

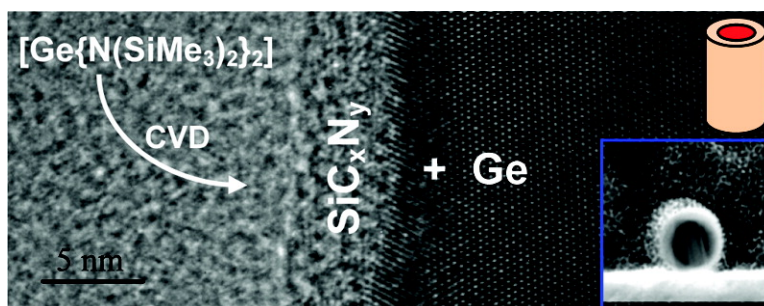
Article

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One-Step Chemical Vapor Growth of Ge/SiC_xN_y NanocablesSanjay Mathur,^{*,†,‡} Hao Shen,[†] Nicole Donia,[†] Thomas Rügamer,[†]
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Abstract: Single-step synthesis of one-dimensional Ge/SiC_xN_y core-shell nanocables was achieved by chemical vapor deposition of the molecular precursor [Ge{N(SiMe₃)₂}₂]. Single crystalline Ge nanowires (diameter ~60 nm) embedded in uniform SiC_xN_y shells were obtained in high yields, whereby the growth process was not influenced by the nature of substrates. The shell material exhibited high oxidation and chemical resistance at elevated temperatures (up to 250 °C) resulting in the preservation of size-dependent semiconductor properties of germanium nanowires, such as intact transport of charge carriers and reduction of energy consumption, when compared to pure Ge nanowires.

1. Introduction

Semiconducting nanowires (NWs) represent a distinct class of matter because their unique size- and dimensionality-dependent electrical, optical, and chemical properties can be substantially modified relative to the bulk counterparts due to the quantum confinement of conduction carriers in reduced dimensions.^{1–5} Germanium is one of the important semiconductors with larger excitonic Bohr radius (~24.3 nm) and higher electron mobility (3900 cm²/V s) when compared to silicon (~4.9 nm, 1400 cm²/V s), which results in more prominent quantum size effects and leads to technologically important applications such as high-performance field-effect transistors and infrared photodetectors.^{6,7} Germanium nanowires with reproducible size, structure, and function offer promising potential as interconnects or active components in nanoscaled electronic and optoelectronic devices, once economically viable synthesis procedures and utilization concepts for these unique building blocks become available.³ Recently, a number of innovative approaches have been demonstrated for synthesizing functional nanowires of different compositions; however, modulation of one-dimensional (1D) nanostructures toward controlled dimensional and chemical configurations remains the most crucial step underlying the technology transfer issues, which mandate detailed understanding and simplification of the growth procedure.^{8,9}

Germanium nanowires have been successfully grown by physical and chemical vapor transport reactions; however, most of the synthesis requires high temperatures (>800 °C) in order to carry out the vapor → liquid → solid (VLS) transformation associated with catalytic growth.^{10–12} As a result, contamination in Ge nanowires, due to diffusion of heteroatoms, and surficial oxidation at high processing temperature are difficult to avoid.¹³ In order to achieve low-temperature synthesis of Ge nanowires, several approaches such as supercritical fluid–liquid–solid (SFLS) (300–450 °C)¹⁴ and chemical vapor deposition (CVD) (~300 °C)^{15–18} have been developed. Given the fact that Ge easily forms unstable oxides on the surface and Ge oxides are soluble in water,¹⁹ effective diameters of Ge nanowires and the corresponding quantum physical properties are expected to change during device operation, and therefore passivation of individual nanowires to prevent the oxidation process is essential. Several reports describing the surface chemistry–electrical property relationship have appeared in the recent past.^{19–24} Their results led to successful passivations toward air-

