

Bottom-up silicon nanowire-based thermoelectric microgenerators

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Abstract. In this work, bottom-up intrinsic crystalline Si nanowire arrays in combination with top-down microfabrication techniques and a vertical device architecture have been proposed to develop an all-silicon nanostructured thermoelectric generator. To fabricate this device, a suitable vertical integration of Si NWs on patterned microstructures, which define the thermoelectric legs of the generator, has been achieved by bonding top and bottom silicon structures through nanowires. The process has been proven to be a feasible approach that employs a regrowth process of the nanowires for bonding purposes.

1. Introduction

Thermoelectric generators (TEGs) are able to convert heat in electrical energy by exploiting the intrinsic properties of the materials that compose them. TEGs possess the potential to become the power generating core of zero-power systems such as sensor networks working in hazardous or remote environments. These prospective applications have led to the development of a broad range of thermoelectric materials with the aim of enabling high performance thermoelectric devices. Among these materials, low-dimensional materials have received particular attention due to the possibility of enhancing the thermoelectric properties of bulk materials through nanostructuring effects, which allow filtering out the low-energy electrons by scattering phonons more effectively than electrons becoming suitable for thermoelectric applications [1-2]. In this way materials such as silicon, considered an inefficient thermoelectric material ($ZT \approx 0.01$) due to its high thermal conductivity, have shown to be a promising material [3-4] that could be integrated in thermoelectric devices.

In this work, silicon nanowires (Si NWs) have been vertically integrated in microfabricated structures to act as the thermoelectric material of a full silicon-based micro thermoelectric generator (μ TEG). A thermoelectric generator is composed by *p*-type and *n*-type material legs, connected electrically in series and thermally in parallel. Figure 1a depicts the basic concept of a single element or thermocouple of the μ TEG presented in this work in which arrays of *p*- and *n*-type SiNWs substitute the thermoelectric legs of a standard TEG device. Achieving different doping types of silicon nanowires within the same substrate entails technological constraints when working with bottom-up nanowires, specifically when *in situ* doping is performed. Therefore, the device concept of this work focuses on the growth of nanowires on two independent substrates and on the bonding of these two structures through an additional growth process step to achieve a complete μ TEG (Figure 1b).



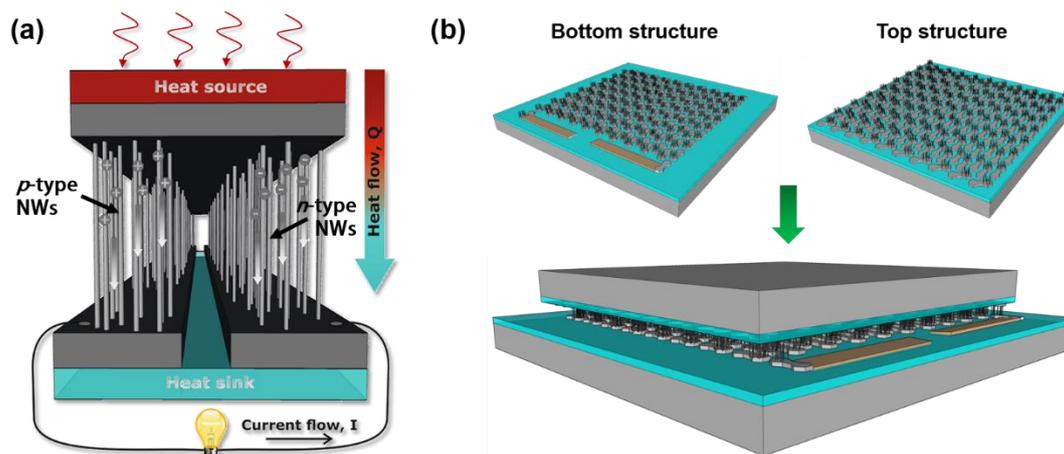


Figure 1. Schematic illustration of the device concept. (a) Thermoelectric elements consisting of *p*-type and *n*-type silicon nanowires arrays are electrically connected in series and thermally in parallel for power generation (Seebeck effect). (b) Once the Si NW legs have been separately grown on two different samples, the top structure is flipped and aligned with the bottom structure with the help of a silicon holder.

