

Chemical Templating of Silicon Nanowires for Energy Applications

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Abstract

Controlling the growth position of a nanowire is important for fabricating devices, especially when involving a large array of nanowires. The growth reproducibility is critically a key parameter in the progress of implementing nanowires in advance applications. The nanopatterning of semiconductors and other surfaces in a controlled manor is of a great interest for industrial application. Nanoscale Chemical Templating (NCT) is a new method of controlling the spatial placement of the growth of silicon nanowires (Si-NWs) seeded with oxygen reactive materials such as aluminum (Al), which is a standard metal in silicon process line. One of the advantages of this technique, in comparison to the conventional ones, it does not require removal of the patterned compound oxide layer. There are several applicationspaces of NCT in nanotechnology devices fabrication including energy production and storage. Si-NWs catalyzed with Al and grown with NCT can be good candidates at PV broad research. Moreover, controlled growth of Si-NWs at VLS-CVD (Vapor Liquid Solid-Chemical Vapor Deposition) process allows us to produce surfaces of economical materials of high thermal absorbance to be integrated with the current thermal energy storage systems increasing the efficiency in terms of amount of the absorbed energy and reducing the charging time. Applying the proposed concept has economical value as it is expected to reduce the required space of thermal tubes considering the extremely high surface areas of a material sheet has nanowires in comparisons to the planar one. Considering that NWs have very high surface to volume ratio, making them ideal components for light and thermal absorption or any related to interface phenomena.

Abbreviations

NCT: Nanoscale Chemical Templating

Si-NWs: Silicon Nanowires

MBE: Molecular Beam Epitaxy

PMMA: Polymethyl Methyl Acrylate

SEM: Scanning Electron Microscope

LPCVD: Low Pressure Conditions

UHVCVD: Ultra-High Vacuum Chemical Vapor Deposition

PV: Photovoltaic

TES: Thermal Energy Storage

NCT: Nanoscale Chemical Templating

Keywords: Si-NWs; CVD; VLS; PV; Thermal Energy Storage

Introduction

The fact that silicon is the basic material in microelectronics makes Si-NWs of special technological interest. The increased sensitivity and faster response time of nanowires is a result of the large surface-to-volume ratio, and the small cross-section available for conduction channels. There are other advantages of implementing Si-NWs in electronic devices fabrication, such as, reducing the strain and thermal expansion between thin grown layers using Molecular Beam Epitaxy (MBE) systems [1–3]. Two

main approaches have been used to synthesize Si-NWs arrays, which can be categorized as etching method known as “top-down” growth methods on the one hand, and growth methods which is known as “bottomup” on the other hand. These are briefly presented schematically below (figure 1), along with more focus on the bottomup approach describing the main steps involved in VLS technique employed at CVD reactor.

