Research Letters

Gravity-Assisted Seeding Control for 1-D Material Growth

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***Abstract*—This letter presents a seeding control scheme by utilizing gravity force to form an agglomeration of molten Co seeds on a patterned inverted silicon nanopyramid. Nanometer sized molten Co seeds formed on a nonwettable inverted pyramid surface can roll along the inclination followed by aggregation to form a singular seed with the size depending on the pyramid size and the thickness of as-deposited Co film inside the pyramid. The proposed scheme allowing the formation of well-aligned catalytic seeds with manipulated size will promise the control growth of 1-D material for practical integrated microelectronic device fabrication.**

***Index Terms*—1-D material, 3D-*IC*, gravity-assisted, integrated nanoelectronic circuit, seeding control.**

I. Introduction

RECENT research progress in the synthesis and characterization of 1-D materials has disclosed potential nanoelectronic device fabrication using the materials, such as zinc oxide nanowire with negative electron affinity suitable for room temperature field emitter application [1], carbon nanotube (CNT) with ballistic conductance good for nanoscale field effect transistor fabrication [2], and tin oxide nanowire with surface-state-dependent conductance right for chemical sensor device making [3]... etc. So far, most of the 1-D materials can be massively produced by chemical vapor phase deposition with appropriate catalytic seeds whose size, composition, and formation have been found as deterministic factors to the microstructure and physical property of the 1-D materials [4], [5]. Because precisely catalytic seed sizing and positioning control would be the next deterministic factors to facilitate device fabrication using the typical "top-down" *IC* manufacturing approach, i.e., the synthetic control in forming a group of stand-alone and well-aligned 1-D material on a substrate for device fabrication, it is still desirable to develop a seeding control method to pave the way for the future integrated nanoelectronic application of 1-D materials.

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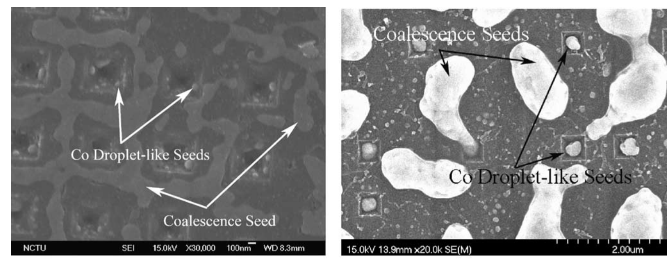


(a) (b)

Fig. 1. SEM micrographs of a 6-nm-thick Co film on a silicon (100) substrate after (a) 800 °C and (b) 900 °C thermal reflow for 10 min, respectively.

Several methods, such as Fe catalyst positioning on a Si pillar array [6], Ni catalytic seed locating in a nonlithographic anodized aluminum oxide (AAO) nanopore template [7], and electron-beam (EB) lithographically seed size and location defining on a blank silicon substrate [8]...etc., have been developed and proposed for the selective growth application of 1-D materials. However, to date, most of the approaches except the EB defining still cannot effectively achieve the required "precise" control in terms of the size, number, and location of catalytic seeds. Even in the EB method, a special lab-made photoresist is required and approximate 10% of the catalyst can be activated for subsequent material growth. Thus, in this paper, a seeding control scheme is proposed and demonstrated by employing gravity force to form an agglomeration of molten Co seeds within a patterned inverted silicon nanopyramid. Because this approach could ensure a group of well-aligned catalytic seeds with fixed size, it is our belief that this technique will be useful for future 1-D material growth control and practical for integrated nanoelectronic device fabrication.

II. Seeding Control Scheme

Fig. 1 shows SEM micrographs of a 6-nm-thick Co film on a silicon (100) substrate after 800 °C and 900 °C thermal reflow for 10 min, respectively, in a chamber purged with $\mathrm{Ar/H_2}$ mixture. The silicon substrate has been micromachined to form inverted 400×400 nm^2 nanopyramids with 1 μm spacing in between. In general, a catalytic metal film should be deposited followed by a thermal reflow on a substrate prior to the growth of 1-D materials from the chemical vapor deposition [4], [9]. During reflowing, the catalytic film would form a group of tiny droplet-like seeds or the coalescence of seeds randomly dispersed on the substrate. However, if these seeds are just formed on the inclined surface of the inverted nanopyramids, which is Si $\{111\}$ plane with a slope of 54.7°, gravity field would exert a force on each seed along the inclination and possibly make the seeds merged to form a large seed right at the bottom of the pyramid. For a several or several 10-nm-thick catalytic seed layer, the average seed diameter right after thermal reflowing is around 45 nm [9]. According to the previous study on the movement of droplet on an inclined surface [10], the nm-sized droplet-like seed would just fall into the regime, where surface tension dominates gravitational force. Since Carter *et al.* have reported that silicon surface is hydrophobic to molten Co [11], the shape of the nm-sized Co-droplet on a horizontal surface can be assumed to be nearly spherical, and the contact length of the droplet to silicon substrate l is

