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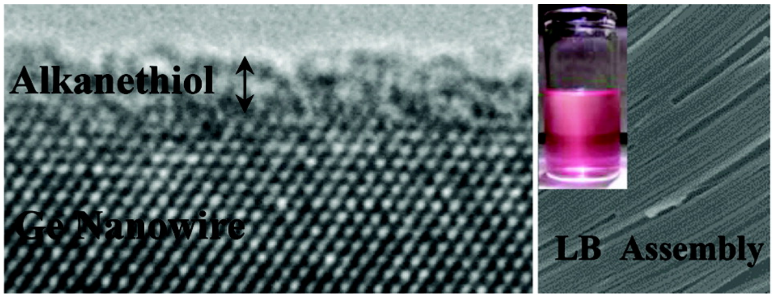
J. Am. Chem. Soc., **2005**, 127 (33), 11871-11875• DOI: 10.1021/ja053836g • Publication Date (Web): 29 July 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Oxidation Resistant Germanium Nanowires: Bulk Synthesis, Long Chain Alkanethiol Functionalization, and Langmuir−Blodgett Assembly

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Abstract: A simple method is developed to synthesize gram quantities of uniform Ge nanowires (GeNWs) by chemical vapor deposition on preformed, monodispersed seed particles loaded onto a high surface area silica support. Various chemical functionalization schemes are investigated to passivate the GeNW surfaces using alkanethiols and alkyl Grignard reactions. The stability of functionalization against oxidation of germanium for various alkyl chain lengths is elucidated by X-ray photoelectron spectroscopy. Among all schemes tested, long chain alkanethiols ($\geq C_{12}$) are found to impart the most stable GeNW passivation against oxidation upon extended exposure to ambient air. Further, the chemically functionalized oxidation-resistant nanowires are soluble in organic solvents and can be readily assembled into close-packed Langmuir−Blodgett films potentially useful for future high performance electronic devices.

Introduction

Germanium is an electronic material with renewed interest for future computing owing to high carrier mobilities than silicon.[1−8] However, several major challenges should be met in order for Ge to become a widely useful material for high performance electronics. The cost to prepare single crystal Ge wafers is high since Ge is a naturally scarce element and mass production is lacking. Methods for efficient formation and usage of crystal Ge should be developed to circumvent this problem. A more fundamental issue is that Ge easily forms unstable oxides on the surfaces.[9] GeO_2 is soluble in H_2O, and the Ge/GeO_2 interface has considerably high surface states.[6,10] Applications of Ge will be limited unless GeO_2-free surfaces and interfaces can be obtained by developing robust chemical passivation of Ge to prevent oxidation.

Among various approaches to high quality single crystalline Ge is simple and low thermal budget synthesis of Ge nanowires at temperatures down to 300 °C using Au nanoparticles as seeds.[4,7] For such a chemical bottom-up approach, however, it is necessary to be able to synthesize bulk quantities of GeNWs and assemble them from random entangled forms into ordered structures to facilitate integration into electronic devices. In terms of surface passivation, various functionalization chemistry for oxidation prevention has been investigated in the past for planar Ge surfaces with well-defined crystallographic orientations.[11−15] Relatively recent is the passivation effort on GeNWs.[15] It remains to be seen whether the various passivation chemistry for planar surfaces can be transferred to curved GeNW surfaces. Also, the efficacy of GeNW passivation by different chemical schemes for molecules with different chain lengths has not been systematically explored. Obtaining GeNWs with truly robust stability against oxidation (e.g., during extended exposure to *ambient* air) remains a challenge.

