placement of Si-NWs has using SiO_2 . PC or PMMA nanospheres can be used similarly, as a mask and Al as the seed material.
- 4- The NCT with PC microspheres method is economic, as it requires fewer steps compared to conventional patterning approaches, not requiring lift off of a metal layer or removal of the mask.
- 5- The methodology used in achieving controlled placement of single NWs seeded with Al is an example of proving the concept of NCT technique, more oxygen-reactive materials such as Sn, Sb, In, Ga, and Ti templated by NCT will have more advanced applications in nanodevices fabrications.

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Conflict of Interest

The author declares that there is no conflict of interest regarding the publication of this paper.

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