$$l \cong \left(\frac{\rho g}{\gamma}\right)^{1/2} R^2 \quad (1)$$

where γ, R, ρ, and g are the surface tension, radius, density of the liquid droplet, and the acceleration of gravity, respectively. Thus, the onset of droplet rolling along the inclination with an angle of ϕ will be triggered as long as the following condition derived based on force equilibrium is satisfied [10]:

$$R \leq \frac{1}{3\sqrt{5}}\sqrt{\frac{\gamma}{\rho g}}\sqrt{\frac{\sin 2\theta}{13 + 12\sin\phi}} \quad (2)$$

where θ is the contact angle of the molten Co on silicon substrate. For instance, for the measured value of surface tension and contact angle of the molten Co on silicon substrate at 1514 k, which are 0.23 N/m and 121°, respectively [12], [13], the maximum radius of liquid droplet for rolling along the Si (111) plane ($\phi = 54.7°$) is about 0.1 mm, which is much larger than the size of the Co droplets formed on the surface of inverted silicon pyramid, indicating that all Co droplets can roll down to the bottom of the pyramid for aggregation. Meanwhile, for the case of rolling droplet, the speed of droplet moving along an inclination v can be calculated as follows:

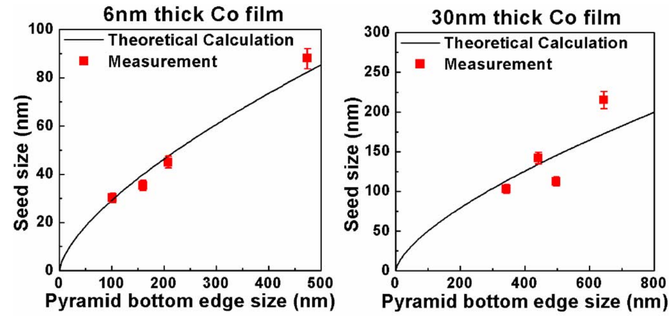
$$v \sim \frac{\gamma^{3/2}\sin\phi}{\mu R(\rho g)^{1/2}} \quad (3)$$

where μ is the viscosity of the Co droplet and can be estimated using the following equation [12]:

$$\mu \sim 0.033\exp\left(\frac{8.2\times 10^5}{RT}\right)\ \text{mPa·s} \quad (4)$$

Therefore, the rolling speed could be enhanced by slightly raising the reflowing temperature for a shorter reflow time for the seed aggregation. In comparison with the two morphologies, as shown in Fig. 1(a) and (b), the appearance of singular seed instead of sparsely distributed Co seeds in the inverted pyramid confirms the tendency via 100 °C reflowing temperature increase.

In addition to the coalescence of seeds at the bottom of the inverted pyramid to achieve the unity and localization of catalytic seed, the seed size could be controlled by the thickness of the deposited Co and the size of the inverted pyramid. In the experiment, a variety of inverted pyramids whose bottom edge lengths ranging from 100 to 500 nm are fabricated on a silicon (100) substrate using KOH silicon-etching technique [14]. The silicon substrate is then deposited with either a 6- or 30-nm-thick Co film for characterizing the correlation between the average size of Co seed, the size of inverted pyramid, and the thickness of deposited Co. Fig. 2 shows the experimental results in which both types of silicon substrates are thermally annealed at 900 °C for 10 min. The results indicate that thinner Co film [6 nm, Fig. 2(a)] deposited on a smaller pyramid produces a smaller catalytic seed, which is about 30 nm in radius in an inverted pyramid with a bottom edge of 100 nm. The seed size is estimated by the law of mass conservation. It is assumed that all the coated Co film on the surface of inverted pyramid would melt, reflow, and agglomerate to form a singular seed at the bottom of the pyramid. Thus, the radius of seed coalescence (R) can be calculated as follows:



(a) (b)

Fig. 2. The bottom length of inverted pyramid versus the size of agglomerated Co seed formed inside. (a) 6-nm-thick Co film deposition. (b) 30-nm-thick Co film deposition. Both substrates are thermally annealed at 900 °C for 10 min.

$$R = \left[\frac{3\sqrt{3}}{4\pi}tL^2\right]^{\frac{1}{3}} \quad (5)$$

where L and t are the bottom edge length of inverted pyramid and the thickness of deposited Co film, respectively. As shown in Fig. 2, the calculation provides a good size prediction, suggesting the seed size can be further reduced by reducing the thickness of deposited Co and the size of pyramid.

Thus, a seeding control scheme from the aforementioned inferences is proposed as follows: A 500-nm-thick plasma enhanced chemical vapor deposited (PECVD) oxide deposited on a (100) Si wafer is coated with a 200-nm-thick ZEP520A photoresist lithographically patterned by EB followed by reactive ion etching (RIE) oxide etching to form an opening for following KOH anisotropic silicon etching. The size of oxide opening, which is related to the lower limit of bottom length of the inverted pyramid, should be controlled as smaller as possible. After KOH silicon etching, the substrate is then sputtered by a layer of Co film followed by thermal anneal at high temperatures with a reasonable time frame (e.g., 1050 °C, 10 min). At last, a singular Co seed can form right at the bottom of the inverted pyramid after removing the surface oxide mask by HF etching.

