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Au-Induced Encapsulation of Ge Nanowires in Protective C Shells**

By *Eli Sutter** and *Peter Sutter*

Semiconductor nanowires (NWs) have attracted significant interest recently due to quantum size effects and novel properties that they will bring to a wide range of electronic and optoelectronic devices, chemical and biological sensors, and photovoltaics. Among the broad range of materials from which NWs can be synthesized, group IV semiconductor (Si, Ge) NWs and NW heterostructures are distinct as they promise materials compatibility and facile integration with conventional Si-based circuits. This promise has stimulated extensive efforts in developing reliable synthesis routes that yield bulk quantities of high-quality group IV NW material, including laser ablation,[1] chemical vapor deposition (CVD) from different precursors and catalysts,[2–6] chemical vapor transport reactions,[7] and low-temperature solution-phase synthesis.[8] Ge offers a number of properties that are superior to those of Si in device applications, for example, higher carrier mobility and larger exciton radius, and hence stronger quantum confinement in a NW, and the prospect of lower processing temperatures and thus easier integration with conventional devices. However, in contrast to Si, which forms a stable oxide with an electronically benign Si/SiO_2 interface, Ge forms oxides with poor chemical stability and unfavorable electrical properties.[9,10] After exposure to air, Ge NWs invariably exhibit surface oxides with thicknesses of about 2–4 nm, a significant fraction of the NW diameter. Methods to inhibit or control surface oxidation, achieve chemical stability under ambient conditions, and thus prevent uncontrolled changes of the electronic properties due to oxidation, will be an important part of any future Ge NW-based device technology. First efforts to address this fundamental issue have been initiated only recently.[11,12]

Layered materials, such as graphite, MoS_2, or BN, in which two-dimensional sheets with complete internal bonding (i.e., no dangling bonds) are joined by van der Waals forces, are chemically inert and could be used to prevent oxidation if assembled as a protective shell around individual Ge NWs. In addition to providing an oxidation barrier, the encapsulation of the semiconductor NWs in a graphitic carbon shell would have the benefit of an already comprehensive understanding of the chemical functionalization of C surfaces, which may open up new avenues for sensing applications based on Ge/C core/shell NWs. In the presence of sufficient C, nanoparticles of some metals (Au,[13] Pb, Sn,[14] Fe,[15] Ni, Co, Cu, Ti[16]) are readily encapsulated in graphitic C shells, as metal surfaces appear to catalyze and template the assembly of ordered C sheets. Surface chemistry and reactivity of most semiconductors, on the other hand, preclude the growth of ordered C sheets, both due to the absence of catalytic effects found for metals and because of the formation of stable carbide compounds.

Here, we use in situ transmission electron microscopy (TEM) experiments to demonstrate the controlled encapsulation of Ge wires in C shells at moderate temperatures. Traces of Au at the NW surface, originating from the Au/Ge catalyst particle used for growing high-aspect-ratio wires, are shown to be critical to the assembly of fragments of graphene C sheets, which then transform into well-defined multilayer shells that completely encapsulate the Ge NWs. Examination of the encapsulated wires after prolonged exposure to ambient conditions shows that the C shells remain intact and unchanged, and provide an efficient oxidation barrier for the Ge wires.

Our variable-temperature in situ experiments are carried out in the temperature range between room temperature and 400 °C on C-supported Ge NWs synthesized prior to the in situ studies using CVD. Figure 1 shows TEM images of the structure and morphology of Ge NWs, obtained at room temperature prior to our in situ experiment; these images are representative of the as-grown starting material in our study. The inset of Figure 1a shows an overview of a group of wires dispersed on the C film of the TEM grid. Our method of NW dispersal creates Ge wire segments severed from the Si substrate, comprising the wire shaft as well as the tip with the residual Au/Ge catalyst particle. The slightly tapered NWs have a typical diameter of 10–50 nm at the tip, 100–200 nm at the base, and are several micrometers long. The wires have monocrystalline cores and well-defined faceted surfaces, and all exhibit a 1–4 nm thick oxide shell, as would be expected after transfer through ambient air.[3,6,11] The TEM images of Figure 1a–c show the detailed structure close to the NW tip for one of the wires from the inset. For all NWs the Au/Ge nanoparticle at the tip shows darker contrast than the Ge wire. In high-resolution TEM images (Fig. 1b and c) the (111) lattice planes of the Au/Ge alloy with separation (0.219 nm) close to the lattice spacing of Au are clearly resolved. The NW axis is aligned with the [111] direction. The high-resolution images show lattice fringes with separation of 0.327 nm perpendicular to the

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[*] Dr. E. Sutter, Dr. P. Sutter
Center for Functional Nanomaterials
Brookhaven National Laboratory
Upton, NY 11973 (USA)
E-mail: esutter@bnl.gov

