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# Synthesis and properties of germanium nanowires\*

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*Abstract*: As a promising electronic material, Ge nanowire (GeNW) has attracted much attention for its low band gaps, high mobilities, and unprecedented dimensions. This article reviews recent research and advancement on this topic and summarizes many aspects of GeNWs, including preparation, surface chemistry, physical properties, functional devices, and controlled assembly. It is shown that GeNWs can be readily synthesized by chemical methods and their electronic properties are comparable or superior to that of the bulk counterparts. Studies of surface chemistry have revealed dominant roles of surfaces on nanowires, and this result led to successful passivations toward air-stable, high-performance functional devices. Finally, controlled assembly to organize chemically synthesized nanowires into functional structures is discussed. Doors are opened up to widely utilize this novel material as excellent electronic building blocks.

*Keywords*: nanowires; chemical vapor deposition; field effect transistors; surface chemistry; assembly.

# INTRODUCTION

In the past decade, innovative research has been actively pursued to develop new semiconductor materials and novel device structures, in order to continue the ever-impressive device scaling trend implemented by the semiconductor industry [1]. As the device dimensions are approaching the theoretical limits, it becomes a daunting challenge to proceed any further unless novel structures with sizes beyond the capabilities of conventional lithographical tools are created [2-6]. In seeking new materials, researchers have focused on substitutes with superior electronic properties to complement and eventually replace Si. Compared with Si, Ge has lower band gaps and higher carrier mobilities, thus offering appealing opportunities for advanced device scaling, such as lower drive voltages and higher drive currents for high-speed electronics [7]. Indeed, Ge electronics has gained renewed interest recently [8]. In the meantime, chemically derived low-dimensional nanomaterials such as nanotubes and nanowires have attracted much attention owing to their unprecedented dimensions and properties [2–6]. They account for a new class of materials with great potential as building blocks for future electronics. As a result of synthetic chemistry development, these materials can be built from the bottom up (i.e., atoms by atoms) with precise controls over their compositions, dimensions, and crystal structures. Toward this end, Ge nanowire (GeNW) satisfies both criteria (i.e., as a new material with novel structures) and is particularly interesting. In fact, it is one of the first semiconductor nanowires that have been reported

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[9], and ever since then tremendous research efforts have been devoted to developing preparation, characterizations, assembly, and devices of GeNWs. This article aims to provide a brief review of GeNWs: the synthetic methods are summarized first, followed by characterizations, particularly on their surface properties; then the chemical treatments intending to functionalize and passivate the nanowire surfaces are discussed in the context of their effects on the electrical properties; finally, the controlled assembly toward device constructions is discussed.

# SYNTHESIS

Chemical methods have been proven successful in creating low-dimensional structures that are often well below the limits of conventional top–down lithographical techniques. Many nanostructured materials, including nanoparticles, nanotubes, and nanowires, have been synthesized via various chemical approaches [2–6]. Nearly every developed approach in making nanomaterials has been utilized to synthesize GeNWs as well, and the results are summarized in Table 1. Based on the media in which the reactions are carried out, the methods can be categorized into two types: solution phase and gas phase.