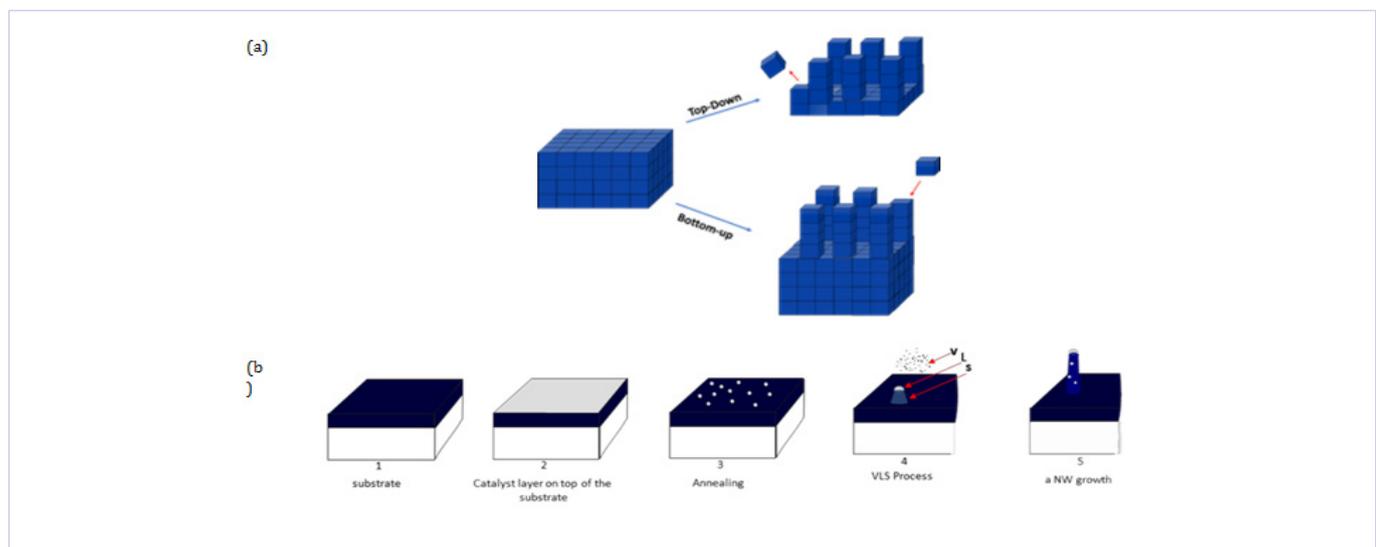


Figure 1: Schematic representations (a) The original substrate, and the two main approaches of creating nanowires “bottom-up” and “top-down”. Notice the building blocks of materials (atoms) are moving towards (depositing) the substrate in the bottom-up process, while atoms are moving away (etching) from substrate in the top-down mechanism. (b) The sequence of the VLS process in five main steps of the bottom-up used in the current study.

The substrate depicted 1 in figure 1(b), can be bulk semiconductor materials or a relatively thin film of a semiconductor on a cheap substrate such as glass or Polycarbonate (PC) or Polymethyl Methyl Acrylate (PMMA) sheets, 2: catalyst thin layer such as Al, 3: catalyst after annealing where it balls up, 4: the sample was placed at the CVD reactor and allowing the precursor gas to flow, temperature reaches the eutectic and three phases co-exists, precipitation begins. 5: growth continues forming a NW; notice the possible incorporation of the catalyst atoms within the grown nanowires. It can be understood that this bottom-up is an analogous to the way that nature works, may show to be a suitable solution to the technological challenges as devices approach atomic size. In CVD-VLS growth [4-6], the metal nanocluster serves as a catalyst at which site the gaseous precursor decompose, providing the gaseous semiconductor reactants. In the case of Si-NWs growth (figure 1), silane (SiH_4) and Al thin film are used as the precursor and catalysts, respectively. Uniform NWs with negligible diameter variation can thus be achieved through careful control of the growth conditions [7-9], as shown in figure 2. The nanowire morphology and crystal structure were studied with an environmental Scanning Electron Microscope (SEM) FEI Co., Eindhoven, The Netherlands, model XL 30. These samples were not coated, as surface charging did not take place inside the experimental chamber of this microscope.

The silicon nanowires presented in this study were grown in a custom-built eight-inch Ultra-High Vacuum Chemical Vapor Deposition (UHVCVD) tool operated under Low Pressure Conditions (LPCVD). A thermal Al evaporator and quartz crystal monitor are installed in the load lock chamber. The details growth parameters were explained technically at previous published studies [9,10]. A promising field for future low cost, medium efficiency solar cell devices is the use of VLS-CVD grown nanowires as the active region of large scale Photovoltaic (PV) devices. VLS has a key advantage for device applications, since it

is possible to template the placement of the NWs by controlling the position of the initial metal seed particle [2,7,8]. 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 reported by Khayyat in 2013 [10,11], the technical details of NCT technique using SiO_2 to template the growth of Si-NWs catalysed with Al, along with silica microsphere lithography and the fabrication process of solar cells [8,12-14]. It is of critical importance to tear down the various parameters involved in the current photovoltaic cells and panels and improve them in one or more directions (properties, performance, costs), by using Si-NWs as an example. Moreover, one of the key goals of the current report is to create new application markets for acrylic such as deploying Poly-Carbonate (PC) AND/OR Poly-Methyl-Methyl-Acrylate (PMMA) in solar engineering and other alternate energy technologies [15-18].