III. Measurement and Discussion

Fig. 3 shows the Auger line scanning spectrum across a singular Co seed at the bottom of the inverted pyramid formed by

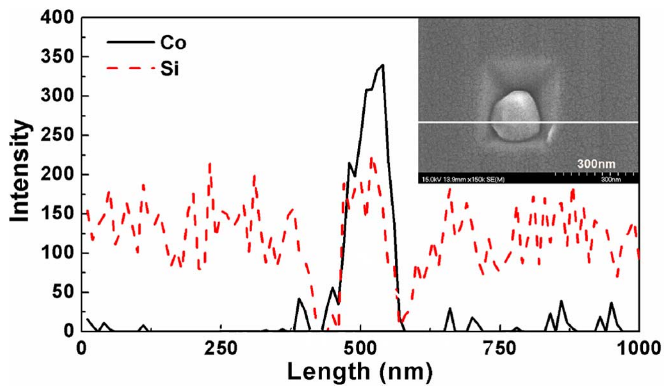


Fig. 3. Auger line scanning spectrum across the region shown in the inset. The inset is an enlarged SEM view on an inverted pyramid with the bottom length of 300 nm inside, which a singular Co seed is formed with the size of 150 nm in diameter.

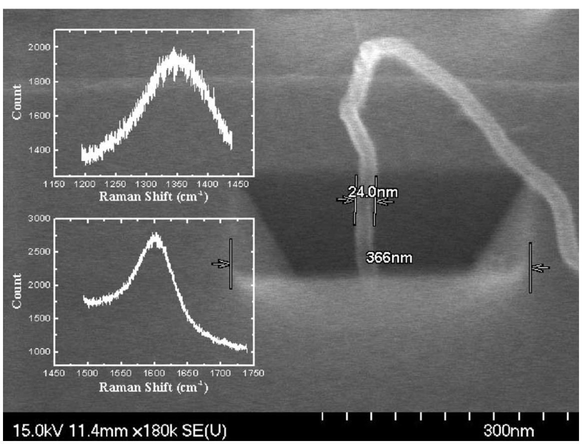


Fig. 4. SEM micrograph of a singular CNT grown from a Co seed formed by the proposed seeding scheme, which is reflowed with a 6-nm Co-seed layer. The insetted Raman spectrum indicates the CNT is a multiwalled carbon nanotube.

the proposed seeding control scheme reflowed with a 30-nm Co-seed layer. The detected 774 eV of Co and 1617 eV of Si signals shown in the spectrum as well as the SEM inset validate the seeding control scheme confirming a singular Co seed with the size of 150 nm in diameter located inside an inverted pyramid with a bottom length of 300 nm. Fig. 4 shows SEM micrograph of a singular CNT grown from a Co seed formed by the proposed seeding scheme, which is reflowed with a 6-nm Co-seed layer. The CNT is grown under the conditions of a reduction treatment at 600 °C for 10 min with mixed gases of H_2 (250 mL/min) and Ar (250 mL/min). Then, C_2H_4 is introduced for another 2 min for CNT synthesis at 850 °C. The respective flow rates for the Ar, H_2, and C_2H_4 are 375, 100, and 25 mL/min, respectively. The insetted Raman spectrum of $1350\ \mathrm{cm}^{-1}$ of D mode and $1598\ \mathrm{cm}^{-1}$ of G mode peaks indicate the grown singular CNT is a multiwalled tube that could be resulted by large seed size. Nevertheless, the size can be further reduced for single-walled CNT synthesis applications via high-temperature anneal in a pure Ar ambient to make a part of seed vaporize [15].

The aforementioned model to describe the movement of Co droplet along an inclined surface is based on the condition of droplet rolling instead of sliding, which is, in fact, the only way to realize the ultimate agglomeration of Co seeds like the phenomenon we have shown in Fig. 3. According to (2), the droplet cannot roll along the inclination once its size is larger than a critical value. In that case, the large droplet will be locally deformed by gravity to form a corner shaped droplet and then stick on the inclination to prevent the formation of agglomeration due to the force balance between the surface tension, gravity, and friction force applied on the droplet [16]. Because the purely rolling behavior is associated with the size, density, and surface tension of the droplet and the interfacial energies of the droplet to the contact surface material, and it only happens while the liquid droplet flows with minute Reynolds and Capillary numbers both indicating low movement speed of droplet [11], further investigations are required for process optimization and seed size control to ensure the unity of Co seed, such as the characterization of the temperature-dependent viscosity and surface tension of liquid Co to the surface of inverted silicon nano-pyramid, the correlation of Co droplet size distribution to the thickness of deposited film at different thermal reflowing temperature, and the reflowing time control for low rolling speed.

IV. Conclusion

The unity and localization of the catalytic seed for the 1-D material growth application has been realized by utilizing the effects of gravity force on the nanometer-sized liquid seeds to form an aggregated singular seed in a patterned inverted silicon nanopyramid. Rolling along an inclined surface is the key mechanism to the coalescence of seeds at the bottom. Experimental results confirm that by well adjusting the thermal reflowing temperature and process time of the catalytic film deposited on the pyramid, the size of the aggregated seed can be controlled by the deposited film thickness and the pyramid size.

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