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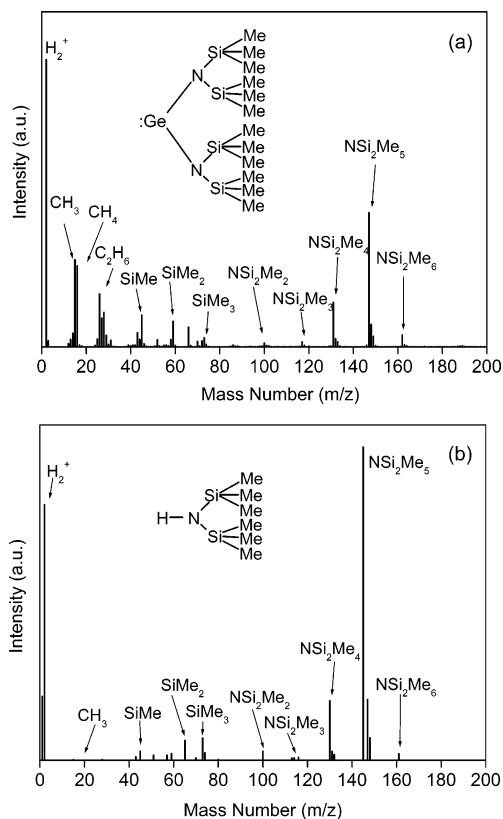


Figure 1. Mass spectra of (a) $[\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2]$ and (b) $[\text{HN}(\text{SiMe}_3)_2]$ precursors recorded during the CVD process.

stable, high-performance functional devices. Surface passivation and modification can conserve the electrical transport behavior of nanowires, which is strongly influenced by depletion layer induced by adsorbed oxygen species and photon interaction.²⁵ Coaxial core–shell semiconductor heterostructures formed by the growth of a chemically stable overlayer on nanowire cores are generally fabricated by **multistep depositions**;^{26–28} however, synthesis of 1D core–shell heterostructures with Ge as core material is not established technology largely due to complexity of multistep processes, the unavailability of precursors with suitable vapor pressure, and the lack of established synthetic principles for growth of the shell material.

CVD of a single-molecule precursor (SMP-CVD) is a bottom-up technique to produce large-quantity and high-quality nanostructures with controllable composition, phase, and dimension. Several reports have showed that the molecular approach is useful to grow nanowires at low temperature and of various compositions such as Ge,^{15,16} GaN,²⁹ IrO₂,³⁰ CoSi,³¹ SiC,³²

Zn_xCd_{1-x}Se,³³ and SiC/SiO₂.³⁴ Preparation of CdS/ZnS core–shell nanowires has been achieved via a one-step metal–organic CVD process with a co-fed single molecular source of CdS and ZnS.³⁵ We report here the first example of a one-step and catalyst-free growth of Ge/SiC_xN_y core–shell nanostructures through CVD of a single molecular precursor $[\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2]$.

2. Experimental Section

Synthesis of $[\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2]$ Precursor. Tri-*n*-butyltin hydride (68.1 g, 0.233 mol) was added to the germanium (IV) chloride (50 g, 0.233 mol) and 1,4-dioxane (40 mL) in a mixture of diethyl ether (50 mL) and *n*-hexane (100 mL) at ambient temperature. Mixing was mildly exothermic, and a white precipitate was immediately formed. The reaction mixture was stirred under nitrogen at room temperature for 24 h. The white precipitate was filtered off, washed three times with *n*-hexane, freed from solvents in vacuum (10^{-2} Torr), and identified by element analysis (exp. (calc.): Ge, 30.8% (31.3%); Cl, 30.1% (30.6%); C, 20.44% (20.7%); H, 3.57% (3.48%)) as the essentially pure $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ (36.67 g, 73% based on GeCl_4).³⁶ The synthesis of $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ was achieved by salt elimination reaction between anhydrous $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ (9.923 g; 0.043 mol) and 2 equiv of $\text{LiN}(\text{SiMe}_3)_2$ (14.34 g; 0.086 mol) in Et_2O and C_6H_6 .³⁷ The reaction mixture was heated up to 60 °C and stirred under nitrogen for 24 h. The precipitated LiCl was removed by filtration. The removal of excess solvent in vacuum gave a yellow-orange viscous liquid which could be distilled under vacuum (10^{-2} Torr) at 90 °C to obtain $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$. The reaction yield was 75% based on $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$.