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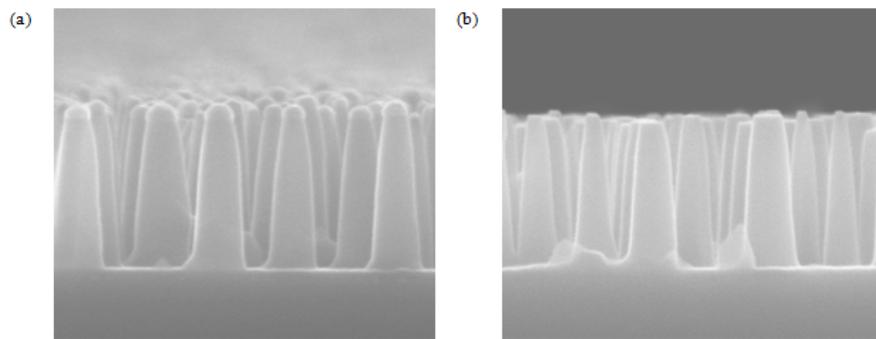


Figure 2: Si-NWs catalyzed with Al on Si(111) substrate. (a) Rounded-tops NWs, shows at the top of the NWs, Al, (b) Flat-tops NWs, after removing the Al from the top of the NWs using HF until complete dewetting.

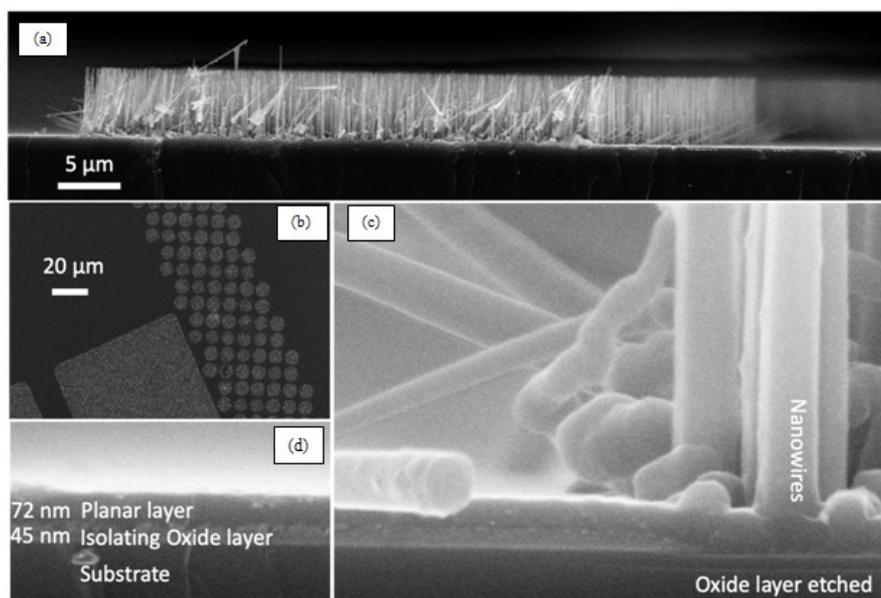


Figure 3: Perpendicular growth of NWs catalyzed with Al, on Si(111) substrate, using Nanoscale Chemical Templating (NCT) technique. (a) SEM micrograph of the side view of NCT growth shows a region where the growth occurs, and regions where there is no growth occurs as Al_xO_x exists (see the thin white layer). (b) SEM image of relatively a low magnification shows bright regions where NWs growth exists and dark regions where there is no NWs 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.