In this article, we present an effort to address these issues and meet the various challenges posed to the synthesis, passivation, and assembly of GeNWs. First, we demonstrate chemical vapor deposition (CVD) synthesis of GeNWs at large scales using supported Au nanoparticle seeds on high surface area silica. Second, a robust surface passivation scheme is identified to stabilize the surfaces of GeNWs using self-assembled crystalline monolayers of long chain alkanethiols (≥12 carbon) for the first time. This imparts chemical stability to GeNWs against oxidation upon exposure to ambient air for ∼1 day. The surface functionalized and passivated GeNWs

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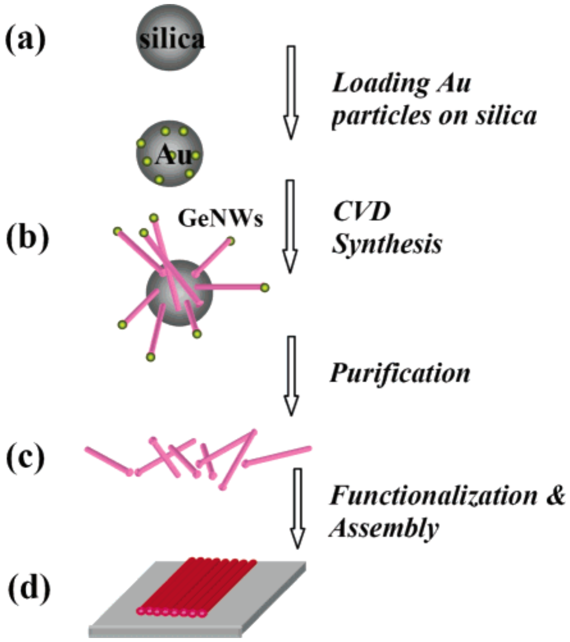

Figure 1. Schematic of the approach used for bulk synthesis, purification, functionalization, and assembly of GeNWs.

exhibit high solubility in organic solvents and can be readily employed to form Langmuir–Blodgett films on various substrates. The current work thus achieves chemically stable (for ~1 day in ambient air) GeNWs in organized forms at large scales, which should facilitate the bottom-up approach to high performance electronics based on Ge.

Results and Discussions

Bulk Synthesis of GeNWs and Purification. Recently we reported understanding and optimization of GeNW synthesis to achieve nearly 100% yield with every Au nanoparticle capable of nucleating and growing a nanowire.[7] The optimized growth condition was utilized here to produce large quantities of intrinsic GeNWs on high surface area support materials (Figure 1, see Supporting Information for details). A typical SEM image of as-grown GeNWs from silica supported Au seeds is shown in Figure 2a. Large numbers of GeNWs emanating from silica particles are observed. After purification by detaching GeNWs from the silica support via sonication and removal of silica by centrifugation and HF etching, we obtain large quantities of pure GeNWs free of any silica residue (Figure 2b). Using monodispersed ~2 mg of 10 ± 2 nm and 20 ± 3 nm Au seeds loaded onto silica, we produced ~0.8 g of 13.5 ± 2 nm and 0.4 g of 23.9 ± 3.7 nm GeNWs, respectively.

Our bulk synthesis of GeNWs is simple, and the idea of loading preformed Au nanoparticles onto APTES modified high surface area silica is novel. By doing so, we are able to obtain large numbers of *monodispersed* growth seeds for the synthesis of bulk quantities of NWs that are uniform in diameter. Conventional methods employ metal salt precursors impregnated onto a silica support and rely on heat treatment to form supported seed catalyst particles. We found that such methods were unable to produce monodispersed Au seeds due to uncontrolled metal aggregation during annealing. Our method of loading preformed monodispersed Au particles onto support materials for NW synthesis can also be generalized for bulk CVD synthesis of other types of nanowires with high uniformity. Previously, bulk quantities of semiconductor nanowires have been reported by using laser ablation[16,17] or high pressure and temperature supercritical fluid solution-phase reactions.[3,18] Compared to these methods, our bulk CVD synthesis has advantages in simplicity, low thermal budget, and high uniformity of nanowires.