	Methods	T <sub>precursor</sub>	T <sub>substrate</sub>	Pressure	Precursors	Seed	Refs.
Solution phase	Solvothermal	275 °C	_	100 atm	GeCl <sub>4</sub> and phenyl-GeCl <sub>2</sub>	-	9
	Supercritical fluidic	350–400 °C	-	13.8–38 MPa	$Ge(C_2H_5)_4, Ge(C_6H_5)_2$	Au	11
Gas phase	Laser	820 °C	_	_	$Ge_{0.9}Fe_{0.1}$	-	13
	ablation	830 °C	690–705 °C	500 Torr	Ge (50 %), GeO <sub>2</sub> (50 %)	-	14
	Vapor	_	400–500 °C	$5 \times 10^{-10}$ Torr	Ge	_	15
	transport	1000–1100 °C	800–1000 °C	30 Torr	Ge and $\text{GeI}_4$	Au	17,18
		900–1100 °C	_	-	Ge	Au	19–21
		1100 °C	1100 °C	10 <sup>-3</sup> Pa	Ge and GeO <sub>2</sub>	-	16
	Chemical	275 °C	275 °C	50-760 Torr	GeH <sub>4</sub>	Au	22,23
	vapor	285 °C	285 °C	-	GeH <sub>4</sub>	Au	26
	deposition	320 °C	320 °C	1300 Pa	GeH <sub>4</sub>	Au	27
		325 °C	325 °C	10 <sup>-2</sup> Torr	$Ge(C_2H_5)_2$	Fe	28
		400–600 °C	400–600 °C	0.04-10 mTorr	Ge <sub>2</sub> H <sub>6</sub>	Au	25

Table 1 Summary of GeNW synthesis.

# Solution-phase-based synthesis of GeNWs

#### Solvothermal synthesis

The first successful synthesis of GeNW was reported in 1993 by Heath and Francoise [10]. In their approach,  $\text{GeCl}_4$  and phenyl-GeCl<sub>3</sub> were mixed with Na, and heated up to 275 °C in hexane. The pressure was maintained at 100 atm during 2–8 days of reactions. Both GeNWs ranging from 2 to 30 nm and amorphous/polycrystalline granular Ge were produced after the reactions were completed. It was discovered that large GeNWs (7–30 nm) had a large number of defects, while small ones (2–5 nm) were defect-free. Phenyl-GeCl<sub>3</sub> was found to play a critical role in the synthesis, without which no nanowires were formed. Therefore, it was suggested that strong chemical potentials between phenyl ligands and the surface of GeNW might favor nanowire structures to maximize surface areas. By altering the ratio of Na in the original mixture, the authors were able to tune the product nanowire sizes. Precise control

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of the nanowires, including sizes and qualities, however, was not achieved due to the lack of detailed understanding of the growth mechanism.

#### Supercritical fluidic synthesis

Almost 10 years after the first solution-phase synthesis of GeNWs, Korgel et al. renovated this solutionphase-based method and developed a supercritical fluidic reaction to prepare GeNWs in 2002 [11]. In their approach, sterically stabilized Au nanoparticles were employed as catalyst and tetraethylgermane (TEG) and diphenylgermane (DPG) were mixed with cylohexane. After reactions at 350–400 °C and 13.8–38 MPa, single-crystalline GeNWs were formed. The growth mechanism was suggested to be vapor–liquid–solid (VLS), a mechanism that was discovered over 40 years ago by Wagner and Ellis [12]. As illustrated in Fig. 1, three stages are involved in this growth mechanism. Initially, precursor molecules containing Ge are decomposed to supply reactive Ge species, which are fed into growth seed (e.g., Au) to form alloy. When the eutectic condition of this binary-phase system is reached, the alloy particle becomes a liquid droplet. Further feeding of Ge causes supersaturation of Ge in the alloy liquid, thus precipitation and nucleation of Ge crystal occur. As more Ge is continuously supplied, this feeding–alloying–nucleation process is continued and Ge crystal prolongs to form a crystalline nanowire.



**Fig. 1** VLS growth mechanism of GeNWs. Left: schematic demonstration of the VLS mechanism, which involves Ge feeding into growth seed, followed by Ge super-saturation and precipitation to form a crystalline nanowire. Right: A TEM picture confirms the tip-growth VLS mechanism. On the bottom of the picture is the growth origin, and on the top is the growth seed as the tip. The nanowire is 20 nm in diameter, which is determined by the size of the growth seed.

The VLS growth offers better control over nanowire sizes since they are essentially controlled by the sizes of growth seed. However, Korgel et al. found a large size distribution of the as-produced nanowires, presumably due to Au nanoparticle aggregation in the solution and uncontrolled deposition of Ge on the surfaces of GeNWs. In addition, sophisticated purification and assembly techniques have

yet to be developed to effectively utilize this method because it is not directly compatible with existing semiconductor technologies.