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Nanowires are excellent photons and phonons absorbers, as it is explained in the schematic diagram at figure 5, where it shows that the rays bounce between the NWs until they get trapped and absorbed by the material. The substrate could be bulk Si or thin layer of Si on a glass or other cheap material, or alternatively thin layer of Si 1 (as depicted in the figure 5(a)), on heavy-duty Al 2, on a glass substrate 3. The surface morphology of NWs

allows them to absorb the incident photon and phonons with distinguished efficiency (figure 5), where Si-NWs can be applied as light trapping option for solar cells, and as thermal absorber. The Si substrate looks absolutely black when we grow NWs on it. The patterned growth of Si-NWs shows isolated nanowires where we controlled their positions using SiO_2 , the unpatterned growth shows Si-NWs growing beside without predefined distancing. When we examine the reflectance of Si-NWs in comparisons to the plane bulk Si (the pristine one), as it is shown in figure 5(d), the reflectance is almost zero, meaning that the absorbance of Si-NWs is approximately 100%. It can be concluded that Si-NWs can be employed in Thermal Energy Storage (TES) systems as it has been used in energy production in PV cells, and improve the overall performance of energy storage [20-22].

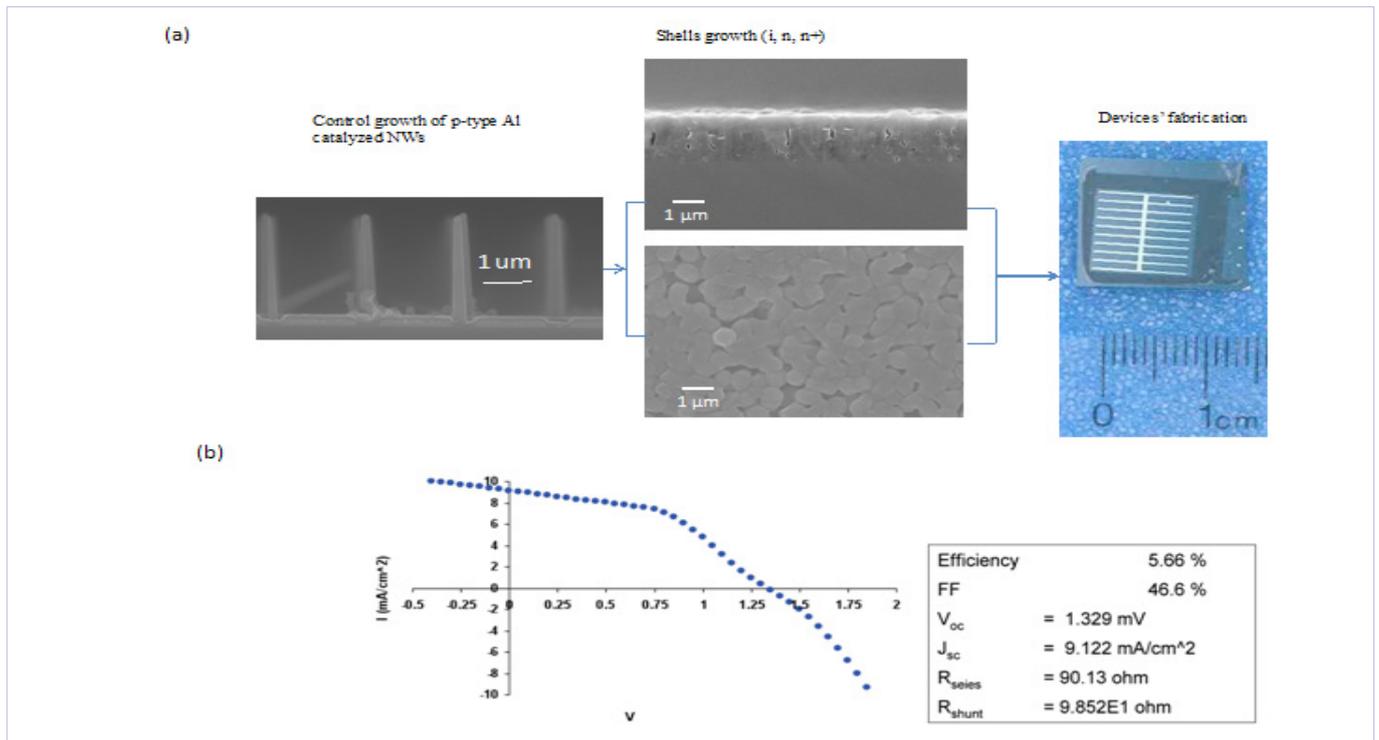


Figure 4a : SEM micrograph of control growth of single Si-NWs (side view) then surface and side views of designed p-i-n junctions (see the voids on the surface and between the perpendicular junctions' wires), then proceeding with fabrication of 1 cm² PV cell (notice the optical photo shows the bus-bars and fingers of the cell). (b) I-V characteristics of the prepared PV cell with sophisticated parameters.