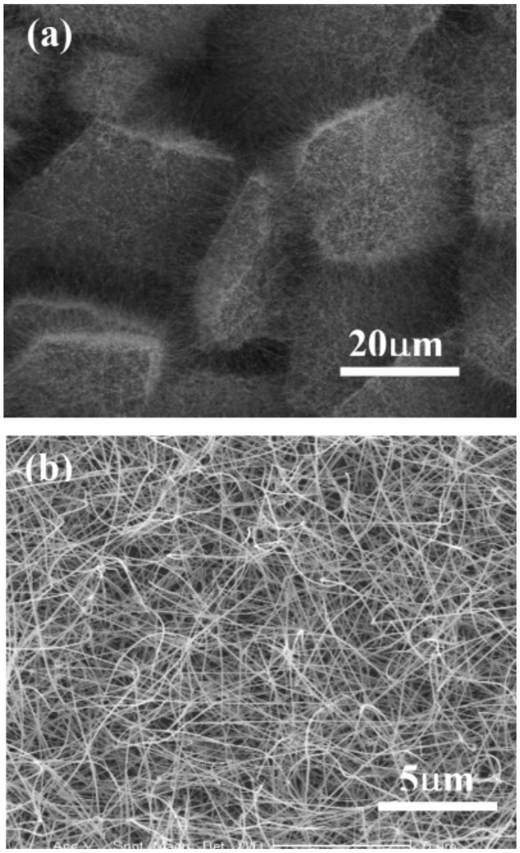

Figure 2. Bulk synthesis and purification of Ge nanowires. (a) An SEM image of high yield of GeNWs grown from Au nanoparticle seeds loaded onto silica particles. (b) An SEM image of purified GeNWs after removal of the silica support.

Passivation of GeNWs via Alkanethiols and Grignard Reactions. A major challenge to Ge is the easily oxidized surface[9] and large numbers of Ge/GeO_2 interface states rendering poor electrical properties to Ge devices.[10] We have found recently significant band bending due to Fermi level pinning by surface states of oxidized GeNWs.[6] Various schemes of functionalization and passivation have been reported previously[11−14,19] to impart oxidation resistance to planar Ge surfaces. In the current work, we focused on investigating GeNW functionalization by various chain-length alkanethiols and by Grignard reactions,[12]as depicted in Figure 3. For both the thiol and Grignard reactions, GeNWs were first treated with diluted HF or HCl to remove native oxides and terminate the surfaces with H (for alkanethiol reactions) or Cl (for Grignard reactions). XPS revealed that the as-cleaned GeNWs after these treatments are indeed oxide free (Figure 4a and b, "as-cleaned" curves), suggesting that Ge NWs terminated with H and Cl are

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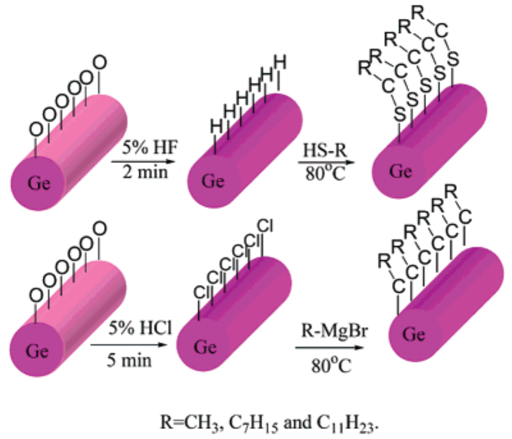

Figure 3. GeNW functionalization schemes using alkanethiols (top) and Grignard reactions (bottom).

stable for at least 10 min in ambient air during sample transfer into the vacuum chamber for XPS measurements. Controlled exposure of functionalized GeNW to ambient air was carried out to investigate the oxidization behavior of GeNWs by high-resolution XPS. Both Ge 2p and 3d binding energies were recorded to monitor the degree of oxidation. Owing to the higher binding energy and smaller escape depth of Ge 2p electrons (1.07 nm) compared with 3d electrons (2.11 nm), a more sensitive probe to the Ge surface properties can be achieved with Ge 2p spectrum.[20] Without any functionalization, H- and Cl-terminated GeNWs are unstable upon exposure to ambient air for 2 h, evidenced by the appearance of a shoulder near the Ge^0 2p peak due to oxidation. After 24 h air exposure, the shoulder grows into an obvious peak corresponding to Ge^{4+} accompanied by a blue shift of the Ge^0 peak (see Figure 4a and b, "control" curves) due to band bending caused by Fermi level pinning by surface states.[6] In stark contrast, GeNWs functionalized by both alkanethiols and the Grignard reactions (for C_2, C_8, and C_{12}) exhibit much reduced oxide signals than the unfunctionalized ones after 1 day of air exposure (Figure 4a and b, "24 hour" curves), pointing to the expected passivation effect. The most stable passivation of GeNWs is achieved with C_{12} alkanethiol (Figure 4b top curves). The C_{12}-thiol coated GeNWs exhibit negligible Ge-oxide signal after 1 day of air exposure.