2. Experimental

Two different substrates (for the top and bottom components) were patterned with defined hexagonal Si structures that shape the thermoelectric legs of the device (Figure 2a). For this purpose, silicon on insulator (SOI) wafers with a 20 μm -thick *p*-type Si (111) device layer and a 0.5 μm -thick buried silicon oxide layer over a 250 μm -thick (100) silicon handle wafer were employed. The device layer of the SOI substrates was structured with a deep reactive ion etching (DRIE) process to define the thermoelectric legs. A thermal oxidation of the substrates was then performed to cover all the silicon exposed areas with an oxide layer and to avoid in this way the exposure of unwanted silicon areas during the further deposition of the nanoparticles employed for the growth of the nanowires. Metal contacts were patterned by means of a reactive ion etching (RIE) process that exposed the areas defined for this purpose followed by the sputtering and lift-off of a tungsten layer. A plasma-enhanced chemical vapor deposition (PECVD) oxide layer was used to passivate the metal contacts. The silicon areas for the selective growth of silicon nanowires were then exposed through a RIE process. At this point, the deposition of the metal catalyst required for the synthesis of silicon nanowires by means of the Vapor-Liquid-Solid (VLS) mechanism took place. The VLS process allows for high-density epitaxial growth of nanowires on free silicon surfaces using catalytic Au nanoparticles as mediators. The Au nanoparticles were deposited by means of the galvanic displacement method, which allows to control the nanoparticle density and diameter distribution. This highly selective method enables the deposition of nanoparticles only on conducting or semiconducting surfaces and the subsequent growth of silicon nanowires only on this (silicon-exposed) areas.

In order to deposit the gold nanoparticles, a solution, consisting of water droplets (reversed micelles) stabilized by a surfactant and emulsified in oil, was prepared. The gold clusters contained in the micelles of the solution are reduced only at the exposed silicon surfaces through a redox reaction. Silicon nanowires were grown on these substrates in a low pressure chemical vapor deposition (LPCVD) furnace at 630°C using a mixture of SiH_4 , H_2 and HCl gases at a pressure of 9 mbar. It is important to mention that the results presented in this work correspond only to intrinsic silicon nanowires.

Highly dense arrays of silicon nanowires with diameters of 84.4 ± 24.7 nm and lengths of 16.7 ± 0.9 μm were selectively grown on two independent substrates for a period of 90 minutes. Figure 2b shows a tilted image of an individual hexagonal thermoelectric leg in which silicon nanowires have been selectively grown.

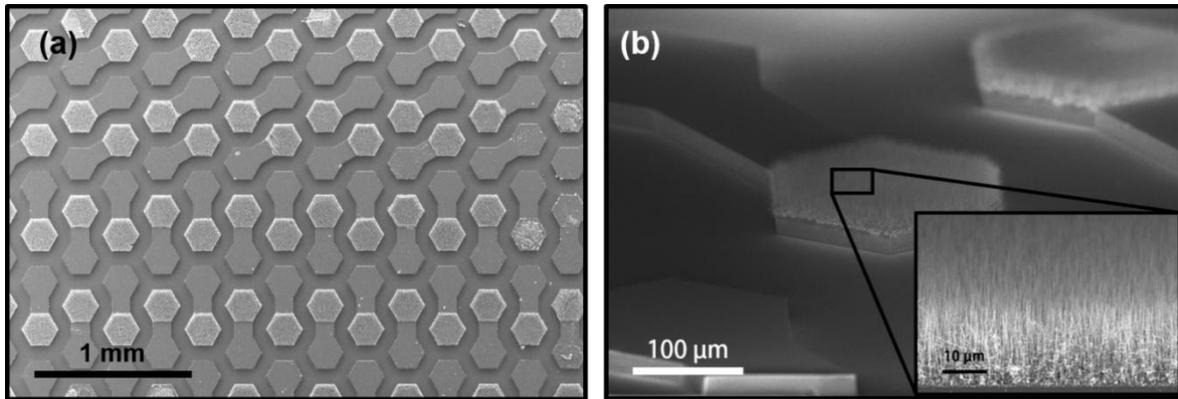


Figure 2. (a) SEM image showing the hexagonal design of the thermoelectric elements comprising the device before bonding the top and bottom structures. (b) Highly dense and ordered arrays of Si NWs have been selectively grown on defined Si structures.

In order to obtain a functional TEG structure, the SiNW arrays, which act as the thermoelectric legs, must provide electrical and mechanical connection between the top and bottom substrates. These two substrates will in turn connect the thermoelectric legs electrically in series and will be exposed respectively to a high and a low temperature source, thus connecting them thermally in parallel.

