Review of the Preparation and Structures of Si Nanowires, Ge Quantum Dots and Their Composites

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Because the motion of charge carriers in nanowires and quantum dots is restricted within nanoscale in two and three dimensions, respectively, both nanowires and quantum dots exhibit many excellent optoelectronic properties. Particularly, with the advantage of being compatible with Si integrated circuits, Silicon nanowires (SiNWs) and germanium quantum dots (GeQDs) have been extensively studied in the past few decades. In order to explore novel physical properties, the integration of SiNWs and GeQDs has attracted great attention recently. In this paper, recent researches on the preparation methods and structures of SiNWs, GeQDs and their composites are reviewed, respectively. The synthesis of SiNWs with random distribution and ordered arrays by using vapor-liquid-solid growth mechanism and metal-assisted chemical etching technique is firstly summarized. Some special structures of SiNWs are also discussed. Furthermore, the development of some novel structures of GeQDs for further improving their optical properties is reviewed. Finally, the growth mechanism and structure evolution of SiNWs/GeQDs composites are illustrated from the view of theory and experiment. The strain in Ge shell layers and SiNWs, the relationship between Ge growth mode and SiNW diameter, and the distribution of GeQDs on the radial and axial directions of SiNWs are discussed in detail. The research about the growth of SiNWs/GeQDs composite structures is in its early stage, so there are many questions that need to be resolved in future.

Keywords: Silicon nanowire; Ge quantum dot; composite structure; core/shell nanowire; ordered array.

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1. Introduction

With the development of nanotechnology, there are increasing demands for smaller and more efficient nanodevices. However, the properties of nanomaterials comprised of a single structure or substance are often unsuitable for such applications. Therefore, many novel nanocomposite materials have been proposed, such as porous nanowires,¹ core-shell nanowires,^{2,3} and carbon nanotube composite materials.^{4,5} In particular, silicon nanowires (SiNWs) are promising potential materials for future nano-optoelectronic information applications due to silicon's important role in the traditional microelectronic and photovoltaic fields. Recently, Si/Ge core-shell nanowire composites have attracted great attention due to their superior performance. Instead of Ge nanofilm layer, the integration of germanium quantum dots (GeQDs) and SiNWs can combine the characteristics of one-dimensional and zero-dimensional nanomaterials, which have promising applications in nanoscale light-emitting diodes,⁶ photoelectric detectors,^{7,8} solar cells,⁹ field-effect transistors¹⁰ (FET) and thermoelectric energy conversion,¹¹ because of the stronger quantum confinement effect of GeQDs. Fortunately, a comprehensive understanding of the preparation, structure and performance of SiNWs and GeQDs has been gained after several decades of research and exploration, laying a good foundation for the study of SiNW/GeQD composite materials.

Currently, some research progress in SiNW/GeQD composite materials has been achieved. Fukata *et al.*¹² pointed out that, theoretically, the critical thickness of the shell layer for transition of Ge growth mode increases with decrease in the nanowire diameter. The smaller the nanowire diameter, the easier it is for Si/Ge core-shell nanowire structures to form. Li *et al.*¹³ proposed a physical model to interpret the evolution of Ge layer growth on the radial surface of SiNWs with increasing nanowire diameter. They demonstrated that the curved surface of the nanowire is conducive to the release of misfit strain. The growth of GeQDs on the radial surfaces of SiNWs was studied experimentally by Pan and Kwon *et al.*^{2,14} under various conditions. However, their results concerning the critical diameter of SiNWs for the transition of Ge growth mode were inconsistent. This indicates that the growth mechanism of GeQDs on the radial surfaces of SiNWs still needs to be further

researched. For the study of electric properties of SiNW/GeQD composites, Dhungana *et al.*¹⁵ confirmed that transconductance of SiNW/GeQD FET is substantially higher than that of SiNW FET, which suggests much higher carrier mobility in the SiNW/GeQD device.

In order to illustrate the research progress about SiNW/GeQD composites clearly in this review, we firstly summarize the recent research advances in the preparation and structures of SiNWs and GeQDs. Then, the growth mechanism and structure evolution of that composites are reviewed from the view of theory and experiment. Some potential issues and possible development directions of that composites for further research are discussed.

2. Synthesis and Structures of SiNWs

In 1964, silicon whiskers were successfully synthesized by the vapor-liquid-solid (VLS) method,¹⁶ which set the basis for the synthesis of SiNWs. In the mid-1990s, abundant SiNWs with nanoscopic dimensions were prepared by laser ablation (LA) techniques,¹⁷ which triggered great interest in SiNW research. After nearly 30 years of development, SiNWs can be fabricated by bottom-up and top-down approaches. Top-down fabrication methods mainly include various dry and wet etching techniques. Bottom-up approaches principally include LA and chemical vapor deposition (CVD). As shown in Table 1, recent research progress on the preparation and structures of SiNWs has made the following three main achievements: (1) the arrangement of SiNWs can be controlled from a random distribution to an ordered array. The diameter of SiNWs in an ordered array can be controlled at about 10 nm.¹⁸ (2) SiNWs with small diameters and large aspect ratios have been prepared. (3) SiNWs with various structures have been produced, such as porous nanowires, *p-n* nanowire superlattices, tapered nanowires, ultra-thin structures, kinked structures and zigzag structures. Additionally, SiNWs' electrical properties (such as field emission characteristics,¹⁹ single electron effects²⁰ and Coulomb blockade effects²¹), photoluminescence²² and photoelectric properties (such as photoelectric conversion.²³ and photoelectric detection²⁴) have been studied extensively.

Table 1. Main preparation methods and structural characteristics of Si nanowires in recent years.

Method	Year	Ordered arrays	Template	Diameter (nm)	Height (μm)	Aspect ratio	Structural characteristics	Ref.
VLS	1964	N	/	100	/	/	Whiskers	16
	1998	N	/	6–20	1–30	166	NWs	25
	2004	N	/	3–30	/	/	NWs	26
	2017	N	/	10–76	60	/	<i>P-n</i> NW superlattices	27
Template + VLS	2005	Y	NSL	70–90	0.25	3	NWs	28
	2016	Y	KSL	220	17	77	NWs	29
MACE	2008	N	/	20–300	5–150	250–500	NWs	30
	2009	N	/	100–200	50	250–500	Porous NWs	31
	2011	N	/	66–115	5.25	46	Tapered NWs	32
	2015	N	/	6–12	9.6	800–1600	Ultra-thin NWs	33
Template + MACE	2007	Y	NSL	180	5.3	30	NWs	34
	2008	Y	AAO	8–20	0.05	2.5–5	NWs	18
	2009	Y	BC	20	4.4	220	NWs	35
	2010	Y	LIL	550	100	182	Pillars	36
	2011	Y	AAO	35–73	/	/	Smooth NWs	37
	2016	Y	NSL	Sub-20	/	/	NWs	38
	2017	Y	NSL	100–550	4–35	8–120	Pillars, kinked and zigzag NWs	39–41

Notes: Y stands for Yes and N stands for No.

2.1. SiNWs in a random distribution

Currently, metal catalysis is one of the major methods used to grow or etch SiNWs. When the positions of metal particles or thin films distributed on the surface of a Si substrate are not limited, Si nanowires can form randomly.