XPS data obtained with Ge 2p electrons can unveil small changes not discernible in 3d data. For GeNWs right after $C_{12}H_{25}SH$ functionalization, peak fitting of the Ge3d spectrum identified no Ge-oxide signal (Figure 4d). However, similar analysis performed on the Ge 2p spectrum clearly identified a small peak corresponding to Ge^{2+} (from GeO) (Figure 4c). This suggested minor oxidation of the as-cleaned GeNWs during sample transfer between acid cleaning and functionalization. The intensity of the peak exhibited no change after 1 day of exposure

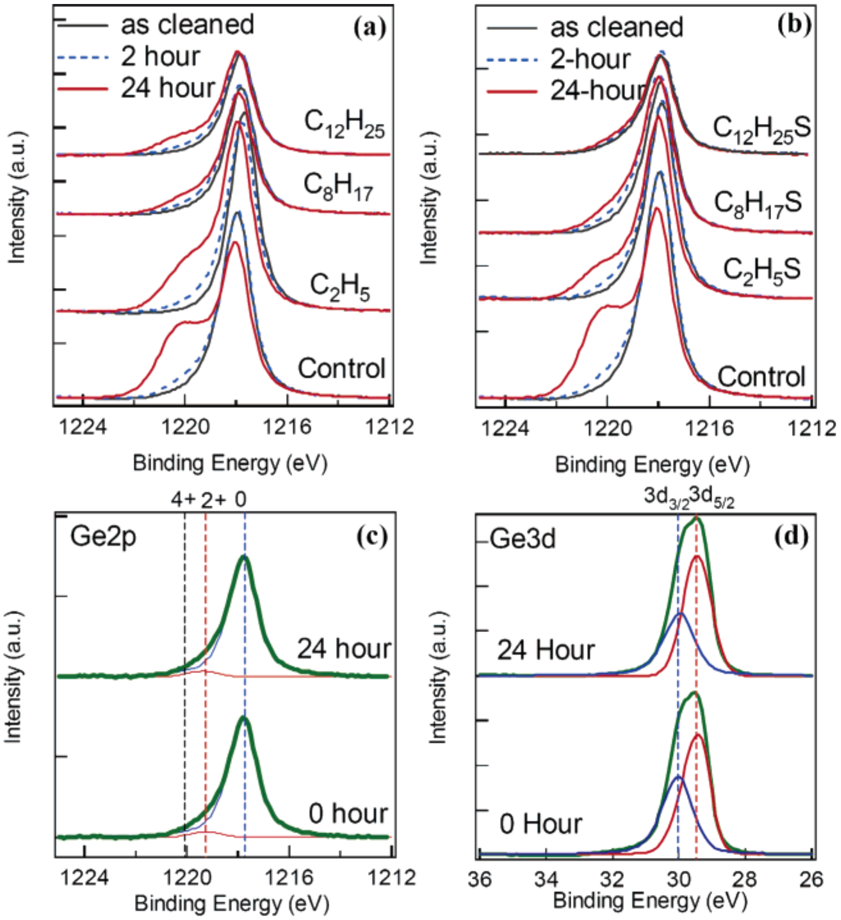

Figure 4. XPS data of GeNWs. (a) Ge 2p spectra for GeNWs functionalized by C_2, C_8, and C_{12} alkyl chains via the Grignard reaction. (b) Ge 2p spectra for GeNWs functionalized by C_2, C_8, and C_{12} alkanethiols. (c) Peak fitting for Ge 2p spectra before and after 24 h air exposure. A small peak due to Ge^{2+} is discerned by data fitting with intensity remaining unchanged after 24 h of exposure to ambient air. (d) Peak fitting for Ge 3d spectra before and after 24 h of air exposure. No GeO peak is discerned here due to lower sensitivity of 3d spectra to surface properties than 2p spectra.