#### Gas-phase-based synthesis of GeNWs

With the understanding of the VLS growth mechanism for nanowire synthesis, it is conceivable that one can prepare GeNWs in many different ways with suitable Ge feeding and appropriate growth seeds. Indeed, GeNWs have been synthesized through a variety of techniques in gas phase, including laser ablation, physical and chemical vapor transport, and chemical vapor deposition (CVD).

#### Laser ablation

Utilizing laser ablation to prepare semiconductor nanowires was developed by the Lieber group, and it has been proven as a successful approach to many materials including Ge [13]. In this technique, a pulsed laser was shined onto a target that contained both semiconductor precursors and growth seed materials. As a result of ablation, nanoclusters of alloys were formed and semiconductor nanowires grew from these clusters via VLS mechanism. For GeNW synthesis,  $Ge_{0.9}Fe_{0.1}$  was employed as the target and the reaction temperature was 820 °C. Although the resulting GeNWs were small (3–9 nm), they were found to have twinning of Ge (111) plans.

Lee et al. also investigated laser ablation method to synthesize GeNWs [14]. In their approach, no catalytic materials were added. Instead, Ge and  $\text{GeO}_2$  were mixed, and the existence of oxide was found to assist nanowire formation. An intrinsic disadvantage of this technique, however, is that as-prepared GeNWs were sheathed with a thick layer of oxide (GeO<sub>2</sub>). Due to poor properties of GeO<sub>2</sub>, applications of these oxide-sheathed GeNWs are limited.

#### Vapor transport

This method involves the generation of Ge vapor and its transport to growth sites, and the growth of nanowires is completed via VLS mechanism or template-confined depositions. It was pioneered by Omi et al., and the first reported synthesis was carried out in a molecular beam epitaxy (MBE) chamber [15]. In their approach, Ge vapor was produced from a boron nitride Knudsen cell, and then transported and deposited onto Si (113) substrate. As a result of anisotropic strain relief, Ge atoms were self-assembled into nanowires along the crystal orientations of the Si substrate. However, as-produced GeNWs had limited applications because they were constrained on Si (113) surfaces and were not single-crystalline. Similar approaches have been attempted by Mei et al. again in 2005 [16], and porous anodic alumina (PAA) template was utilized to define the sizes and shapes of Ge nanorods. The Ge vapor was created by heating Ge and GeO<sub>2</sub> mixture at 1100 °C for several hours, and it was then nonspecifically deposited into PAA pores to form crystals. The quality of as-produced Ge nanorods was limited by the qualities of the PAA used in the synthesis. Structure perfection remained a challenge for this approach.

Vapor transport synthesis of GeNWs was advanced by Yang et al. [17]. They introduced volatile chemicals  $\text{GeI}_4$  to facilitate vapor generation/transport, and employed Au nanoclusters as growth seeds. Through VLS mechanism, the growth was improved and single-crystalline GeNWs were obtained. The same group later carried out systematic studies of GeNW growth mechanisms using transmission electron microscopy (TEM) observations of individual nanowire growths heated in situ [18]. The VLS growth mechanism was confirmed unambiguously in their experiments.

Similar vapor transport methods have also been employed by several other groups to synthesize GeNWs [19–21]. Although detailed procedure varies, the same characteristics are shared by most approaches. A high-temperature heating is typically required to produce Ge vapor, and either chemical (GeI<sub>4</sub>) or physical (inert gas flowing) method is used to transport the vapor to growth site. An inherent disadvantage is unspecific deposition of Ge vapor, which is often found to coat sidewalls of the nanowire surfaces. Also, due to high processing temperatures, nanowire surface is more susceptible to oxidation if any O<sub>2</sub> impurities exist in the system.