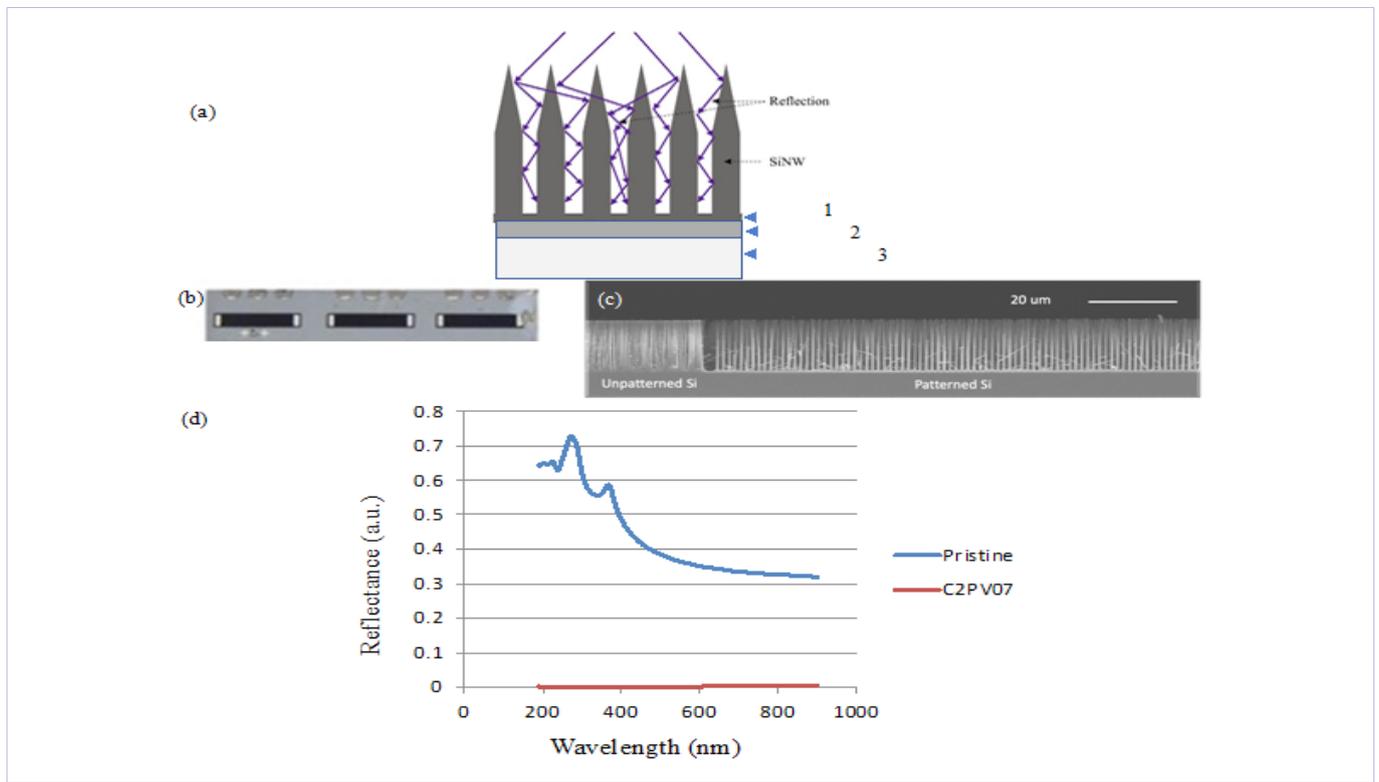


Figure 5a: Schematic diagram of Si-NWs where the rays (light or thermal) might get reflected between the nanowires with high absorbance probability, the substrate could be layers as follows: 1: thin layer of Si, 2: heavy-duty of Al, 3: glass substrate. (b) grown Si-NWs where the surface looks black. (c) SEM side view of patterned NWs grown using NCT, and unpatterned NWs, (d) the reflectance is almost zero from Si-NWs in comparison with pristine Si.

TES is a promising technology system that stores thermal energy by heating or cooling a storage medium, paraffin wax as a phase changing materials, to be used later for space heating and cooling, power generation and wider use of solar PV technology applications [19]. The use of TES systems has significant benefits in improving the performance and reliability of energy system, better economics; reduce operation costs, and less pollution and carbon dioxide emissions [20]. Our research has highlighted that today's mainstream storage technologies, which are unlikely to be sufficient to meet future flexibility requirements resulting from further decentralisation and decarbonisation efforts [21,22]. With major work to remove the excess thermal power generation and scale up renewable energies, the widespread adoption of energy storage continues to be described as the key game changer for electricity systems. Affordable storage system is a critical missing link between intermittent renewable power and 24/7 reliability and strategic resilience. Thermal Energy

Storage TES systems consists mainly of the following parts; source heat, storage unit, load resistance, as shown in figure 6. To improve the overall performance and increase the efficiency of the system several approaches can be considered [23-26]. This document is focusing on the implementing available heat sources considering increasing the output efficiency and reducing the overall cost of the integrated system. The experimental work is in progress in a parallel way, on the storage unit design [27] and storage materials development [28-31]. The suggested integration of standard PV, CSP, CPV or fuel cells will enable cost-effective deployment of energy storage. Our research highlighted that today's mainstream storage technologies are unlikely to be sufficient to meet future flexibility requirements resulting from further decentralization and decarbonization efforts. The photos at figure 6(a) presents view of the Paraffine Storage Units and the completed solar installation, which is connected with the solar panel field located in the building roof.