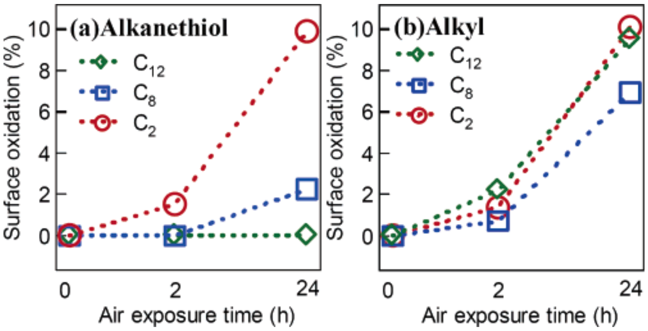

Figure 5. Oxidation behavior of various functionalized GeNWs. The percentage of surface oxides (GeO_2) is extracted from peak fitting of Ge 2p spectra. (a) Data for various alkanethiols functionalized NWs. (b) Data for various alkyl Grignard reactions. The C_{12}-thiol functionalization in (a) gives the most effective passivation.

in ambient air (Figure 4c) owing to the $C_{12}H_{25}SH$ passivation layer. The result here strongly suggests that Ge 2p spectra should be used to analyze surface functionalization effects by various molecules to afford high sensitivity.

Chain Length Effect. We carried out a systematic investigation of the alkyl chain length (C_2-C_{12}) effect to the oxidation resistance of GeNWs after functionalization by thiols and Grignard reactions. The degree of oxidation (to GeO_2) of GeNWs was extracted from peak fitting of Ge 2p binding energies and plotted against the exposure time to ambient air in Figure 5. For alkanethiol functionalized GeNWs, the stability of the wires monotonically increases with the alkyl chain length, with the dodecanethiol ($C_{12}H_{25}SH$) functionalized GeNWs exhibiting essentially oxide free surfaces after 1 day of air exposure (Figure 5a). Similar dependence of oxidation resistance to alkyl chain length has been reported previously for metal surfaces (e.g., Cu) with self-assembled monolayers (SAM). As for the SAM protected metals, we suggest that the enhanced oxidation resistance of GeNWs by longer chain alkanethiols is owing to the better packing of the molecules resulted from stronger interchain van der Waals interactions and thus more crystalline and denser molecular films formed on the GeNW surfaces. This affords better blocking of oxygen and therefore higher oxidation resistance.[23] Since the GeNWs employed in the current work are ~10−20 nm in diameter and significantly larger than the molecular chain length (up to ~1 nm for C_{12}), dense crystalline alkanethiol SAMs can still be formed on these relatively large wires. For NWs with diameters approaching 1−2 nm, different passivation strategies will be necessary since close packing of ~1 nm long molecules on the NWs will be difficult due to the high curvature of the wires.