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#### Chemical vapor deposition

CVD was one of the most successfully developed methods to produce one-dimensional nanostructures, and the best-established example was found in carbon nanotubes. For a typical CVD synthesis, reactive species are decomposed to feed into the catalyst clusters, and nanostructures are derived from the catalyst clusters. Compared with other methods, CVD syntheses often have gentler conditions and the reactions are more specific. Growth parameters can be easily tuned to eliminate undesirable deposition of reagents on the nanowire sidewall, and growth locations can be defined by positioning of catalyst clusters. Despite the extensive applications of CVD on carbon nanotube synthesis, relatively few examples of CVD synthesis of semiconductor nanowires have been performed, particularly for GeNWs.

We reported the first CVD synthesis of GeNWs, in which  $\text{GeH}_4$  was used as feeding stock and preformed Au nanoclusters served as growth seeds [22]. A striking finding was that with reactive  $\text{GeH}_4$ , high-quality single-crystalline GeNWs were readily produced at temperatures down to below 300 °C. It represents the modest conditions that have been employed to grow high-quality semincondutor nanowires in gas phase. Further studies revealed that optimum growth results could be obtained only when the feeding of Ge species and diffusion of Ge in growth seed was balanced [23]. As a result of short diffusion distance, smaller nanowires could be produced at lower temperatures while larger ones were produced at higher temperatures. Based on this understanding, deterministic one-to-one synthesis of GeNWs with regard to growth seeds was achieved and utilized to prepare GeNWs from individually patterned Au nanoparticles. By supporting preformed Au particles on high-surface-area silica particles, gram-scale GeNWs were also obtained in a single growth from a one-inch tube furnace [24]. This result opened up opportunities to synthesize bulk quantity of high-quality GeNWs with monodispersed sizes that are defined by Au nanoparticle sizes.

After the first report, CVD synthesis of GeNWs has been studied by various groups intensively [25–28]. In addition to GeH<sub>4</sub>, Ge<sub>2</sub>H<sub>6</sub> [25] and Ge(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> [28] have also been employed as precursors. Most of the reactions resemble the VLS mechanism except the one reported by Mathur et al. [28]. They discovered that with Fe as growth substrates, a base-growth mechanism that differs from VLS could produce GeNWs, in which the catalyst clusters did not move while nanowires grew.

## SURFACE CHEMISTRY

#### Band bending

It is well known that surface states affect semiconductor electronic properties, and this effect can be dominant as the structure dimensions decrease down to nanometer scales. Therefore, the study of surface states effect on nanostructure electronic properties is of fundamental and practical importance to unravel a detailed understanding of the relationships. Furthermore, the understanding can elucidate methods to eliminate surface states for high-performance electrical or optical devices, therefore facilitating applications of nanostructures [29].

We first carried out systematic X-ray photoelectron spectroscopy (XPS) on p- and n-type GeNWs [30]. By comparing the difference of core levels with regard to Fermi levels, we detected significant band bending on both types of GeNWs and the bending directions were found to be opposite. For p-type GeNWs, the Fermi level is bent upwards, and for n-type GeNWs it is bent downwards, so both of them are pinned by the inter-band states, as shown in Fig. 2. Surface states due to surface oxides were attributed to cause the band bending. Simple calculations showed that small surface potential could dominate nanowire bulk properties as the sizes of nanowire are scaled down.

Korgel et al. performed similar studies with combined scanning transmission electron microscopy and energy loss spectroscopy (STEM-ELS) on intrinsic GeNWs [31,32]. They also found that the Ge 3d ionization edge was very sensitive to surface oxidation and up to 0.3 eV shift was reported. In addition, they discovered that the volume plasmon energy was a strong function of GeNW sizes, and it increased up to 0.8 eV as nanowire diameter decreased from 25 to 8 nm.