In metal catalysis-induced growth methods, SiNWs have been synthesized from bottom to top mainly by CVD, MBE and LA techniques based on the VLS growth method.⁴³ The name VLS method refers to the fact that silicon from vapor passes

through a liquid droplet and finally ends up as a solid. Many metals, such as Au, Cu, In, Ga, Ni, Pt and Ti,^{44,45} can catalyze a gaseous silicon precursor (e.g., SiH_4 , Si_2H_6 or SiCl_4) to form SiNWs under certain temperatures. The VLS growth process has two stages: firstly, small liquid metal-Si alloy droplets form on the substrate surface. Secondly, the silicon supplied by the gaseous silicon precursor causes the droplet to become supersaturated with Si until silicon freezes out. This process is schematically presented in Fig. 1. The diameter of the SiNWs

Fig. 1. Vapor-liquid-solid mechanism for nanowire synthesis, (a) schematic of VLS growth of Si NW from a liquid Au catalyst seed, which floats on top of the NW as it grows. (b) Enlarged view illustrating the kinetic steps for NW growth. Reprinted with permission from Ref. 42. Copyright 2010 Chemical Reviews.

is determined by the size of the metal-Si, their length is decided by the flow velocity and reaction time.

One of the advantages of VLS growth is that the diameter of SiNWs can be controlled below 10 nm. Based on the VLS growth method, Wu *et al.*²⁶ prepared monocrystalline SiNWs with diameters of 3–30 nm using CVD technique. They demonstrated that the growth directions of SiNWs are dependent on their sizes. The smallest diameter SiNWs grew along $\langle 110 \rangle$ direction, while the larger SiNWs grew along $\langle 111 \rangle$ direction. SiNWs with a diameter of 10 nm and length $> 1 \mu\text{m}$ were also obtained by the LA technique.⁴⁶

The VLS growth mechanism also allows for precise control of the composition and doping of SiNWs at nanoscale, which is a benefit for fabricating SiNW device with p - n junction.^{5,27,47} Usually, p - and n -type doping of SiNWs can be performed during the VLS growth process using CVD by introducing the diborane and phosphine, respectively, in addition to the silane. Compared with the phosphorus doping of SiNWs, there are many problems in boron doping of SiNWs, such as morphological changes or amorphous shell overgrowth.²⁷ Because boron can serve to catalyze the decomposition of silane (SiH_4) under proper conditions, resulting in the increase of radial growth rate and overgrowth of a Si shell on nanowire sidewall. The sidewall becomes rough due to the gold-cluster migration from the main catalyst during the overgrowth process. Hydrogen chloride (HCl) was employed to improve the surface morphology of p - and n -doped SiNWs. The SiNWs with smoother surface and reduced tapering

were observed by Gentile *et al.*⁴⁷ after using the HCl with dopant gases, which was attributed to the limitation of gold diffusion from the catalyst. This approach provides a valuable solution for limiting the gold contamination in SiNWs. The gold contamination is harmful for the performance of nanowire device, because it will create traps and reduce minority carrier lifetimes.⁴⁸

Recently, Hill *et al.*²⁷ explored the effect of temperature and HCl: SiH_4 ratio on the p -type SiNW growth. As shown in Fig. 2, as the HCl flow is low and the temperature is below 700°C in region I, the overgrowth of Si shell occurs, leading to the appearance of tapered SiNWs with bases thicker than the original catalyst diameter. In region III, higher HCl flow over the same temperature regime, SiNW grows slowly. Between these two regimes is region II, where reliable SiNW nucleation and stable growth is achieved. In region IV, unstable SiNW growth is observed. The temperature-dependent kinetics of Si chlorination provide a basis for understanding the origin of the different growth regimes.

Metal-assisted chemical etching (MACE)⁴⁹ has been proposed as another preparation method of SiNWs due to its low-cost fabrication process with easy controllability and reproducibility. In this technique, the Si atoms under the noble metal are oxidized due to hole injection, where a rapid etching rate of Si is observed in $\text{HF}/\text{H}_2\text{O}_2$ solution. Hence, the diameter of the nanowires is dependent on the size of the noble metal particles and their length is determined by the etching solution and etching time.

Fig. 2. (a) Qualitative analysis of p -type NW growth conditions depended on temperature and HCl: SiH_4 ratio. (b) Dark-field microscopy images (left) and schematics (right) exemplifying NWs grown in regimes I–IV, scale bars, $4 \mu\text{m}$. (c) Schematic of the microscopic chemical process that can occur during p -type NW growth. Reprinted with permission from Ref. 27. Copyright 2017 ACS Appl. Mater. Interfaces.

In 2008, Zhang *et al.*⁵⁰ investigated the influences of different Si substrates and different etching conditions on the structural characteristics of SiNWs. The nanowires obtained after etching p-Si (100) substrates are perpendicular to the silicon substrate. While, the angle between the nanowire and the Si substrate is about 40°, as the crystal orientation of the substrate with (111) direction was selected. In addition, the effects of the etching solution's H₂O₂ concentration on nanowire morphology and density are important. The higher the H₂O₂ concentration, the faster the etching reaction, leading to more Si being dissolved.

At present, one of the major researches on the preparation of SiNWs using the MACE method is focused on how to obtain SiNWs with small diameter and large aspect ratio. Honchbaum *et al.*⁵¹ prepared SiNWs with diameters ranging from 20 to 300 nm and aspect ratios of up to 500 by using an AgNO₃ and HF acid mixture. However, the distribution of nanowire diameters was large and the size uniformity was poor. In 2015, ultrathin SiNW arrays were fabricated by Tan *et al.*³³ using ion beam-assisted chemical etching. As shown in Fig. 3, the average diameters were less than 10 nm and the aspect ratios reached 1600. In their experiment, after implanting Ag ions into the thin Au film, which was grown on the surface of the Si substrate, large quantities of Au–Ag particles were formed beneath the surface of the Si substrate at an appropriate dose. These Au–Ag particles were used as catalysts in MACE for fabricating SiNWs. It can be

seen from Fig. 3(c) that the diameters of SiNWs were distributed between 6 nm and 12 nm, which shows that the SiNWs had a uniform distribution of diameters. And the ultrathin SiNWs could be easily gathered together due to the ultra-large aspect ratio. In this technique, ion implantation was employed to disperse Au–Ag alloy catalysts into the Si substrate, which will greatly reduce the size of the catalysts. In addition, one-dimensional porous SiNWs were also prepared by a one-step MACE method to etch *p*-doped Si substrates.³¹ This nanostructure was used as the anode of a lithium-ion battery, which had fast charge–discharge and superior cycling performance due to the high surface area of the anode.¹

2.2. Ordered Si nanowire arrays

The preparation of ordered Si nanowire arrays has become a research hotspot because the photoelectric properties of nanomaterials in ordered arrangements can be improved significantly due to the collaborative effect and coupling effect.⁵² Additionally, nanowires in ordered arrays are separated by a certain distance rather than being gathered together. This lays a good foundation for exploring the modification of SiNWs by cladding them with another material.⁵³

A template is necessary to prepare well-organized nanostructures in ordered arrangements. The quality of the template determines the diameter and uniformity of the ordered SiNW arrays. Currently,

Fig. 3. (a) A top view SEM image of the ultra-thin SiNWs fabricated using IBCE. (b) The cross-sectional SEM image of the ultra-thin SiNWs. (c) A higher magnification SEM image of the SiNWs. The inset shows the diameter distribution of these SiNWs. (d) A HR-TEM image of a SiNW obtained using IBCE. Reprinted with permission from Ref. 33. Copyright 2015 Nanoscale.

common templates for the fabrication of ordered SiNW arrays mainly include anodic aluminum oxide (AAO) templates, photolithography masks, and nanosphere templates.