Instrumentation. Ge/SiC_xN_y nanowires were synthesized in a horizontal CVD reactor in which a high-frequency field was used to inductively heat the substrates by placing them on a graphite susceptor (700–900 °C). $[\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2]$ was introduced in the reactor through a glass flange by applying dynamic vacuum (10^{-4} Torr) and heating the precursor reservoir to the desired temperature (70–85 °C). The precursor flux was regulated following the feedback of the pressure measurement in the reactor during the CVD process. The gaseous byproducts were detected by an online quadrupole mass spectrometer coupled to the CVD reactor. Room-temperature powder X-ray diffraction (XRD) was obtained on a Siemens D-500 diffractometer using Cu K α radiation. Scanning electron microscopy (SEM) analysis was performed on an EDX-coupled scanning electron microscope JSM-6400F (JEOL). The substrate-bound nanowires were mechanically scraped and sonicated in ethanol and deposited on copper grids for TEM measurements performed on a Philips 200 FEG (200 kV) transmission electron microscope. The composition of Ge/SiC_xN_y was determined by XPS which was performed on a Surface Science Instrument, M-Probe, operating with an Al K α radiation and total resolution of ~ 0.8 eV.

For determining the electrical behavior, a suspension of the nanowires was applied between interdigital electrodes (IDE) using a glass capillary. A suspension of nanowires was made in isopropyl alcohol by ultrasonication of nanowire samples for several seconds. The IDEs were fabricated on quartz substrates by sputtering a platinum film of 50-nm thickness. Each IDE is composed of 50 pairs of comb electrodes with a pitch of ~ 1 μm . IDE was connected to an external circuit by mounting on an 8-pin IC socket (DIP) using conducting adhesives. The samples were built in a chamber of a homemade sensing characterization system in which the samples can be heated (up to 250 °C, 1 h) and regenerated

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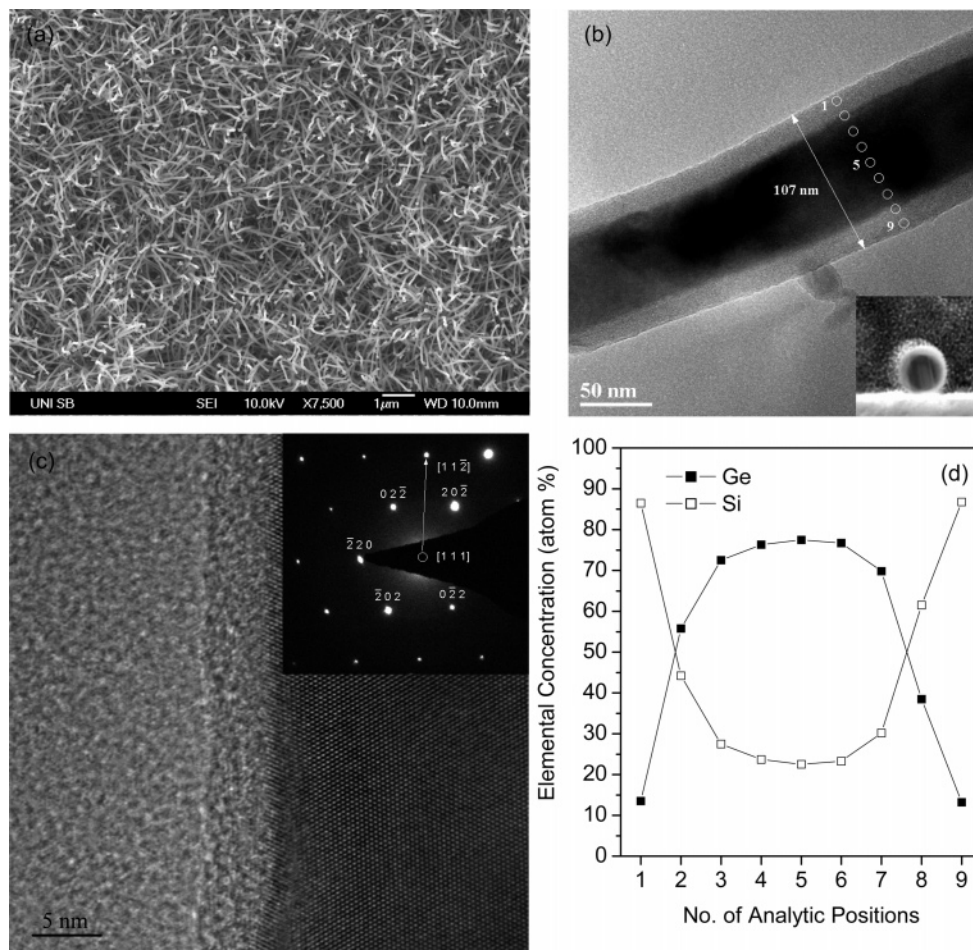
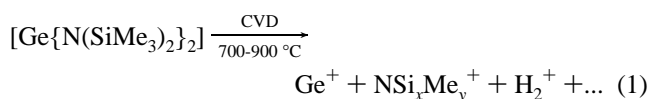