**Fig. 2** Band structure of GeNWs. With data extracted from ref. [30], band bending due to surface states can be determined for p- and n-type nanowires. The values are 0.3 and 0.1 eV, for p- and n-type, respectively. Therefore, the surface/interface states are expected to be in the mid-gap, as indicated in the picture.

# Surface passivation

A variety of chemical methods have been attempted to alter Ge surfaces for better chemical stabilities and fewer surface states since more than 40 years ago [33]. Only with proper surface modifications can this material be widely used in practical applications. As aforementioned, surface effects are more prominent for nanostructures such as nanowires. Within this context, chemical passivation of GeNWs is of great importance. We and other groups have investigated various reactions that have been successfully applied to planar Ge wafers on GeNWs and found that long-chain alkanethiols provide the best stabilities [24]. This is different from the results that have been reported on planar Ge surfaces, in which long-chain alkyl passivation was found to be the most stable [34,35]. While more studies are still needed to fully understand this difference, it was hypothesized that the structures of nanowire surfaces may play a role. Large curvature and complicated surface atom geometries may change the arrangements of long alkyl chain molecules on GeNWs, therefore change the stabilities.

# **PROPERTIES AND DEVICES**

### **Transport properties**

Despite the fact that Ge has many intriguing electrical properties, reports on transport properties of Ge are relatively scarce compared with Si. And there have been even fewer studies on GeNWs. The successful fabrication of high-performance GeNW field effect transistors (FETs) was first reported by our group in 2003 [36]. The devices were fabricated with CVD-grown GeNWs that were p-doped by co-flowing  $B_2H_6$  as a doping source. Both thermally grown SiO<sub>2</sub> and atomic layer deposition (ALD) of HfO<sub>2</sub> were employed as gate dielectrics. Peak hole mobilities of 600 cm<sup>2</sup>/V<sup>-s</sup> and high on/off current ratios were achieved in our studies. The device characteristics are comparable to those fabricated on planar Ge wafers, suggesting that GeNW is a promising candidate for high-performance electrical applications. Later on, Lieber et al. fabricated similar devices with both p- and n-type doped GeNWs and observed similar device characteristics [26]. In their studies, however, the authors developed a different doping scheme, in which dopant atoms were deposited on the surfaces of GeNWs after growth and diffused into the nanowire channel through thermal annealing.

GeNW FETs have also been attempted by Gu et al. [19] and Korgel et al. [32]. with GeNWs synthesized by physical vapor transport and supercritical fluidic methods, respectively. Although the device geometry was identical to ours and those by Lieber et al., poor performance was observed independently by both groups. It was argued that unintentional doping could be attributed to such behavior, whereas detailed studies were still lacking.

#### Functionalization effects on electrical properties of GeNW

As has been discussed in the earlier part of this paper, surface states play important roles in determining the electrical properties of nanostructured materials. The consequences include hysteresis in  $I-V_g$ sweeping and significant device performance degradation. This problem becomes dominant as nanowire diameter is decreased to the scale of several nanometers, which are comparable to the depletion depth of the surface potential so that the channel properties are dominated by the surfaces. In this context, for nanowire devices fabrication in general, proper functionalization of the surfaces to reduce and/or eliminate surface states is necessary.

In addition to the chemical stability effect, alkanethiol functionalization on GeNWs was also found to improve device electrical properties significantly. For back-gated GeNW FETs, drastic performance improvement is achieved for those with functionalizations. This difference is manifested in Fig. 4a. Representative drain current  $(I_{ds})$  is plotted vs. gate voltage  $(V_{gs})$  for both GeNWs with and without functionalizations. It is clearly demonstrated that GeNW without functionalizations has on-current in the p-channel almost one order of magnitude lower than that with functionalizations under the same measurement conditions. A similar effect has been observed on more than 20 devices from two batches of samples. Considering both types of devices with and without functionalizations have similar geometries and dimensions, the difference is significant.