De *et al.*⁵⁴ pointed out that it is easy to fabricate perfectly-ordered SiNW arrays in an area of several square centimeters by the laser interferometric lithography (LIL) technique. With more advanced equipment, a defect-free pattern can be gained on the whole 300 mm wafer.⁵⁵ In Fig. 4, the shape of these Si nanowires is appropriately square and the periodic pattern is not limited to being hexagonally symmetric, which makes them suitable for use in electronic and thermoelectric devices. In their experiment, the diameters of the Si nanowires ranged between 65 nm and 350 nm and had a surface density greater than $2 \times 10^7 \text{ mm}^{-2}$.

Park *et al.* proposed a bottom-up approach to fabricate ordered SiNW arrays using Au nanodisks formed by combining KrF stepper lithography (KSL) and CVD followed the VLS mechanism.²⁹

Fig. 4. (a)–(c) Laser interference lithography (LIL) combined with O_2 plasma etching is employed to produce arrays of photoresist posts. (d) Metal evaporation, (e) lift-off and (f) metal-assisted etching leads to vertically aligned arrays of Si nanowires, shown in (g). The wires have a diameter of around 350 nm, a periodicity of 710 nm and a length of several micrometers. The TEM image in (h) shows the foot of a nanowire and the substrate. The high-resolution magnification in (i) proves that the wire and substrate form a single crystal. The scale bars are 2 μm , 10 nm and 5 nm in (g), (h) and (i), respectively. Reprinted with permission from Ref. 54. Copyright 2010 Nanotechnology.

The KSL technique can obtain nanometer-to-micrometer-scale patterns in an area of 1 cm^2 . The SiNWs arrays in a perfect hexagonal array were obtained with the diameter of 220 nm and length of 17 μm , as shown in Fig. 5. The smooth surface, straight morphology and single-crystalline of SiNWs have been proved by TEM.

Although large-area and highly-ordered SiNW arrays have already been obtained by the LIL and KSL technique, these techniques still require expensive equipment and complicated processes, which impedes the application of ordered SiNW arrays. Therefore, reducing cost becomes another expected breakthrough. Many other techniques are proposed, such as nanosphere lithography (NSL), and AAO template method.

Kim *et al.*³⁷ studied the influences of an Au/Ag bilayered metal mesh on the surface morphology of nanowires by combining the AAO template and MACE method. Often, Ag can be anodically dissolved in an etchant solution containing an HF and

Fig. 5. (a) 20° tilt-view SEM image of v-SiNW arrays having high fidelity in large area. (b) Low-magnification TEM image of a SiNW. Inset of (b) shows the SAED pattern indexed for single crystalline Si. (c) HRTEM image taken from the area designated in (b). Reprinted with permission from Ref. 29. Copyright 2016 Chem. Asian J.

H₂O₂ mixture, leading to SiNWs' surface roughening.^{50,56,57} To solve this problem, they proposed a novel metal mesh structure with an Au/Ag-stacking configuration. In this structure, Ag film contacts the polished surface of the Si substrate. During MACE reaction, Au is inert against oxidative dissolution in a solution of HF and H₂O₂. Thus, the upper Au layer effectively prevents not only undesired structural disintegration of the underlying Ag layer, but also tapering of the SiNWs. Furthermore, Au film can still act as a catalyst for H₂O₂ decomposition on an Ag surface. Figure 6 shows that the surface of the SiNWs is relatively smooth, and the sizes of the nanowires at the top and bottom are consistent without showing a tapered morphology. This is attributed to the inert nature of the Au layers in the bilayered metal mesh against anodic dissolution.

To gain smaller SiNWs in ordered arrays, Huang *et al.*¹⁸ prepared ordered SiNWs arrays with an average diameter of about 10 nm by controlling the pore size in the AAO template and the metal thickness. The distribution of these diameters ranged between 8 nm and 20 nm, and their surface densities were up to 10¹⁰ cm⁻². The surfaces of the

SiNWs are smooth, but the uniformity of nanowire heights is poor.

NSL is another potential technique for fabricating ordered SiNW arrays and has the advantages of low cost and simple operation. This approach starts with the self-assembly of a monolayer of polystyrene (PS) spheres arrayed on a Si substrate. The pattern of this array has a hexagonal close-packed structure. Fuhrmann *et al.* fabricated the ordered arrays of SiNW by using NSL without reducing their size and MBE followed the VLS mechanism.²⁸ Gold was directly deposited on the hexagonal close-packed nanosphere arrays. After annealing, the nanosphere was removed and ordered arrays of gold particles was formed. With the deposition of Si atoms by MBE, SiNWs with diameter of 70 nm and length of 250 nm were synthesized by the catalysis of gold. The arrangement of SiNWs displays a hexagonal structure.

In addition, the size of PS spheres in the arrays can be reduced by reactive ion etching (RIE),³⁴ plasma etching⁵⁸ or ion beam etching,⁵⁹ which transfers the close-packed spheres into nonclose-packed ones. In this way, the size of SiNWs and

Fig. 6. SEM micrographs of (a) AAO membrane and (b) Au/Ag bilayered metal mesh. (c) Typical plan-view SEM image of extended arrays of vertically aligned SiNWs obtained by MaCE of Si(100) wafers by using Au/Ag bilayered metal mesh. (d,e) Cross-sectional SEM images of vertically etched Si(100) wafers, showing SiNWs with different diameters; (d) 63.9 ± 9.2 and (e) 39.5 ± 4.2 nm. (f) A magnified cross-sectional SEM image of a vertically etched Si(100) wafer taken near the etching front. (g) Histogram showing the diameter distribution of SiNWs shown in panel c, together with a Gaussian fit (solid line) of the measured statistical data. Reprinted with permission from Ref. 37. Copyright 2011 Acs Nano.

interval distance between SiNWs can be modulated according to the need of experiment. In 2007, Huang *et al.*³⁴ fabricated larger scale SiNW arrays with controlled nanowire diameters, lengths and densities. In their research, the diameter of the PS nanospheres decreased from 360 nm to 180 nm by adjusting the time of RIE. The length of nanowires increased from 1.3 μm to 5.3 μm with an increase of MACE etching time. However, after the diameter of the PS spheres decreased to nearly 50 nm, the morphology of the nanospheres became irregular rather than circular, which is disadvantageous for the preparation of SiNWs with uniform shape. In order to gain small diameter nanowires, Li *et al.*³⁸ proposed a novel method combining chemical etching and thermal oxidation. In their experiments, SiNWs with diameters of 95–200 nm were first prepared by the conventional NSL technique. After oxidizing, the SiNWs at 950°C for 1 h, Si/SiO₂ core-shell nanowires were formed. The SiO₂ shell on the SiNWs was removed by a buffered oxide etching solution (40% NH₄F: 49% HF = 6:1) for 3 min. As a result, vertically aligned, sub-20 nm SiNW arrays were formed. In Fig. 7(a), tapered SiNWs are evident, which may be attributed to accelerated oxidation at the nanowire tip.