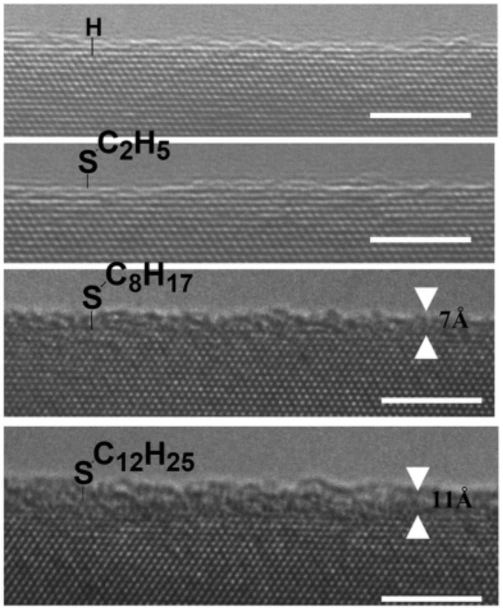

Figure 6. TEM images of GeNWs functionalized with thiols of different alkyl chain lengths. (a) As-cleaned GeNWs without functionalization. (b) Ethanethiol (C_2), (c) octanethiol (C_8), and (d) dodecanethiol (C_{12}) thiol functionalized wires. Scale bars in all pictures: 5 nm.

The overall Ge^0 signal intensity monotonically decreases for GeNWs modified by longer chain alkyl groups via both thiol and Grignard reactions (under the same data collection condition, Figure 4a and b). This is consistent with the formation of thicker molecular layers for longer alkyl chains. We also carried out TEM imaging of the molecular passivated GeNWs and found that the thickness of the coating on the nanowires consistently increased with the alkyl chain length (Figure 6). For GeNWs reacted with C_2H_5SH, $C_8H_{17}SH$, and $C_{12}H_{25}SH$, the thickness of the coating layers over the GeNW crystalline lattices were ~0 Å, ~7 Å, and ~11 Å, respectively.

The chain length dependence of GeNW stability after alkyl Grignard functionalization somewhat differs from those functionalized by alkanethiols. While the C_8- and C_{12}- Grignard functionalized GeNWs are significantly more oxidation resistant than the C_2 Grignard functionalized ones, the C_8 and C_{12} passivations are rather similar (Figures 4a and 5). We speculate that this could be a result of interplay between the molecular packing/film thickness effect and reactivity differences of molecules with various chain lengths. Longer chain molecules may exhibit lower reactivity with the GeNWs toward Ge−C bond formation, giving little advantage for C_{12}-passivation over C_8-passivation.

Relative stability of alkanethiol and alkyl Grignard functionalized GeNWs. Unlike the C_{12}-thiol passivation, none of the C_2-, C_8-, and C_{12}-Grignard functionalization investigated here imparted high oxidation resistance to GeNWs (Figures 4 and 5). This is in agreement with the result of Korgel et al.[15] but seemingly differs from previous reports that alkyl monolayers on planar Ge (111) and (100) surfaces via Ge−C bonding provide better passivation than alkanethiols.[12,14,19] It has been suggested that such stability stems from stronger Ge−C bonding than Ge−S bonding.[19] Nevertheless, in the literature, systematic experimental and theoretical data of Ge−C vs Ge−S bonding properties for various well-defined Ge crystal surfaces appear lacking. In one reference, we find that that the bonding energy of Ge−C (460 kJ/mol) is suggested to be lower than that of Ge−S (534 kJ/mol),[24] opposite to the suggestions based on functionalization stability studies. Therefore, the relative bonding strengths for Ge−C and Ge−S remain to be fully elucidated and may not apply to interpreting the relative stability of thiol and alkyl functionalized GeNWs.

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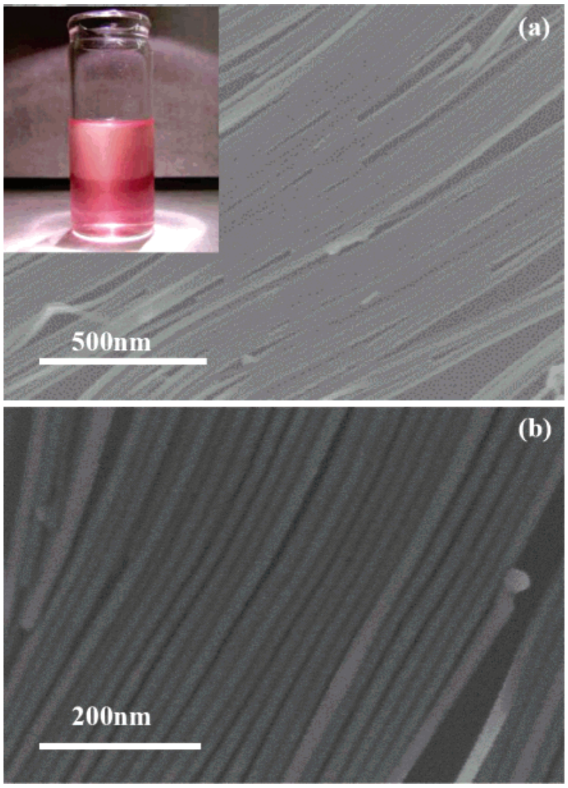