The ability of SiNWs to connect two silicon surfaces has been previously reported for horizontal architectures in which two pre-fabricated silicon electrodes or structures are bridged through a large number of highly directional nanowires [5-7]. In the case of TEG devices, a vertical architecture that allows a good thermoelectric leg integration and an efficient exploitation of naturally occurring thermal gradients would be desired. The vertical bonding of the two, top and bottom, structures was achieved using a microfabricated silicon holder that served to align the samples and bond them through an additional nanowire growth process step. Since the silicon nanowires on the samples have been synthesized using a bottom-up technique (i.e. the VLS process) the catalyst gold nanoparticle, which remains on top of the nanowires, allows to resume the growth as depicted in figure 3. The Au nanoparticle is responsible for the passage of silicon from vapor phase (SiH_4), through liquid phase (in the Au-Si alloy), to solid phase (in the NW's body). Since the nanoparticles stay on top of the wires, it is reasonable to expect that, by reintroducing an array of already grown SiNWs in the LPCVD system and by recreating the same growth conditions, the growth of the NWs can be resumed and their length further increased. Therefore, the vertical nanowire arrays of the thermoelectric legs continue to grow reaching the opposite surface and achieving an epitaxial contact between the two structures.

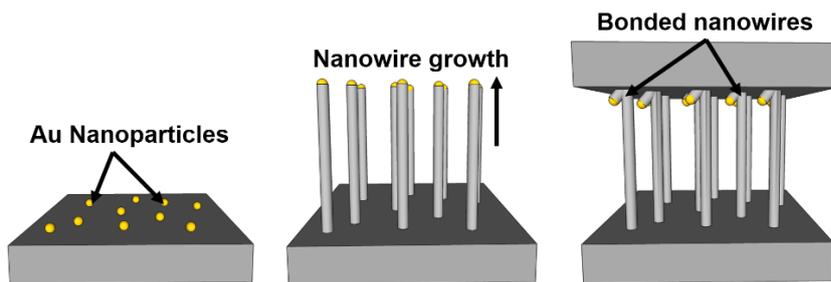


Figure 3. Schematic illustration of the bonding mechanism. Vertically aligned arrays of silicon nanowires grown on a silicon substrate bond with a top silicon surface.

3. Results

To prove the existence of a regrowth mechanism, silicon nanowires were grown on (111) Si substrates for a period of 60 minutes after which the samples are removed from the LPCVD and analyzed using SEM imaging. Then these samples are reintroduced in the LPCVD chamber, and the same growth procedure is reapplied. SEM images after this process reveal that, as expected, the silicon nanowire arrays continue to grow in the $\langle 111 \rangle$ direction (figure 4).

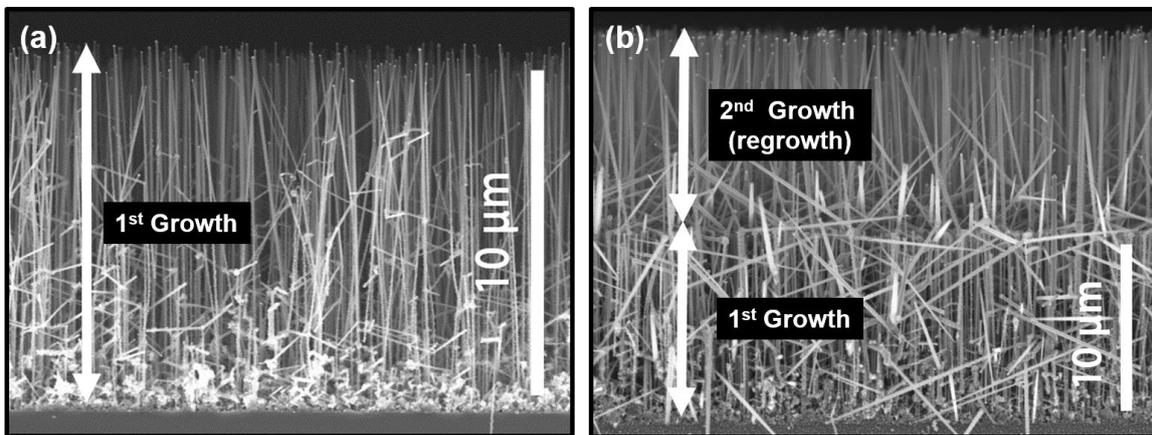


Figure 4. SEM images showing the feasibility of resuming the growth of silicon nanowires. (a) A single growth of silicon nanowires yielded a length of $12.4 \pm 0.5 \mu\text{m}$ for a 60 minutes period growth. (b) The same sample is reintroduced in the LPCVD chamber and the same growth procedure is performed on the sample. A homogeneous second regrowth process yielding a total length of $24.8 \pm 0.7 \mu\text{m}$ is achieved.