Most studies on the preparation of ordered SiNW arrays are focused on the fabrication of vertical and straight nanowires. However, some ordered SiNW arrays with novel structures have been reported recently, such as kinked⁴⁰ and zigzag nanowires.⁴¹ In order to form these nonstraight nanowires, an alternating MACE method was proposed by Chen *et al.*⁴⁰ In this approach, a Si substrate is etched alternately by different types of etchant. By adding some organic additives into the etchant, such as methyl alcohol, ethyl alcohol, 2-propanol or

Fig. 7. (a) SEM image of sub-20 nm SiNWs fabricated after two-step oxidation (at 950°C for 60 min and 20 min, respectively) and SiO₂ shell removal; (b) size distribution of the sub-20 nm SiNWs. More than 150 NWs were counted to obtain adequate statistics; (c) TEM image of a single sub-20 nm SiNW without removing the SiO₂ shell; (d) HRTEM image of a single sub-20 nm SiNW on supporting TEM carbon film after SiO₂ shell removal. The inset is a high-magnification HRTEM image showing lattice fringes. Reprinted with permission from Ref. 38. Copyright 2016 Nanotechnology.

acetonitrile, the etching direction will be changed because organic additives can lower the surface tension of the etchants and decrease the etching rate along the vertical direction. Kinked nanowires with two or more kinks, with segments of the same or different lengths, and with small or large kinking angles, are shown in Fig. 8(a). The number of kinking points is determined by the number of times

Fig. 8. (a) Periodically multiply kinked nanowires with four kinks after changing etchant four times; (b) Zigzag NWs formed in 10 mL of HF, 2 mL of H₂O₂, 5 mL of glycerol and 15 mL of DI water with etching time is 10 min. Reprinted with permission from Refs. 40 and 41. Copyright 2017 Nano Letters and 2017 Nano Letters.

the type of etchant is changed. The angle of the kinks is related to the surface tension and viscosity of the etchant. Moreover, they also developed a diffusion-controlled MACE method to fabricate another form of nonstraight nanowires — zigzag nanowires, as shown in Fig. 8(b). By adjusting the composition of etchant to change its diffusivity, etching direction and etching time, various zigzag nanowires were formed.⁴¹ They found that the etchant's viscosity plays a significant role in zigzag nanowire fabrication.

3. Preparation and Structures of GeQDs on Planar Substrate

Since the dislocation-free GeQDs were proven by Eaglesham and Mo *et al.*^{60,61} via TEM in 1990, GeQDs have attracted wide attention because of their special properties, such as their small band gap, nontoxicity, compatibility with well-developed Si technology and the long service life of their carriers.^{62,63} Over the last three decades, a deep understanding of Ge growth mode, the evolution of island size, density, shape, and the relationship between components and strain under various conditions has been attained.^{60–82} The growth mechanisms of Ge islands have been analyzed using thermodynamic and kinetic theories.^{65–67} Furthermore, by modulating their optical and electrical properties, many photoelectric and electronic devices, such as infrared detectors,⁶⁸ near-infrared light emitting diodes⁶⁹ and single-electron transistors⁷⁰ have been explored.

Some research progress on the microstructural and optical properties of Ge quantum dots over the past five years is listed in Table 2. Clearly, current researches mainly focus on the improvement of

Fig. 9. PL spectra of GeSi QDs with 0.9 nm Ge deposition on a miscut Si (001)/4° substrate at 30, 70, 150, 200 and 300 K. The spectrum at 300 K is multiplied by a factor of 10. The integrated intensity of PL peak versus the temperature is shown in the inset, which is fit by $I(T) = I(0)/[1 + C_1(\exp(-E_1/kT) + C_2(\exp(-E_2/kT))]$. Reprinted with permission from Ref. 71. Copyright 2014 APL Materials.

luminescence properties by acquiring quantum dots with high density, uniform sizes and other special structures. Zhou *et al.*⁷¹ observed a quite strong Photoluminescence (PL) peak of dense GeQDs on a miss-cut substrate even at 300 K, as shown in Fig. 9, which was attributed to the good confinement of excitons in dense GeQDs due to the absence of the wetting layer. The absence of the wetting layer also leads to a transition of the growth mode from the Stranski–Krastanov (SK) mode to the Volmer–Weber (VW) mode. Extremely dense QDs with a density of $2 \times 10^{11} \text{ cm}^{-2}$ were formed on the miss-cut Si substrate with 6°. The steps induced by the miss-orientation of the Si substrate can significantly

Table 2. Statistical results of some research results on the microstructure and optical properties of Ge quantum dots in the past years.

Structure characteristic	Layer number	Year	Density (cm^{-2})	Size (nm)	PL temperature	PL intensity enhanced	Ref.
QDs on miscut substrate	Single	2014	1×10^{11}	/	RT	Y	71
Circularly ordered array	Single	2011	5×10^{11}	40–75	30–200 K	Y	72
Ultrasmall size	Single	2012	/	8	15–100 K	/	73
QDs on RSG virtual substrate	Single	2014	/	/	175 K	/	74
Super-dense array	Single	2014	8×10^{12}	3	/	/	76
QDs+B ions implantation	Single	2014	/	/	/	Y	76
Ge/Si/Ge CQDs	Multi	2015	/	24	/	Y	77
3D QD crystals	Multi	2015	8×10^{10}	/	/	Y	78
QDs+Ge ion bombarded	Multi	2017	/	/	RT	Y	79
Disk + small laterally ordered	Multi	2017	/	50–140	RT	/	80

reduce the surface diffusion length of adatoms and favor the formation of dense GeQDs.

In 2015, Kuo *et al.*⁷⁷ designed a novel structure with multifold Ge/Si/Ge composite quantum dot (CQD)-stacked heterostructures, which was able to effectively suppress dislocation generation in superlattice materials. The structure of multifold CQD is shown in Fig. 10. Multifold CQD refer to the overlapped growth of Ge and Si layers in a single quantum dot. Unlike traditional Ge quantum dots, a Si spacer is inserted into two Ge layers in a double-fold CQD. The interface between the Ge and Si layers is kept clear by controlling the growth parameters. Similarly, three layers of Ge thin film are separated by two layers of Si spacer in a triple-fold CQD. These multifold Ge/Si/Ge CQD were employed to grow 40-period multilayered quantum dots with a 50-nm thick buffer layer. PL spectra show that increases in the fold number per stack in the CQD-stacked heterostructures significantly improve the PL intensity with invisible PL

broadening, whereas the TO/NP peaks from the Si spacer layer become weaker. Based on these CQD, a visible-to-near-infrared photodetector for optical interconnect applications was produced. Typical responsivity values of this photodetector at 850 nm and 980 nm are 250 mA/W and 204 mA/W, respectively. The responsivity of the CQD/Si photodetector at 980 nm is greater than that of commercially-available silicon photodetectors. Improvements in photocurrent, photoresponsivity and external quantum efficiency are attributed to increased Ge volume, which facilitates efficient absorption and enhances the built-in E -field resulting from photocarrier confinement within the CQDs/Si system.