Figure 2. (a) SEM and (b,c) TEM images of Ge/SiC_xN_y nanowires obtained at 850 °C. (d) Elemental distribution of Ge and Si obtained by nanoprobe EDX analysis.

with 100 sccm synthetic air. *I*–*V* curves were obtained under different heat-treatment conditions monitored by a PC-controlled HP 2400 source meter.

3. Results and Discussion

Chemical Vapor Deposition of Ge/SiC_xN_y Nanowires. The decomposition behavior of [Ge{N(SiMe₃)₂}₂] was studied by on-line mass spectral analysis, which revealed NSi_xMe_y⁺ species with high spectral weight (Figure 1a). For comparison and differential peak analysis, the mass spectrum of the free ligand [HN(SiMe₃)₂] was recorded under similar CVD conditions, which showed a high peak for atomic hydrogen in the case of [Ge{N(SiMe₃)₂}₂], whereas this peak was less prominent in the case of the free ligand [HN(SiMe₃)₂] (Figure 1b). Based on the fact that Ge–N bonds are more labile than Si–N bonds (Ge–N: 55 kcal/mol; Si–N: 78 kcal/mol),³⁸ the decomposition pattern of the precursor molecule can be outlined as follows (eq 1):



The analysis of gaseous byproducts suggested that decomposition produced Ge feedstock which led to the preferential

crystallization of Ge core apparently due to higher sticking coefficient and mobility of ad-atoms. In a later step, NSi_xMe_y⁺ species condense on the growing Ge NWs to form a homogeneous overlayer. Since the concentration of Ge and NSi_xMe_y⁺ species in the gas phase is constant, the growth process is self-terminating. The amount of atomic hydrogen plays an important role in the control of radial dimensions and uniform growth of Ge nanowires,³⁹ it is thus possible that atomic hydrogen plays a role in the growth process of Ge/SiC_xN_y core–shell structures.

Microstructure Analysis. The CVD deposits on different substrates (Si, Fe, Al₂O₃, and MgO) exhibited wire-like morphology, indicating a single-step growth of Ge/SiC_xN_y nanowires and substrate-independent nature of the observed structural features. Morphology and microstructure analyses (Figure 2) confirmed a catalyst-free growth and core–shell configuration where single crystalline Ge core was covered by an amorphous SiC_xN_y overlayer. The HR-TEM image (Figure 2c) of individual wires revealed single crystalline Ge with *fcc* structure and a preferred growth direction [112̄]. Elemental mapping using EDX analysis (spot diameter, 5 nm), performed perpendicular to the wire axis (Figure 2b), displayed a Ge-rich core, whereas Si was found to be concentrated in the overlayer (Figure 2d). In order to perform a 3D analysis of the core–