For GeNW FETs without functionalizations, S/D contacting metals with different work-functions do not yield obvious device characteristic difference due to the presence of surface states and consequent Fermi-level pinning in the contacting region and depletion in channel region. This suggests that the device performance is dominated by surface states. This imposes a great challenge in measurements of physical properties of GeNWs. However, this challenge can be met by reducing surface states, and intrinsic properties of the materials are accessible through proper surface treatments such as long-chain alkanethiol functionalization. As shown in Figs. 3 and 4, FETs of intrinsic GeNWs are either p-type with relatively high work function metal contact of Ti, or ambipolar for relatively low work function metal contact of Co. Examinations of the band diagram in the metal/semiconductor regions of these two types of devices clearly explain this difference. For Ti contact, the work function is close to conduction band of Ge. Therefore, transmissions of holes have high probabilities, thus p-type FET characteristics are obtained. For Co contact, on the other hand, the work function is close to the mid-gap. As a result, transmissions of both hole and electrons are comparable, thus ambipolar FET characteristics are observed.

The ambipolar devices with Co contact offer opportunities to directly measure the band gap of GeNW. It is known that the maximum resistance of semiconductor is [7]:

$$R_{\max} = R_c + R_{\text{off}} \exp\left(\frac{E_g}{2KT}\right) \tag{1}$$

From this equation,  $E_g$  can be derived by measuring maximum resistance at different temperatures. Figure 3 shows a set of  $I-V_g$  data at different temperatures from 300 to 400 K at  $V_{ds} = 10$  mV. The maximum resistance is extracted from the minimum point of the current and plotted with regard to temperatures. By fitting to eq. 1,  $E_g$  is estimated to be 0.64 eV. Atomic force microscopy (AFM) was then carried out, and the GeNW was found to have a diameter of ~17 nm. This is in good agreement with the value of bulk Ge. Similar measurements have been performed on GeNWs with other diameters down to 10 nm as well, and variations of  $E_g$  have been observed. Nevertheless, the trend of band structure change with regard to GeNW sizes is not clear thus far and more studies are still needed for rigorous conclusions.

The surface-passivated nanowires open up opportunities for air-stable high-performance GeNW FETs. Figure 4 shows a p-type GeNW FET with surface treatment. At room temperature, the device shows high on/off ratios at various biases. High saturation current is achieved, and current density at



**Fig. 3** Measurement of GeNW band gap. Intrinsic GeNWs passivated with alkanethiols can be contacted with Co electrodes to show ambipolar characteristics. (a) Typical  $I-V_g$  plots at various temperatures. (b) The minimum conductance points are extracted to fit eq. 1, and the band gap of 0.64 eV is calculated. Inset: AFM picture of the measured nanowire, scale bar: 500 nm. The nanowire is 17 nm in diameter.



**Fig. 4** High-performance FETs based on GeNWs with surface passivations. (a) Typical  $I-V_g$  characteristics before (blue) and after (red) surface passivations. Higher conductance and improved gating effect is obtained by passivating the surface states. (b)  $I-V_g$  and (c)  $I-V_d$  plots at different  $V_d$ , and  $V_g$ , respectively. (d)  $I-V_g$  plots at different temperature. The conductance does not decrease as temperature is decreased, suggesting ohmic contact to the nanowire devices and negligible surface states.

 $V_{\rm ds} = 1$  V is estimated to be 380  $\mu$ A/ $\mu$ m, comparable to that of planar bulk Ge devices. Quasi-ohmic contact is achieved as demonstrated by the temperature-dependent measurements, in which conductance does not drop significantly as temperature is decreased from 300 down to 4 K. Nevertheless, further improvements are needed to achieve truly ohmic contact GeNW FETs reliably.