In 2017, Groiss *et al.*⁷⁹ observed that the PL intensity could be improved as epitaxial GeQDs were bombarded with Ge ions in vertically stacked samples. In their design, one to two Ge ions impinged on a single quantum dot, creating an amorphous region with a depth of a few nanometers. During growth

Fig. 10. CTEM micrographs, schematic structural diagrams and energy band diagrams of triple-, double-, and single-fold Ge/Si CQD heterostructures. Reprinted with permission from Ref. 77. Copyright 2015 Optical Letters.

process, these amorphous regions partly recrystallized by solid phase epitaxial regrowth (SPER) starting from neighboring QD regions that remained crystalline. Based on the design of Ge ion-bombarded epitaxial Ge quantum dots (GIB-QDs), 11-fold multi-stack samples were prepared to study the influence of the growth temperature of the Si spacer layers on the PL properties. As shown in Fig. 11, for samples grown at 350–500°C, no PL signal is present. It shows that SPER breaks down as the temperatures are too low. The carriers are depleted by the abundance of nonradiative recombination centers resulting from dislocation. However, a strong PL peak can be observed at room temperature at the temperatures of 500–600°C. The PL intensity for an 11-layer GIB-QD stack is 650% higher than that for single-layer samples. When the temperature is higher than 625°C, the extended point defects can migrate out of the GIB-QD, leading to PL quenching.

In addition, the growth of GeQDs on concave substrate surface and/or convex substrate surface has also been studied with theory and experiment,^{83–85} which lays a good foundation for exploring the growth of GeQDs on the sidewall of SiNWs. Li *et al.*⁸⁴ developed a theoretical model to elucidate GeQDs formation on different curved patterned substrate surface. They pointed out that

Fig. 11. Room-temperature PL spectra from a single layer of GIBQDs (gray) and from a 11-fold multi-stack (blue) for which TSi was 500–600°C. For the multi-stack sample for which the growth parameters were not optimized (TSi=350–500°C), no PL signal was recorded (red) (color online). Reprinted with permission from Ref. 79. Copyright 2017 Semiconductor Science Technology.

the formation energy of GeQD on a convex substrate was lower than that on a planar and concave substrate surface, as shown in Fig. 12, when the occupancy area of GeQD was larger than the periodicity of the patterned substrate surface. It suggested that the formation of GeQD on a convex substrate surface was more favorable. Conversely, when the occupancy area was smaller than the periodicity of the patterned surface, the formation

(a)

(b)

Fig. 12. QD formation energy as a function of QD volume on three different substrate surface curvature, -0.01 nm^{-1} (blue line), 0 (black line), and 0.01 nm^{-1} (red line). (a) Occupancy area by QD is larger than the periodicity of the patterned substrate surface; (b) occupancy area by QD is much smaller than the periodicity of the patterned substrate surface. In our calculation, the shape of QD is pyramid and contact angle $\alpha = 11.3^\circ$. According to the geometrical relations, shape factors, A_1 , A_2 and A_3 , can be given by $A_2 = (6/\tan\alpha)^{2/3}$, $A_1 = A_2/\cos\alpha$, $A_3 = 0.9922 \tan\alpha$ (color online). Reprinted with permission from Ref. 84. Copyright 2013 Physical Chemistry Chemical Physics.

energy of GeQD on a concave substrate surface is lower than that on a planar and convex substrate surface, which suggested that it was more favorable for GeQD to form on a concave substrate surface.

4. SiNW/GeQD Composite Materials

As mentioned above, as typical one-dimensional and zero-dimensional nanomaterials, SiNWs and GeQDs have already been widely studied, which lays a solid foundation for exploring the preparation and structures of SiNW/GeQD composite materials.

In 2000, single-crystal *p*-type and *n*-type SiNWs were prepared by doping boron and phosphorus elements in nanowires.⁸⁶ Based on this, axial *p-n* junction nanowire photodetectors were reported in 2011 by Kim *et al.*⁸⁷ which invoked research interest in SiNW photoelectronic devices. Furthermore, because *p-i-n* junction devices have higher detection sensitivity and luminous efficiency than *p-n* junction devices, as a desirable intrinsic material, GeQDs have great potential to be integrated into SiNW devices. In this chapter, the growth mechanism and structures of SiNW/GeQD composite materials will be discussed from two aspects: QD growth on (1) radial and (2) axial surface of SiNWs.

4.1. Coaxial SiNW/GeQD composite materials

4.1.1. Theoretical studies

It is well known that the growth of a Ge thin film on a flat silicon substrate follows the S-K mode due to

the 4.2% lattice mismatch between Ge and Si. Growth starts in a layer-by-layer mode up to a critical thickness of about 0.4–0.6 nm. Then, the strain energy that accumulates with an increasing thickness of Ge is partially relaxed through the formation of GeQDs.^{13,14} Nevertheless, the radial surfaces of SiNWs are not flat and have a certain nanoscale curvature. Existing theoretical models of the growth of Ge layers on planar and patterned substrates are not appropriate for such growth on surfaces with nanoscale curvatures. Therefore, new theoretical models are urgently needed to understand the basic physics involved in strain-induced growth on the radial surfaces of SiNWs.

In 2012, Fukata *et al.*¹² calculated the stresses in the Si core and Ge shell regions of Si/Ge core-shell nanowires by analyzing X-ray diffraction measurements. Figure 13 shows the evolution of the average lattice constants of Si cores and Ge shells with increasing shell growth time. It can be seen from Fig. 13(a) that the average lattice constant of Si cores is greater than that of bulk silicon and increases with shell growth time. This indicates that Si cores bear tensile stresses, as the Ge shells grow on the radial surfaces of nanowires. The tensile stresses increase with Ge shell thickness. In Fig. 13(b), the average lattice constant of Ge shells is lower than that of bulk Ge and increases with shell growth time. The Ge shell bears compressive stresses originating in the Si core. The compressive stresses are weakened by increasing the Ge shell thickness. These results indicate that the lattice mismatch between Si cores and Ge shells may be less than 4.2%. Consequently, the critical thickness of

Fig. 13. Dependence of the average lattice constant of Si/Ge core-shell NWs on the shell growth time. The lattice constant of (a) the Si core in the i-Si/n-Ge and p-Si/i-Ge core-shell NWs, (b) the Ge shell in the i-Si/n-Ge and p-Si/i-Ge core-shell NWs. (c) Schematic illustration of the stress induced by the formation of Si/Ge core-shell NWs. Reprinted with permission from Ref. 12. Copyright 2012 ACS Nano.

the Ge shell for S-K growth is higher than that of Ge thin film grown on a planar surface. This implies that heteroepitaxial growth on the radial surfaces of SiNWs can accommodate larger stress.

