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Relaxing the electrostatic screening effect by patterning vertically-aligned silicon nanowire arrays into bundles for field emission application

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A B S T R A C T

Top-down fabrication strategies are proposed and demonstrated to realize arrays of vertically-aligned silicon nanowire bundles and bundle arrays of carbon nanotube–silicon nanowire (CNT–SiNW) heterojunctions, aiming for releasing the electrostatic screening effect and improving the field emission characteristics. The trade-off between the reduction in the electrostatic screening effect and the decrease of emission sites leads to an optimal SiNW bundle arrangement which enables the lowest turn-on electric field of 1.4 V/μm and highest emission current density of 191 μA/cm^2 among all testing SiNW samples. Benefiting from the superior thermal and electrical properties of CNTs and the flexible patterning technologies available for SiNWs, bundle arrays of CNT–SiNW heterojunctions show improved and highly-uniform field emission with a lower turn-on electric field of 0.9 V/μm and higher emission current density of 5.86 mA/cm^2. The application of these materials and their corresponding fabrication approaches is not limited to the field emission but can be used for a variety of emerging fields like nanoelectronics, lithium-ion batteries, and solar cells.

1. Introduction

One dimensional nano-material has attracted a tremendous amount of attention in recent years due to their interesting electronic and optical properties and a diverse array of potential for nano-scale device applications [1–6]. Owing to their fascinating properties and applications in a variety of important fields like nanoelectronics, lithium-ion batteries, and solar cells, carbon nanotubes (CNTs) and silicon nanowires (SiNWs) are the most suitable candidates whose properties can be coupled to have a widespread impact [7–10]. Among the promising nanoelectronic applications, field emission is of great interest in vacuum microelectronic devices, such as field emission displays, microwave devices, and X-ray sources [2]. Reports have shown that CNT-based field emitters exhibit excellent field emission properties due to its superior thermal and electrical characteristics. However, the wire number density of as-grown vertically-aligned CNTs is usually around 10^{10} wires/cm^2 [11]. Such a dense CNT structure would suffer from so-called electrostatic screening effect provoked by the proximity of neighboring wires which results in limited field emission performance. Alternatively, a pillar array of aligned CNT bundles grown by chemical vapor deposition (CVD) and patterned by photolithography was used to release the electrostatic screening effect [12]. In this case, every CNT bundle is regarded as an individual field emitter due to its high wire-number-density, thus the CNTs inside the bundle do not efficiently contribute to the generation of emission current. Further scaling down the diameter of CNT bundles to increase the number of effective field emitters may require submicron patterning of metal catalysts using complex lithography and lift-off processes for the following CNT growth. Post-patterning as-grown CNTs into bundle arrays could be an alternative solution but the poor adhesion between CNTs and silicon substrate is the roadblock because the CNTs may not be able to withstand for the spin-coating process to deposit the photoresist (PR) layer. In addition, it is also difficult to maintain the verticality of CNT bundles as the bundle diameter shrinks to submicron scale.

Silicon nanowire (SiNW) is also an attractive material for field emission applications not only because of its low work function and sp^3-bonded crystal structure but also due to the mature silicon processing technologies and the possibility to be integrated with other opto-electronic devices [1–5]. However, since SiNWs inherently have the drawbacks of poor thermal conductivity and oxidized surface, SiNW-based field emitters usually have high turn-on electric field and low

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emission current. Dense SiNW array also suffers from serious electrostatic screening effect. Recently, SiNWs with modified morphologies were fabricated aiming to release this issue [1,3,4]. However, none of them tried to solve the problem by forming an array of aligned SiNW bundles, which similar idea has been applied in CNT material system for realizing high performance field emitters [12]. For field emission applications, the use of CNTs as the emitter material would benefit from its metallic-like property and high thermal conductivity while the advantages of using SiNWs would be the availability of mature and flexible processing technologies for silicon and the possibility to be integrated with other optoelectronic devices. As a result, recently researchers focus on the synthesis of hybrid CNT–SiNW heterojunction array in order to take the advantages from both material systems for breakthrough findings in not only high-performance electron field emitters but also many other emerging technologies [7–10].

In this work, we firstly focus on the synthesis of an array of vertically-aligned SiNW (VA-SiNW) bundles, aiming to release the electrostatic screening effect and to boost its emission current. A sequence of fabrication procedure is developed to make this material feasible for practical production over a large wafer area, as shown in Fig. 1(a). Instead of bottom-up vapor–liquid–solid growth method, VA-SiNWs are realized by top-down metal-induced etching process using a thin silver film as the catalyst [13]. A top-down scheme for post-patterning the as-fabricated SiNWs is proposed and demonstrated by means of simple photolithographic patterning and chemical etching processes such that mesa-type arrays of VA-SiNW bundles could be realized. The verticality of SiNW bundle is therefore independent of the bundle dimension. The bundle arrangement of SiNWs is optimized in order to boost the field amplification by maximizing the field enhancement factor. To investigate if the existence of SiNWs inside the bundles can contribute to the field emission, an array of planar silicon bundles with the same orientation is also fabricated for comparison, as shown in Fig. 1(b). We realize that CNT is inherently a superior emitter material but is difficult to be processed with flexibility. Instead of using CNTs as both field emitter material and supporting structure to obtain certain aspect ratio in conventional CNT bundle arrays, this work then proposes to use vertically-aligned SiNWs as the supporting structure while CNTs only serve as the emitter material, as shown in Fig. 1(c). The main advantage of this proposed hybrid material is the possibility for further scaling down the diameter (periodicity) of the bundles (bundle array) while maintaining the verticality of the supporting structure. In this case, the underlying SiNW bundle array serves as a structured template for the growth of coarse CNT mats on their top surfaces. With proper design in SiNW bundle array such as the inter-bundle distance, bundle diameter and height, the electrostatic screening effect in this hybrid material could be reduced. Though the electric field on the SiNWs is shielded by the CNTs such that the SiNWs may not be able to contribute to the emission current, the existence of SiNWs beneath would enables the growth of coarse CNTs with lower wire-number-density. The wire-number-density of as-grown CNTs atop SiNWs is expected to be lower than the density of the underlying SiNWs which is at least one order of magnitude lower than the density of CNTs grown on flat silicon surface [11]. Generated emission current from coarse CNTs as the emitters atop SiNW bundle array would be enhanced due to the release of electrostatic screening effect that typically limits the emission performance in dense CNTs [5]. The comparison of field emission characteristics among planar SiNWs, an array of SiNW bundles, planar CNT–SiNW heterojunction and an array of CNT–SiNW heterojunction bundles is conducted to verify the merits of the proposed method.