# **Optical properties**

Compared with Si, Ge has a relatively large Bohr radius of ~24 nm, suggesting more pronounced quantum confinement effect can be observed on Ge nanostructures [37]. One of the most promising probing methods would be phonon confinement effect. While such effects have been widely reported on Ge nanocrystals and noticeable phonon confinement effect was observed on nanocrystals as large as 7 nm by UV–vis absorption [38], similar studies on one-dimensional GeNWs were lacking, and the only study to our best knowledge in the literature was conducted by Lee et al. [14]. In their studies, GeNWs sheathed with a thick oxide layer were synthesized by laser ablation. By comparing Raman spectrum of GeNWs with diameters ranging from 6–17 nm, both peak broadening and an extension of the Raman peak toward low frequencies were observed. The reason was attributed to the quantum confinement of optical phonons in the GeNWs.

# CONTROLLED ASSEMBLY

Although chemical methods hold great promise in producing nanostructures from the bottom up, assynthesized nanomaterials are typically in random dangling forms, which significantly limits the successful utilizations for functional devices. For practical applications, well-controlled assembly must be developed to organize nanomaterials into ordered forms. Toward this goal, two general methods have been reported: (1) assembly of as-grown GeNWs from their growth sites and (2) assembly of collected GeNWs in large scale.

# Deterministic synthesis and post-growth assembly

As have been discussed earlier in this article, deterministic GeNW growth was achieved by carrying out the synthesis under optimum conditions with 100 % yield [23]. Due to the VLS tip-growth process, one of the ends of an as-grown GeNW is anchored on the substrate (from where the nanowire is grown) and can act as a pivotal point for the wire. After a stream of DI  $H_2O$  is flowed across the substrate surface, we find that the nanowires are reoriented toward the flow direction and become quasi-aligned while maintaining the same spacing between their pivoted ends.

# Langmuir-Blodgett assembly

The Langmuir–Blodgett (LB) technique has been widely applied for molecular films and for various nanomaterials such as nanoparticles, nanorods, and nanowires [39–43]. The GeNWs functionalized by both alkanethiols and alkyls form uniform and stable suspensions in organic solvents such as chlorobenzene and chloroform [24]. Upon adding functionalized GeNW suspensions drop-wise to a subphase of ethanol/water in an LB trough, we observed that the droplets spread out quickly on the water surface. The organic solvent quickly vaporized to leave the functionalized GeNWs floating on the water surfaces. These floating GeNWs formed a close-packed dense film upon compressing with the nanowires oriented perpendicular to compressing direction or parallel to the edge of the trough, and were transferred onto various substrates and ready for characterization or integration into device structures (Fig. 5). Simple calculation suggests that ~0.7 mg GeNWs (20 nm in diameter) is needed to form an LB film to cover a full 4-inch wafer. This quantity can be easily afforded by our bulk synthesis that yields ~0.4 g of pure GeNWs in a single growth run. Thus, this approach is promising for large-scale



**Fig. 5** Controlled assembly of GeNWs. (a) Deterministic growth from pre-patterned Au nanoparticles, followed by post-growth fluidic assembly, adopted from ref. [23]. (b) LB film of parallel nanowire arrays, adopted from ref. [24].

productions of LB films of high-quality, single-crystal GeNWs with close packing and excellent alignment. These NW films can be used as wafer materials for fabrication of various types of devices such as FETs with channel length parallel to the nanowire orientations.

# CONCLUSIONS

The development of nanomaterial synthetic chemistry has provided a wealth of methods to growing novel structures with excellent controls. The applications of these methods to produce high-quality GeNWs are summarized in this article in the context of nanowire synthesis in general. It is shown that among the developed approaches, CVD offers compelling advantages in synthesizing high-quality GeNWs with the minimum yield of undesirable by-products. Studies of the surfaces reveal that surface states play important roles in determining GeNW properties, and the result is general to other nanostructured systems as well. Successful chemical passivation methods that lead to air-stable, high-performance devices have been discussed as well. Finally, controlled assembly toward functional devices is summarized. The results presented in this article represent the up-to-date advancement of GeNW research, and great potentials of their applications as appealing electronic materials are opened up.

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