The smaller the nanowire diameter, the larger the stress effects. Thus, the modified growth of the Ge shell strongly depends on the diameter of the nanowires. In 2014, Li *et al.*¹³ established a theoretical model to interpret strain-induced growth on the radial surfaces of SiNWs with increasing nanowire diameters. In their calculations, a two-dimensional layer with a thickness of θ monolayers was considered on a curved surface. The energy required per atom to add a layer from the islands at a chemical potential of μ_{island} is

$$\Delta\mu = \mu_{\text{layer}} - \mu_{\text{island}}, \quad (1)$$

where μ_{layer} is the energy change of the epitaxial layer from n atoms to $(n+1)$ atoms. To minimize the total energy and achieve a stable condition, the system needs to balance the energies of the layer and islands. Therefore, the condition for stability is

$$\mu_{\text{layer}} = \mu_{\text{island}}. \quad (2)$$

If $\mu_{\text{layer}} < \mu_{\text{island}}$, the layer is going to grow thicker, while if $\mu_{\text{layer}} > \mu_{\text{island}}$, the layer will not grow and island growth is favored. The chemical potential of the bulk epitaxial material with no strain is used as the reference value ($\mu = 0$) in order to determine the values of μ_{layer} and μ_{island} . In this case, the energy changes of an epitaxial layer from n atoms to $(n+1)$ atoms is determined by the surface energy and elastic strain energy of the layer:

$$\mu_{\text{layer}} = \Omega\gamma(h)k + \Omega\frac{\partial\gamma(h)}{\partial h} + \Omega\varepsilon_{\text{layer}}, \quad (3)$$

where Ω is the atomic volume, $\gamma(h)$ is the surface energy density of the layer with thickness h ($h = \theta h_0$ and h_0 is the thickness of the monolayer (ML)),⁸⁸ k is the surface curvature and $\varepsilon_{\text{layer}}$ is the elastic strain energy density. The strain energy density can be calculated as $\varepsilon_{\text{layer}} = 2G[(1+\nu)/(1-\nu)]\varepsilon^2$,⁸⁴ where G and ν are the shear modulus and Poisson's ratio, and ε is the strain mismatch of the layer. The first term reflects the influences of surface curvature and the second term represents changes in surface energy with layer thickness. The last term represents the contribution of the elastic strain energy.

Based on the above physical model, they studied the relationship between the growth mode of Ge shell layer on the radial surfaces and the nanowire

Fig. 14. The values of μ_{layer} and μ'_{island} as the function of the Ge layer thickness on the surface of Si NWs with different diameters of (a) 40 nm, (b) 80 nm and (c) 120 nm. The insets in (a), (b) and (c) show the schematic three growth modes, the FM mode, the LIL mode and the SK mode, respectively. Reprinted with permission from Ref. 13. Copyright 2014 Nanotechnology.

diameter. Figure 14 displays the values of μ_{layer} and μ'_{island} as a function of the Ge thickness with various diameters. The chemical potential of a layer is always smaller than that of an island at a diameter of 40 nm. Generally, the growth mode of a Ge thin film is inclined to be one with lower chemical potential. Thus, it is unfavorable to form islands on such thin nanowires. At this moment, the Frank-van der Merwe (F-M) growth mode of Ge film on the radial surfaces of SiNWs is favorable. The Ge shell layer still maintains layer-by-layer growth when the thickness of Ge shell reaches 20 nm. This is different from the growth mode of Ge film on a planar substrate. However, when the SiNW diameter is 120 nm, the growth mode of Ge shells turns to the S-K mode and the critical thickness for the formation of islands on the nanowire is 4 MLs. Differently, the chemical potential curves of Ge film and islands have two intersecting points for the diameter of 80 nm [Fig. 14(b)], indicating that a complicated transition occurs. The growth mode of Ge film transitions from “layer growth” to “island growth” and then to “layer growth” again, so this mode is named *layer-island-layer* (LIL). Furthermore, it is estimated from their calculations that the Ge shell layer exhibits an F-M growth mode when the diameter of the SiNWs is less than 70 nm but turns to the S-K mode with the diameter exceeding 100 nm. The nanoscale curved surface of the nanowires can

help release mismatch strain in a process of *self-relaxation*. Hence, as Ge thin film grows on the radial surfaces of SiNWs, the types of mismatch strain relaxation may include Ge island relaxation, self-relaxation of the epitaxial layer and relaxation of dislocation. The competitions among them determine the growth of Ge shells.

Additionally, the distribution of Ge quantum dots on the radial surfaces of nanowires has also been studied. Schmidt and Wang *et al.*^{89,90} used a surface perturbation model to describe the distribution pattern of GeQDs after depositing Ge thin film on a SiNW backbone. Their calculations show that at certain diameters, the misfit strain in core-shell nanowires can propagate along their length and self-assemble into a periodic pattern that minimizes the total strain energy.^{91,92} As shown at the top of Fig. 15, periodic GeQD arrays in one of

several unique growth modes can be formed due to the initial instability of Ge shell layers. The nanowire diameter determines the distribution of the quantum dots. The periodic strain fields distributed into the core nanowire is corresponding to the distribution of periodic QDs arrays. For example, the alternating coherent strain distributed inside the core is shown at the bottom of Fig. 15. Because the lattice constant of Ge is larger than that of Si, tensile strain (+ signs) is created in Si cores below the interfaces of GeQDs, while compressive strain (− signs) is produced, accordingly, at the opposite side. GeQDs are preferentially formed at the tensile-strained surfaces of Si cores. As a result, an anti-correlated zigzag organization of GeQD arrays is distributed on SiNWs through strain modulation, which reduces the total elastic energy of the system. Besides, the periodic distance (L) between quantum dots at the same side is inversely proportional to the diameter of the nanowires.

Fig. 15. (Top) Schematic of possible surface instability modes of Ge shell on Si core nanowires. Homogeneous Ge shell and four different types of inhomogeneous growth modes are shown: $n = 0, 1, 2$ and 5 . (Bottom) Alternating coherent strain distribution inside the core is shown as + (tensile) and − (compressive) signs for an $n = 1$ mode growth. The QD wavelength L is defined as the periodic distance between QDs on the same side of the wire. Reprinted with permission from Ref. 13. Copyright 2014 Nanotechnology.

4.1.2. Experimental studies

The fabrication of a coaxial SiNW/GeQD composite material was first reported by Pan *et al.*² in 2005. In their experiment, GeQDs were grown on the radial surfaces of SiNWs using the CVD and VLS method. The growth modes of Ge thin films were proven by transmission electron microscopy (TEM). Their experimental results demonstrated that the growth mode of Ge shell layer on the sidewalls of SiNWs was determined by the diameter of the nanowires. The growth of Ge shell exhibited the F-M growth mode when the nanowire diameters ranged between 10 nm and 50 nm, and formed Si/Ge core-shell nanowire structures. However, when the diameters exceeded 50 nm, the Ge shell showed an S-K growth mode and formed a SiNW/GeQD composite structure. This tendency agrees with the simulation results reported by Li *et al.*, but the LIL growth mode was not observed in the experiment. The morphology of GeQDs grown on the radial surfaces of SiNWs with a diameter of 100 nm is shown in Fig. 16. The shape of the GeQDs on the nanowires is asymmetric and their crystal facets are (002), (111) and (112). These facets are different from the facets of quantum dots on the planar surface, which are surrounded by (15 3 23), (113) and (105) facets. Furthermore, several (111) stacking faults and {111} type twins are present in the GeQDs. These stacking faults are likely bounded by

Fig. 16. (a) Bright-field TEM and (b) ADF STEM images of the Ge islands deposited on Si nanowires with Moiré fringes clearly seen. The inset in (b) shows a thin Ge-rich layer at the surface of Si nanowire. (c) The corresponding SADP with extra spots consistent with the Moiré fringes in (a) and (b). (d) Higher magnification TEM image of an island on the same nanowire with the arrows pointing to the misfit dislocations. (e) HRTEM image of an area in (d) with stacking faults and twin boundary (marked by arrows) clearly seen. Reprinted with permission from Ref. 2. Copyright 2005 Nano Letters.