Figure 7. Langmuir–Blodgett film of GeNWs. (a) SEM image of a GeNW film with dodecanethiol (C_{12}) functionalization. Inset: photo of a GeNW suspension in chloroform. (b) SEM image of a GeNW film with octyl (C_8) functionalization.

Another likely factor is the different reactivity of molecules employed in our functionalization and passivation. It is known that long chain Grignard reactions with Ge require more rigorous reaction conditions or longer times to complete than alkanethiols[12] due to the relatively low reactivity of long chain Grignard reagents. It is therefore probable that our C_8 and C_{12} Grignard reactions afford lower coverage on GeNWs than the same length alkanethiols and thus giving less passivation effect.

Langmuir–Blodgett Film. The Langmuir–Blodgett (LB) technique has been widely applied for molecular films and for various nanomaterials such as nanoparticles, nanorods, and nanowires.[25–30] The GeNWs functionalized by both alkanethiols and alkyls form uniform and stable suspensions in organic solvents such as chlorobenzene and chloroform (Figure 7a inset). This is one of the key elements for successful LB film assembly of GeNWs. Without functionalization, GeNWs do not form stable suspensions in these organic solvents and sink into water due to the hydrophilic oxide surfaces. Upon adding functionalized GeNW suspensions dropwise to a subphase of ethanol/water in an LB trough (see Supporting Information for experimental details), 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 (Figure 7) and were transferred onto various substrates and ready for characterization or integration into device structures. The subphase of ethanol in H_2O was another key to our successful GeNW LB film formation. We found that without the addition of 5% ethanol in water, monolayer formation of GeNWs on a pure H_2O surface was difficult as the nanowires tended to overlap and form bundles due to strong hydrophobic interactions between functionalized GeNWs. As a result, multilayers of GeNWs or overlapping wires without good alignment were obtained after transferring to solid substrates. On the other hand, high concentrations of ethanol in the subphase (>10%) are also undesirable since the functionalized nanowires tended to submerge into the solution without floating on the surface.

Simple calculation suggests that ~0.7 mg of GeNWs (20 nm in diameter) is needed to form an LB film to cover a full 4-in. 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, the approach presented here (Figure 1) is promising for large scale 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 field effect transistors with the channel length parallel to the nanowire orientations.

Conclusions

We have demonstrated the synthesis and purification of bulk quantities of high quality single crystalline GeNWs by CVD on high surface area silica supported monodispersed Au seeds. We investigated various surface passivation schemes for GeNWs and found that the best method among all tested schemes to protect GeNWs from oxidation in ambient air is to use self-assembled crystalline monolayers of long chain alkanethiols (≥12 carbon). By no means can this passivation method provide indefinite protection of Ge nanowires against oxidation especially under harsher conditions, and the quest for optimum Ge passivation will continue. Our surface functionalized GeNWs exhibit high solubility in organic solvents and can be readily employed to form Langmuir–Blodgett films on various substrates. Thus, we achieve oxidation resistant GeNWs in organized forms at large scales, which should significantly facilitate the bottom-up approach to high performance electronics based on single-crystal germanium.

Acknowledgment. We would like to thank Profs. Nathan Lewis, Chris Chidsey, and Nicholas Melosh for insightful discussions and suggestions. This work was supported by Stanford INMP, a DARPA 3D Program, and SRC/AMD.

Supporting Information Available: Materials and Methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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