2. Concepts and experiments

In a typical metal-induced chemical etching procedure, the silicon beneath the noble metal is etched much faster than the silicon without noble metal coverage. As a result, the noble metal penetrates into the silicon substrate, generating pores or wires in the silicon substrate. The synthesis of random SiNWs can be done by immersing clean silicon wafers in metal contained aqueous solution such as $HF/AgNO_3$ [14], or by immersing metal-distributed silicon wafers in oxidizing hydrofluoric acid solution such as HF/H_2O_2 [15]. Ag, Au, and Pt are the most

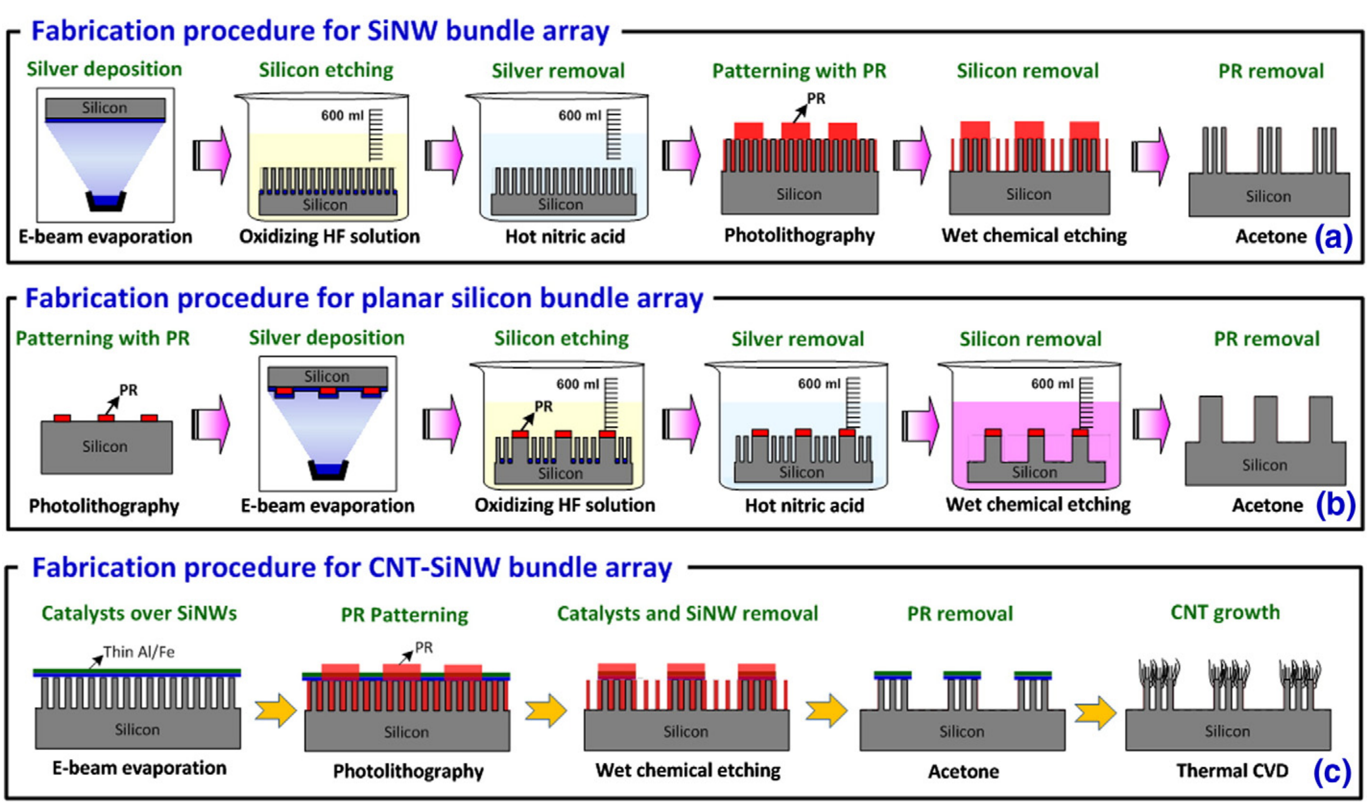

Fig. 1. Fabrication procedure for realizing (a) arrays of SiNW bundles, (b) arrays of planar silicon bundles, and (c) bundle arrays of CNT–SiNW heterojunctions.