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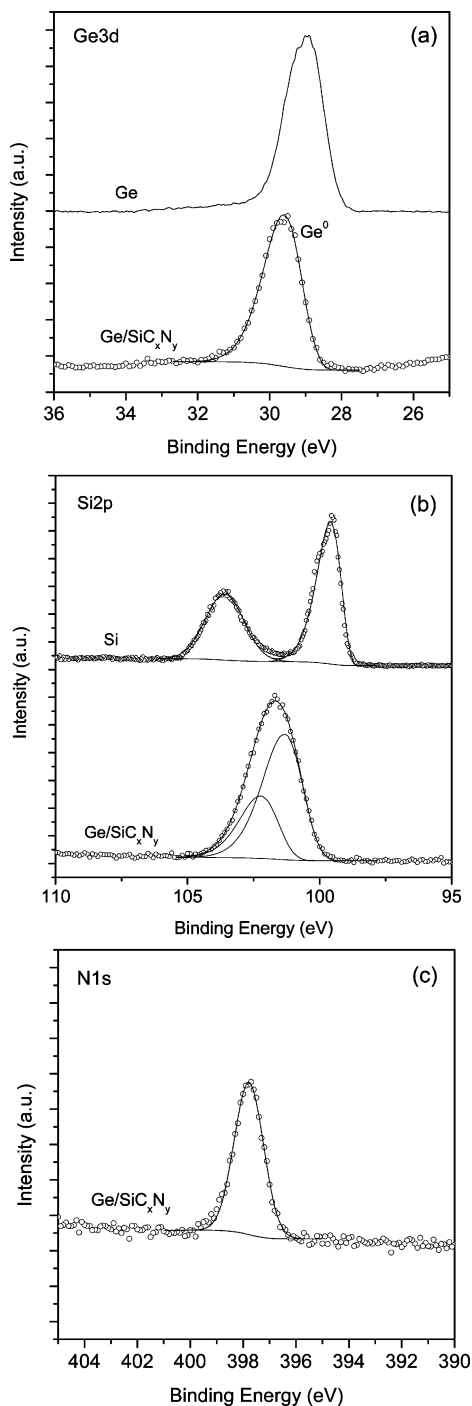


Figure 3. XPS spectra of Ge/SiC_xN_y nanowires: (a) Ge 3d, (b) Si 2p, and (c) N 1s.

shell NWs, cross-sectional lamellae of Ge/SiC_xN_y NWs spread on a Si substrate were prepared using focused ion beam technique followed by HR-TEM analysis. Figure 2b (inset) confirmed the core (Ge)–shell (SiC_xN_y) configuration of our nanowires.

Chemical composition of the shell material was unambiguously identified by high-resolution XPS analysis, which delivered chemical shifts of Ge 3d, Si 2p, and N 1s peaks as finger prints for the chemical bonding within the core–shell structure (Figure 3). Compared to polycrystalline Ge (~29 eV), the Ge 3d peak in Ge/SiC_xN_y NWs is shifted toward higher binding energy (~29.7 eV), which can be attributed to the insulating

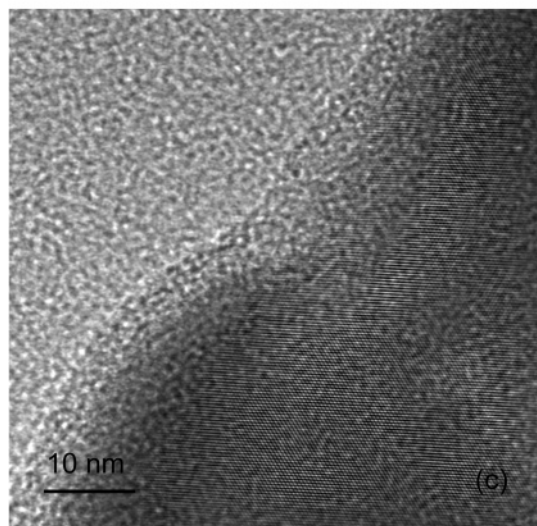
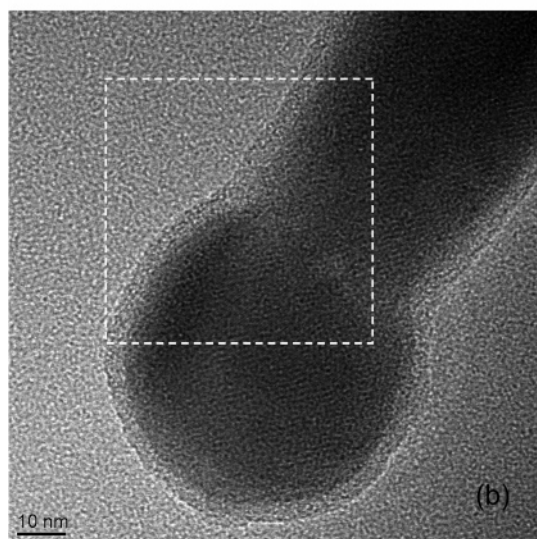
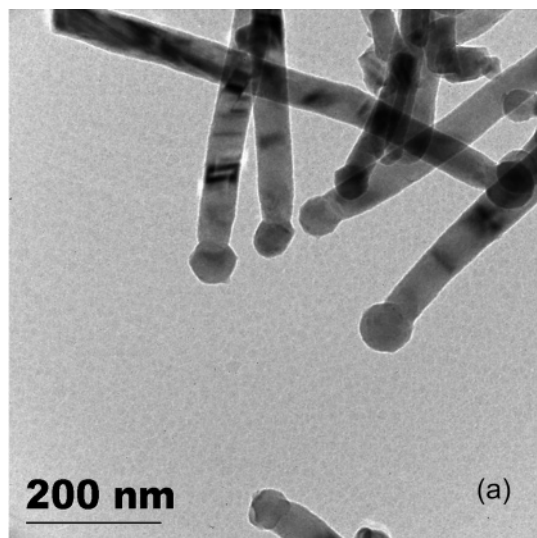