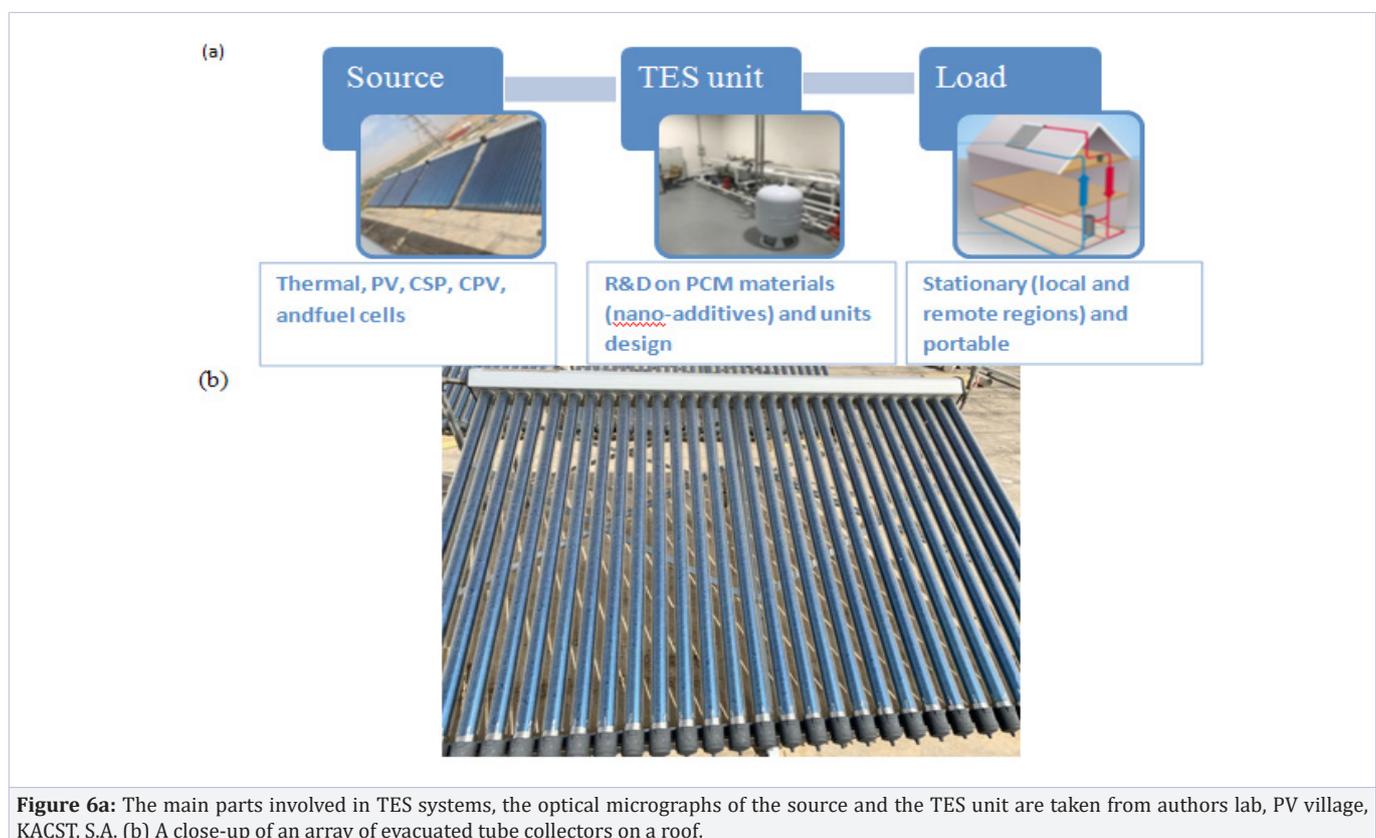


Figure 6a: The main parts involved in TES systems, the optical micrographs of the source and the TES unit are taken from authors lab, PV village, KACST, S.A. (b) A close-up of an array of evacuated tube collectors on a roof.

The solar field was launched and cooperated with the heating storage system, supplying it with energy obtained from solar radiation at the PV village at KACST's remote site outside Riyadh city, Aloyaynah, Saudi Arabia. The amount of energy obtained from the solar field operation on July 26th, 2021. It can be seen, that the approximate operating range of the solar field, which shows more precisely what amount of heat was recovered from the field is between 12 – 18 kW after the temperature stabilized, while the designed power of the solar field is 24 kW. The work efficiency stated at 50-75% in the summer season. However, this difference can be minimized by applying remedial actions. The

working conditions of the TES system, particularly the heat source unit, can be improved by several approaches. One of the possible plans of developing the thermal absorbers. The evacuated tube collector shown in figure 7 consists mainly of a glass tube to surround the absorber with high vacuum and effectively resists atmospheric pressure and reduces convection and conduction heat loss achieving greater energy conversion efficiency [20]. The absorber can be curved metal absorber sheets. Heat transfer fluid can flow in and out of each tube or being in contact with a heat pipe reaching inside the tube. The proposed concept here is to replace the regular metal absorber sheet with Al sheets (could be