Shockley partial dislocations at the core/island interface that act as misfit dislocations, as indicated by the arrow in Fig. 16(d).

In 2012, Kwon *et al.*¹⁴ reported the first experimental study of correlated GeQD arrays on the radial surfaces of SiNWs and their diameter dependence. Several distinctively different modes of GeQD ordering on SiNWs were observed, such as an anticorrelated pattern, single side growth and the covering of all exposed surfaces. The diameter of nanowires plays an important role in determining the morphology and distribution of GeQD arrays. In Fig. 17, periodic GeQDs arrays with an anti-correlated pattern form when the SiNW diameter is about 20 nm. In anticorrelated patterns, if there is one quantum dot located on the right sidewall of the nanowires, no quantum dots are observed at the opposite position on the left sidewall, while quantum dots can form above or below the opposite position on the left side, as shown in Fig. 18. On the same sidewall, GeQDs are separated by a certain

distance. The formation of an anti-correlated pattern is attributed to modulation of the strain field distributed within the Si core nanowire. As a GeQD is formed on the sidewall of Si core, tensile strain is created within the Si core underneath the quantum dot, and compressive strain is also produced at the opposite position within the core. The region with compressive strain is unfavorable for the growth of GeQDs. As a consequence, an anti-correlated pattern of GeQD arrays presents and decreases the total elastic energy of the system. Similarly, the effects of modulation of the strain field have also been reported in studies of multilayer quantum dot structures. In a multilayer QD sample, the strain field within the Si spacer will modulate the growth of QDs in the upper layer.^{93,94} However, this anticorrelated pattern disappears when the nanowire diameter is less than 15 nm. For nanowires with a diameter of 11 nm, GeQDs only grow on a single side of the SiNWs, as shown in Fig. 17(e), and the nanowires exhibit a bending curvature with GeQDs

Fig. 17. TEM images of Ge QDs on Si nanowires. Both Si core and Ge QDs were grown at 470°C. (a) and (b) Representative TEM images of anti-correlated quantum dots with 20 ± 2 nm core diameters. (c) High resolution TEM showing the defect-free single crystal Si core and Ge island. (d) FFT of the TEM image in (c). Note that the $[0\bar{1}1]$ and $[\bar{1}01]$ FFT spots are composed of twin peak signals (lower inset). (e) and (f), morphology of Ge dots on small (11–13 nm) and large (> 50 nm) Si cores. Scale bar, 50 nm for (a), (b), (d) and (e) and 5 nm for (c). Reprinted with permission from Ref. 14. Copyright 2012 Nano Letters.

on the convex surfaces. Such bending can be attributed to the high flexibility of this thin nanowire. In addition, when the nanowire diameter increases to 57 nm, GeQDs are distributed randomly on all exposed surfaces of the SiNWs [Fig. 17(f)] with an arrangement and density similar to that of GeQDs on planar substrates.

Fig. 18. Evolution of Ge QDs as a function of growth time. (a–c) TEM images showing anticorrelated array of Ge QDs at different Ge growth time; 3.5 min, 5 min, and 10 min from left to right. Scale bars, 20 nm. Reprinted with permission from Ref. 14. Copyright 2012 Nano Letters.

Pan and Li *et al.* reported that the Ge shell layer was favorable to grow in a layer-by-layer mode as Si nanowire diameter is less than 50 nm. However, QDs were still observed with SiNW diameters of about 20 nm in Kw's experiment. These inconsistent results suggest that the growth mechanism of Ge shell on the radial surfaces of SiNWs needs further exploration.

In the above works, both Ge thin films and SiNWs were prepared by VLS method. Possible contamination by noble metals may affect the growth of Ge shell on the sidewalls of nanowires. Thus, Ye *et al.*⁹⁵ also studied the structure of GeQDs grown on the radial surfaces of SiNW by combining MACE and CVD method, instead of VLS. The diameters of SiNWs ranged between 50 nm and 200 nm, and the diameters and heights of GeQDs were 40–70 nm and 14–20 nm, respectively. The GeQDs were distributed randomly on all exposed surfaces of the SiNWs. The size and density of the GeQDs could be controlled effectively by changing the growth parameters. A red shift of the Ge–Ge and Si–Si peaks in Raman spectra was investigated due to the stress and thermal effects.

Generally, a large surface defect density on SiNWs is produced by using MACE method, which is adverse to the growth of GeQDs on the sidewall of SiNWs and the potential application of SiNWs in photoelectronic devices. Therefore, surface defect density should be eliminated as much as possible. Before loading SiNWs into the vacuum chamber for the further growth of GeQDs, Ye *et al.*⁹⁵ adopted the polishing solution and standard Radio Corporation of America (RCA) method to eliminate surface defects and make the surface of SiNW sidewall smooth. In addition to RCA chemical cleaning, Wu *et al.*⁵² also grew a thicker Si buffer layer on the sidewall of SiNW to improve the growth of Ge shell layer.

In 2015, the growth of Ge particles on ordered SiNW arrays was reported by Pan *et al.*¹¹ They, firstly, fabricated the ordered SiNW arrays by combining MACE and NSL technique, and then deposited a polycrystalline layer of Ge on the surface of SiNWs using electron-beam vapor. The TEM image [Fig. 19(h)] showed that Ge particles were randomly distributed on the sidewall of SiNW. The improvement of thermoelectric efficiencies has been proved after Ge particles doping on SiNWs.

However, the growth modulation of GeQDs on ordered SiNW arrays still needs to be further

explored to study their photoelectric properties. The PL efficiency of Si/Ge core-shell nanowires in ordered arrays can be obviously improved by the optical resonance coupling effect (as demonstrated by Wu *et al.*⁵²), which suggests that ordered coaxial SiNW/GeQD composites have great development potential.

4.2. Axial SiNW/GeQD composite materials

In addition to coaxial SiNW/GeQD composite structure, the fabrication of axial SiNW/GeQD composite structure is another important research direction. As we know, SiNWs are a type of one-dimensional material. Therefore, the movement of current carriers on the radial direction of nanowires is restricted while their movement along the axial direction is free. When the thickness of axial heteroepitaxial materials on nanowires is designed to be relatively small, the axial movement of current carriers is also restricted. In this case, the movement of current carriers for heteroepitaxial materials will be restricted in three dimensions, even if no islands can be formed on the axial surfaces of nanowires. This structure can also be defined as axial quantum dot/nanowire composite.

Fig. 19. Fabrication process of Ge-doped SiNWs and the corresponding SEM and TEM images. (a) and (b) Spin-coating of the PS beads (red spheres) on a silicon substrate. (c) and (d) Etching of the PS beads by isotropic RIE. (e) Gold (short yellow lines) assisted chemical etching in HF and H₂O₂ solution. (f) SEM image of the standing SiNWs. (g) Deposition of Ge nanoparticles (black spots) on SiNW. (h) TEM image of the lattice structure of the nanowires. The black spots are Ge particles (color online). Reprinted with permission from Ref. 11. Copyright 2015 Applied Physics Letters.