Figure 4. TEM images of the tips of Ge/SiC_xN_y nanowires.

nature of the shell material and also to the reduced dimensions of nanowires. The chemical configuration of Si is complex due to the broadness of the peak which is probably due to the overlapping of Si–N and Si–C features; however, a comparison with chemical shifts observed in the Si/SiO_x reference sample

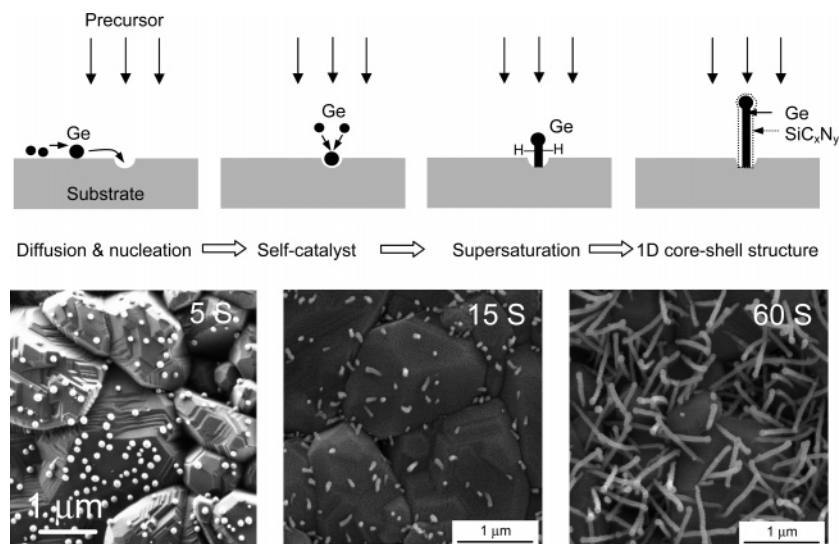


Figure 5. Proposed self-catalytic growth mechanism for Ge/SiC_xN_y nanowires and SEM images of Ge/SiC_xN_y nanowires formed in 5, 15, and 60 s.