The alignment of bonded structures was verified by manually detaching the top and bottom samples of the device. As expected, SiNWs successfully bond the two substrates. SEM inspection confirms that the nanowires grow from the bottom to the top substrate (and vice versa) providing linkage between the two structures. As shown in figure 5, silicon nanowires break where they have reached and contacted the opposite substrate, whereas misaligned nanowires, lacking of a top structure where to bond and make contact, are left intact.

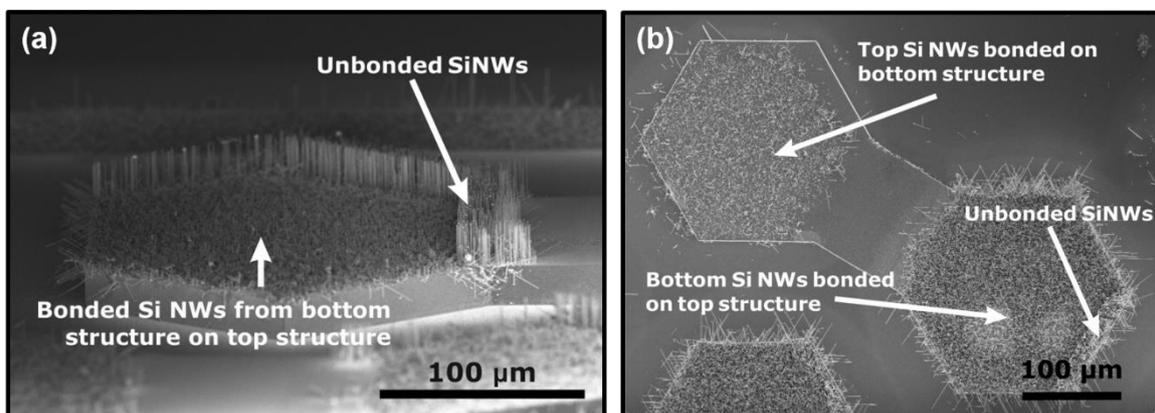


Figure 5. SEM images showing the areas where the top and bottom patterns have been aligned and bonded. The Si NWs on these areas have broken when detaching the samples, whereas the misaligned NWs, which have not been bonded with the opposite structure, have continued to grow. A minimum misalignment of $30 \mu\text{m}$ has been achieved using a microfabricated silicon holder.

Devices with 276 hexagonal elements connected through intrinsic silicon nanowires have been fabricated yielding a total electrical resistance of $4.4 \pm 0.53 \text{ k}\Omega$ at room temperature. Although further efforts have to be performed to reduce the internal resistance of the device through doping of the nanowires, these preliminary results together with the SEM analysis performed after detaching the samples prove the feasibility of integration of two different types of silicon nanowires on future thermoelectric microgenerators and provide the basis of a fabrication process to produce a functional device.

4. Conclusions

In this work, the feasibility of a thermoelectric microgenerator with a vertical structure in which the thermoelectric legs consist of silicon nanowires has been proven. Selective growth of VLS-synthesized silicon nanowires has been achieved on defined silicon structures that shape the legs of the thermoelectric device.

The regrowth of silicon nanowires was successfully carried out by applying the same growth conditions for a second time in samples with arrays of silicon nanowires. The results obtained allow to exploit this mechanism to assemble two different substrates on which nanowires have been already grown and doped separately. By vertically growing silicon nanowires in two separate silicon substrates, flipping one of these substrates over the other and performing a second growth step, the possibility of bonding a top and a bottom sample was demonstrated.

Integration of *p*- and *n*-type silicon nanowires and further characterization to ensure a good electrical connection of the NWs and a good thermal connection of the substrates to the thermal interfaces is needed to confirm the feasibility of this design for thermoelectric applications.

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