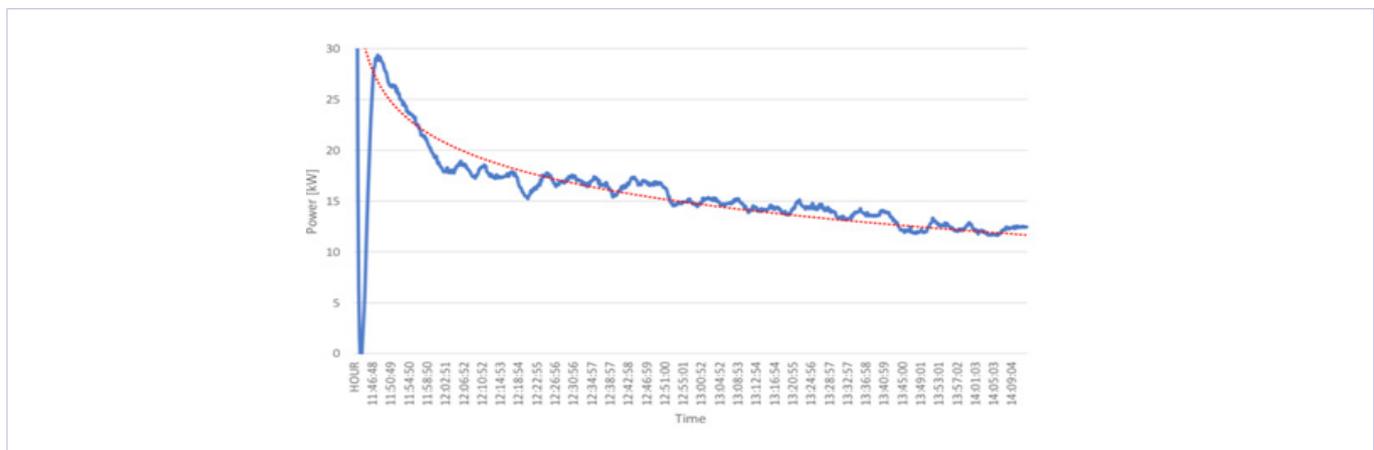


Figure 7: Solar field operation on July 26th, 2021 for 2 hours around 12 noon- 2 pm

Al heavy-duty sheets) that has Si-NWs (as explained previously in figure 5). Growing Si-NWs on heavy-duty Al foil can be done at the CVD chamber at 490 °C / 500 mTorr SiH₄ / 30 min.

Conclusion

To sum up, the main concept and some experimental validations of Nanoscale Chemical Templating (NCT) method has been explained to achieve controlled spatial placement of Si-NWs by using patterned SiO₂ as a mask and Al as the seed material. The main advantage of this method lies in its suitability for the oxygen-reactive seed materials which are of great interest for electronic applications. The NCT method can also have fewer steps compared to conventional patterning approaches, not requiring lift off of a metal layer or removal of the mask. The method is also flexible, as it is amenable to both standard lithography techniques and self-assembled patterning techniques like microsphere lithography. These Si-NWs which includes aluminum can be used for applications such as solar cells and Thermal Energy Storage systems. The size of electronic components keeps decreasing as more computing power is packed into the volume of a personal computer. There are also clear advantages to shrinking sensors and other electronic devices; they will be lighter, smaller and require less power. More functionality can then be added to portable instruments, whether they are cellular phones or uniforms for soldiers. In the quest for miniaturization, nanotechnology is an obvious field of study. Nanostructures can have properties that differ from those of the bulk material, for example size-tunable effective band gap or high sensitivity to surface preparation due to the large surface-to-volume ratio. This can lead to miniaturized components with completely new properties.

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