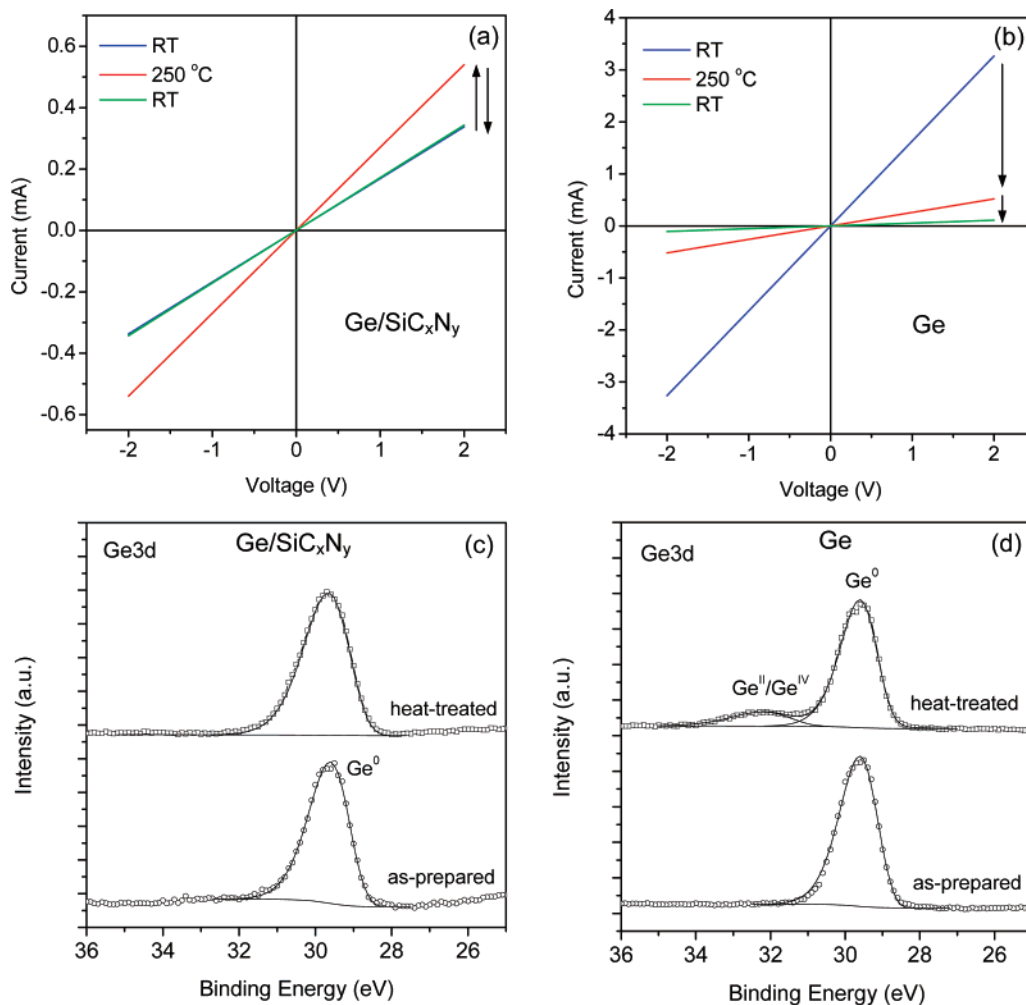


Figure 6. *I*–*V* characteristics and the corresponding XPS spectra of Ge 3d peaks of Ge/SiC_xN_y (a and c) and Ge (b and d) nanowires.

suggests that Si is bonded to less electronegative partners (C, N) than O. The sharp N 1s peak at 397.8 eV indicates a single Si–N phase in the samples. The carbon has at least two distinct configurations which can be assigned to graphitic carbon (contamination due to residual organics) and carbidic phases, respectively.⁴⁰ The above data confirmed the chemical composi-

tion of the amorphous overlayer to be SiC_xN_y, whereas the core consisted of pure Ge. Since CVD of the protonated ligand (HN-

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{SiMe₃}₂) has been shown to produce SiC_xN_y films,⁴¹ it can be envisaged that the ligand moieties (–N{SiMe₃}₂) present in the precursor molecule decompose to similar composition due to a preformed N–Si–C backbone in the molecule. Higher partial pressure of hydrogen in the synthesis of Ge NWs has been shown to have a diameter-governing influence due to the passivation of NW surface by H atoms.³⁹ The high amount of atomic hydrogen (Figure 1a) observed in the CVD of [Ge–{N(SiMe₃)₂}₂] is responsible for the uniformity of the NW diameter, and the SiC_xN_y coating is apparently controlled by the chemical reaction between terminal H atoms and unsaturated ligand fragments.

Growth Mechanism. Core–shell nanostructures were grown on various substrates (Si, Fe, Al₂O₃, and MgO) without any external catalyst or template. Despite the absence of any catalytic metal nanoparticles or growth templates, the as-grown nanowires displayed a spherical tip that showed no difference in chemical composition compared to the body of the nanowire (Figure 4). Further, the lattice fringes of the wires (Figure 4c) were epitaxially extended to the tips without depicting any variation in contrast due to composition variation. SEM analysis of time-dependent nanowire growth stages (Figure 5) showed 1D morphology to be pertinent from the onset of the deposition process. High-resolution SEM images of the sample deposited in 5 s (Figure 5) showed that nanowires preferentially nucleate at defect sites, steps, and/or grain boundaries of the polycrystalline alumina substrate with unusually high growth rates (~1 μm/min). The growth of Ge/SiC_xN_y nanowires is possibly initiated by randomly formed Ge droplets, which are liquefied at the growth temperatures (700–900 °C) and used as “catalysts” to promote anisotropic growth due to the dissolution of precursor fragments followed by precipitation due to supersaturation. The axial growth is kinetically driven, which was examined by a systematic temperature variation. We assume that in our case the rate-determining step of the nanowire growth is the preferential decomposition of precursor molecules on initially formed Ge droplets (Figure 5). In view of the favorable intermixing of Si–Ge, a possible alloying of Si-containing organic fragments with Ge can be ruled out by Raman investigation (Supporting Information) because the finger print of Ge (~300 cm⁻¹) instead of SiGe (~400 cm⁻¹) was observed.