In 2009, axial SiNW/GeQD composite structure was reported by Wen *et al.*⁹⁶ In order to avoid the interface diffuseness between Si and Ge using VLS mechanism, they synthesized the axial SiNW/GeQD composite structure by using the VSS growth mechanism. Because the VSS growth is impractically slow for conventional Si and Ge reactants, they adopted AlAu alloy catalyst to raise the growth rate

Fig. 20. (a to c) Frames extracted from a movie recorded during growth of a Si nanowire (diameter 28 nm) in 3×10^{-5} torr disilane as the temperature was reduced from 570°C to 503°C: (a) immediately before solidification of the catalyst (507°C); (b) just after solidification (503°C), which is evident from the faceted shape of the catalyst; (c) 14 s after (b), growth rate 5 nm/min. The growth rate is 22 nm/min in the VLS mode at 570°C. (d to i) Formation of a Si-Ge-Si heterojunction in a Si nanowire (diameter 14 nm). The Si nanowire in (d) was first grown at 510°C with 1×10^{-5} torr Si_2H_6 for 2 h and then cooled to 360°C. The faceted surface after cooling indicates the solid state of the catalyst. (e) After flowing 5×10^{-6} torr Ge_2H_6 at 360°C for 1 min, Ge growth has begun and the catalyst has become less sharply faceted. (f) After 7 min, formation of a thin Ge layer that appears as a dark band at the Si-catalyst interface. (g) After 8.5 min of Si growth at 360°C and 1×10^{-5} torr Si_2H_6 . (h) After 14 min of Si growth, the catalyst has resumed the strong facets on its surface seen in (d). (i) For demonstration purposes, the catalyst was exposed to 5×10^{-6} torr Ge_2H_6 at 360°C for 1 min again, resuming the shape seen in (f). The growth rates of the Ge and Si segments measured in (h) are 0.4 and 0.2 nm/min, respectively. The growth direction of the wires is Si[111]. The dark contrast on the Si segment in (g) to (i) is due to conformal deposition of Ge on the Si sidewalls. Reprinted with permission from Ref. 96. Copyright 2009 Science.

of Si and Ge. Firstly, they grew long SiNWs in the VLS mode due to its larger growth rate. Then, a Si-Ge-Si heterostructure is formed by VSS growth mechanism after cooling the growth temperature below eutectic off temperature. The results showed that the interface between GeQD and Si layer was compositional abruptness. The diameter of SiNWs is 14–28 nm, and the height of GeQD is about 3 nm, as shown in Fig. 20. Based on their results, axial SiNW/GeQD superlattice structures are expected to be developed. The structure is similar to an axial Ge/Si superlattice nanowire structure,^{97,98} but the thickness of the Ge layer in an axial SiNW/GeQD structure is lower than that in an axial Ge/Si superlattice nanowire structure.

Since ordered nanowire arrays can form optical whispering gallery microcavities (WGMs), the quantum efficiency of QDs can be improved significantly by embedding them into nanowires.^{99–101} Therefore, the growth of GeQDs on the top surface of larger SiNWs has been studied recently. Zhou *et al.*¹⁰² investigated the growth of GeQDs on the tops of periodically arranged SiNWs with diameters of 350–450 nm. As shown in Fig. 21, for nanowires with a diameter of 450 nm, four small hut-like GeQDs are symmetrically distributed at the edges of the top terraces of the SiNWs. The QDs have heights of 13.3 ± 0.9 nm and sidewalls with {105} facets. This is attributed to local potential minima appearing at the corners of the tops of SiNWs with larger diameters, where Ge atoms will be in favor of nucleation. For nanowires with a diameter of 350 nm, one large dome-like QD is located at the center of the top terrace of the nanowire. This indicates that the SiNW diameter determines the distribution and morphology of the GeQDs. After

Fig. 21. AFM images of the surface morphologies after 10 ML Ge deposition on SMPs of (a) ρ_{600}^{450} and (b) ρ_{450}^{350} at 580°C. Reprinted with permission from Ref. 102. Copyright 2014 Nanoscale.

Fig. 22. AFM images ($2 \times 2 \mu\text{m}^2$) of self-assembled Ge nanostructures on the ordered Si nano-pillars via the two-step procedure with the Ge deposition of, (a) (0.8 nm at 500°C and $0.1 \text{ \AA/s}$) + (1.0 nm at 520°C and $0.025 \text{ \AA/s}$), (b) (0.8 nm at 500°C and $0.1 \text{ \AA/s}$) + (1.0 nm at 580°C and $0.025 \text{ \AA/s}$), (c) (0.8 nm at 580°C and $0.025 \text{ \AA/s}$) + (1.0 nm at 480°C and $0.1 \text{ \AA/s}$). The inset in (a) shows the height profile along the dotted line AB in (a). The color bar is shown at the right (color online). Reprinted with permission from Ref. 103. Copyright 2016 Scientific Reports.

embedding QDs at the edges of the top terrace and close to the sidewalls of the nanowires, strong light-matter coupling phenomena such as resonance radiation and Purcell effects are expected if the spontaneous radiation of quantum dots can match the WGM resonance mode. Wang *et al.*¹⁰³ proposed a two-step growth method to control the uniform growth of Ge atoms at the edges of the tops of SiNWs. In their experiment, 0.8 nm of Ge was first deposited at 500°C at a rate of $0.1 \text{ \AA/s}$. After the growth was interrupted for 1 min, another 1 nm of Ge was deposited at different temperatures at a rate of $0.025 \text{ \AA/s}$. In Fig. 22, when the temperature of the second Ge growth was 500°C , four uniform QDs were formed at each edge of the top terrace. With the temperature increased to 580°C , a quantum ring was acquired at the top of the nanowire. With the temperature decreased to 480°C , no quantum dots or quantum ring occurred.

5. Conclusions

In this review, recent research progress on the fabrication and structures of SiNWs, GeQDs and SiNW/GeQD composites was introduced, respectively. Firstly, ordered nanowire arrays with small diameters, large aspect ratios and special structures become the hot research topics. Then, the researches about GeQDs focus on improving their luminescence properties by designing novel structures, such as GeQD crystals, Ge/Si/Ge CQD, and GIB-GeQDs. In experimental studies of coaxial SiNW/GeQD composites, there are inconsistent conclusions regarding the critical SiNW diameter for the transition of Ge growth from the F-M to the S-K mode. Simulations show that growth of Ge thin

films on SiNWs is more inclined to form Si/Ge core-shell nanowires as the nanowire diameter becomes smaller, whereas it is easier to prepare SiNW/GeQD composite structures with larger diameter nanowires. A physical mechanism has been put forward to understand the transition of Ge growth mode on SiNWs with increasing nanowire diameter. It has also been found that the curved surfaces of SiNWs help to release the strain induced by lattice mismatch. Furthermore, the axial SiNW/GeQD composite structure have already been demonstrated by VSS method. For the potential application, axial SiNW/GeQD superlattice structures are expected to be developed. In summary, the studies about SiNW/GeQD composites have raised a lot of interesting questions, which need to be resolved in future. By reviewing the research on the preparation methods and structures of SiNW/GeQD composite materials, we hope to facilitate more intensive study of such materials and their potential applications.

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