Oxidation Resistance. Finally, the superior potential of Ge/SiC_xN_y core–shell structure against pure Ge nanowires (grown by CVD of [Ge(C₃H₅)₂])¹⁶ was demonstrated by recording *I*–*V* characteristics (Figure 6a,b) of both systems under ambient and high temperatures (250 °C). Upon heating, the resistance of Ge/SiC_xN_y wires decreases, indicating the typical thermoelectronic behavior of semiconductors. The original resistance value was recovered upon cooling the sample to room temperature. On the contrary, the resistance of pure Ge wires decreased at 250 °C and exhibited further irreversible decrease after cooling down to room temperature. The experiment showed that electrical properties of Ge/SiC_xN_y nanowires were relatively unaltered due to the protective function of the SiC_xN_y overlayer, whereas pure Ge nanowires suffered rapid oxidation resulting in thickening of the native germanium oxide on the surface and less conduction (Figure 6a,b). Phase evaluation in both systems by surface-sensitive X-ray photoemission spectroscopy showed the appearance of Ge 3d spectral features at

the higher binding energy corresponding to oxidized Ge species in pure Ge NWs, whereas the Ge⁰ phase in Ge/SiC_xN_y samples showed no change before and after heat-treatment (Figure 6c,d).

The charge carrier transport in nanowires depends on the surface states and potential distribution between the material surface and surroundings. The unique structural and electrical properties of Ge/SiC_xN_y nanowires exhibit promising potential for device applications, such as the following:

(i) effective passivation of germanium nanostructures by the SiC_xN_y shell necessary for preserving size-dependent semiconductor properties of germanium nanowires, enabling ballistic transport of charge carriers and reduction of energy consumption,

(ii) the insulating and barrier properties⁴² of the SiC_xN_y coating would not only minimize the surfacial roughness but also prevent the diffusion of foreign ions/atoms, thereby reducing the background current (noise) in nanowire-based devices,

(iii) the surface passivation of Ge by SiC_xN_y can lead to enhancement of emission performance. Direct optical emission of germanium due to size confinement is usually quenched due to the coexistence of surface defects and interface states. In addition, the broad band gap in SiC_xN_y (~3.8 eV)⁴² when compared to that of Ge makes the shell material optically transparent which would allow directly addressing the core without substantial influence of the shell material.

4. Conclusion

In summary, we have reported on the first self-controlled and single-step synthesis of Ge-based 1D coaxial heterostructures. Since both Ge and the organic part of the single metal–organic source are consumed in the formation of the core–shell structure, it is a simple and cost-effective strategy to grow Ge-based nanostructures in high yield with a greater degree of reproducibility when compared to other reported procedures. The directive force of chemical configuration is obvious in the conformal coverage of the Ge core with SiC_xN_y shell, which is chemically resistant. Given the choices available for tuning the organic periphery (nature of the ligand), this molecular approach would be useful for targeted construction of inorganic nanostructures.^{43–45} For instance, the replacement of hexamethyldisilazane ligands in [Ge{N(SiMe₃)₂}₂] with cyclopentadienyl groups ([Ge–(C₅H₅)₂]) produced pure Ge nanowires because the chemical bonding of the departing C_xH_y ligands on Ge surface is energetically less favorable.¹⁶ In addition, the strength of the metal–ligand bond can be modulated by an appropriate choice of ligand moieties, which could produce high-purity nanowires at low synthesis temperatures and which influence the local atomic arrangement and dimensions (radial and axial) of the nanostructures.

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Supporting Information Available: XRD and Raman patterns and SEM image. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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