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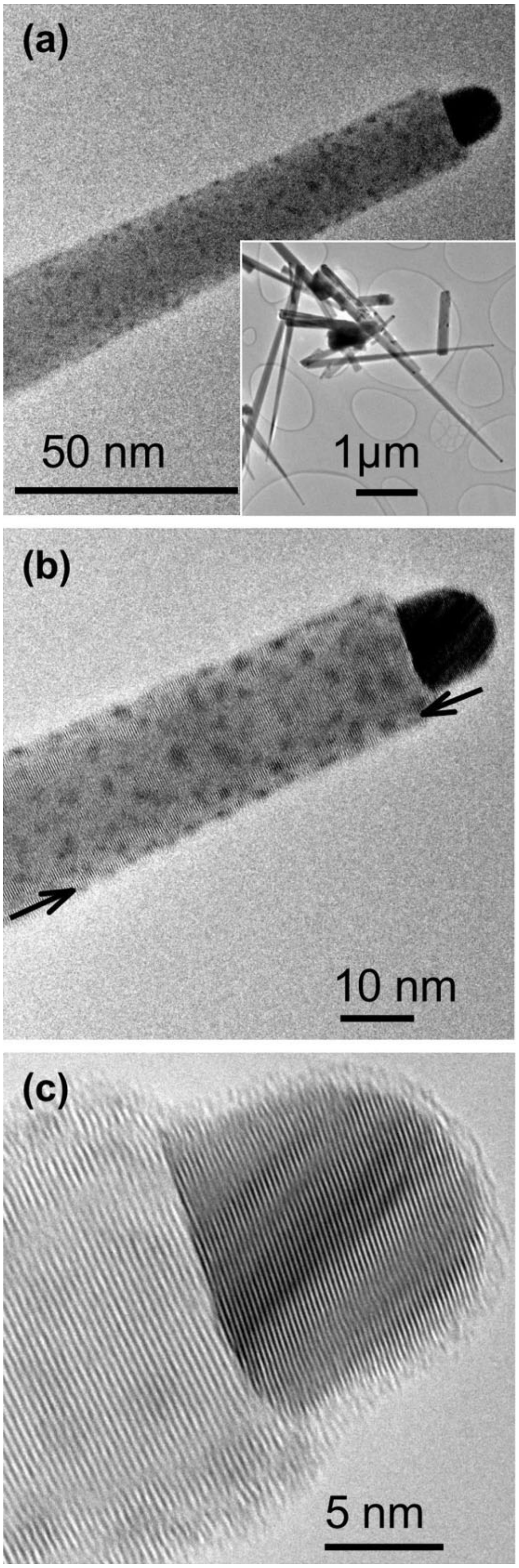

Figure 1. TEM images of as-grown Ge NWs taken at room temperature prior to the annealing experiments. The inset of (a) shows an overview of a group of wires dispersed on a C film. b,c) High-resolution TEM images of the area close to the tip of the Ge NW from (a).

NW axis, consistent with the spacing of (111) planes in bulk Ge. Importantly, the contrast from the Ge wires is not homogeneous. Spots exhibiting darker contrast can be clearly seen. A combination of several experimental observations conclusively demonstrates that these spots represent accumulations of Au on the surface of the Ge NWs. Local energy-dispersive X-ray spectrometry analysis along the NWs away from the Au-rich tip shows the presence of small but measurable amounts of Au (together with Ge). In high-resolution TEM a few larger spots show lattice fringes consistent with the (111) lattice spacing of Au. The Au appears bunched along the projected edge of the wires, consistent with Au aggregates that are not randomly dispersed throughout the Ge matrix, but instead are clustered on the surface (see arrows). During in situ annealing, the Au aggregates are observed to ripen rapidly into larger, elongated crystalline clusters aligned with the NW axis. Such facile rearrangement of Au at somewhat elevated temperatures (< 400 °C) provides additional evidence for the localization of the Au clusters on the NW surface and is consistent with scanning tunneling microscopy observations of Au chain assemblies on extended Ge surfaces.[17] The presence of small Au aggregates on the Ge NW surface is not surprising. The Au-rich eutectic nanoparticle has been observed to shrink during Si-wire growth,[18] suggesting a slow loss of Au from the particle. The solubility of Au in Ge is already very low at the growth temperature of our wires ($\ll 10^{-6}$ at %[19]), and decreases even further upon cooling to room temperature. Given the small diameter of our wires, surface segregation would be a likely pathway to expulsion of excess Au from the Ge lattice during cooling.

Figure 2 shows the process of the reduction of the initial, thick surface oxide and the gradual assembly of a C shell around the Ge NWs and the Au/Ge tip during an in situ annealing experiment in the transmission electron microscope. The Ge NW shown in Figure 2a at room tempature before heating was chosen as it exhibited a thick (4 nm on average) layer of oxide. The inset of Figure 2a shows in detail the interface between the Ge wire and the GeO_x surface layer. The oxide layer is amorphous, and its interface with the Ge surface is atomically sharp. Upon heating of the wires to 180 °C we observe that the thickness of the GeO_x layer decreases over a course of minutes, creating large areas of the NW surface that are entirely oxide free. Figure 2b shows the process at a stage at which the oxide thickness has decreased to ca. 2.5 nm, and Figure 2c shows the oxide entirely removed over large parts of the surface (Fig. 2c, inset). Along the length of the NW some oxide patches remain that are completely removed after the temperature is increased to 290 °C (Fig. 2d). This observed removal of the native GeO_x from the NW surface can be caused by the thermal or electron-beam-induced desorption of the oxide, or may involve its reduction by C diffusing from the amorphous C support at elevated temperature.

Following the removal of the surface oxide, the Ge NWs undergo a striking further modification. At a temperature of 290 °C the assembly of graphene C fragments is initiated at the tip of the NW adjacent to the Au/Ge nanoparticle, similar

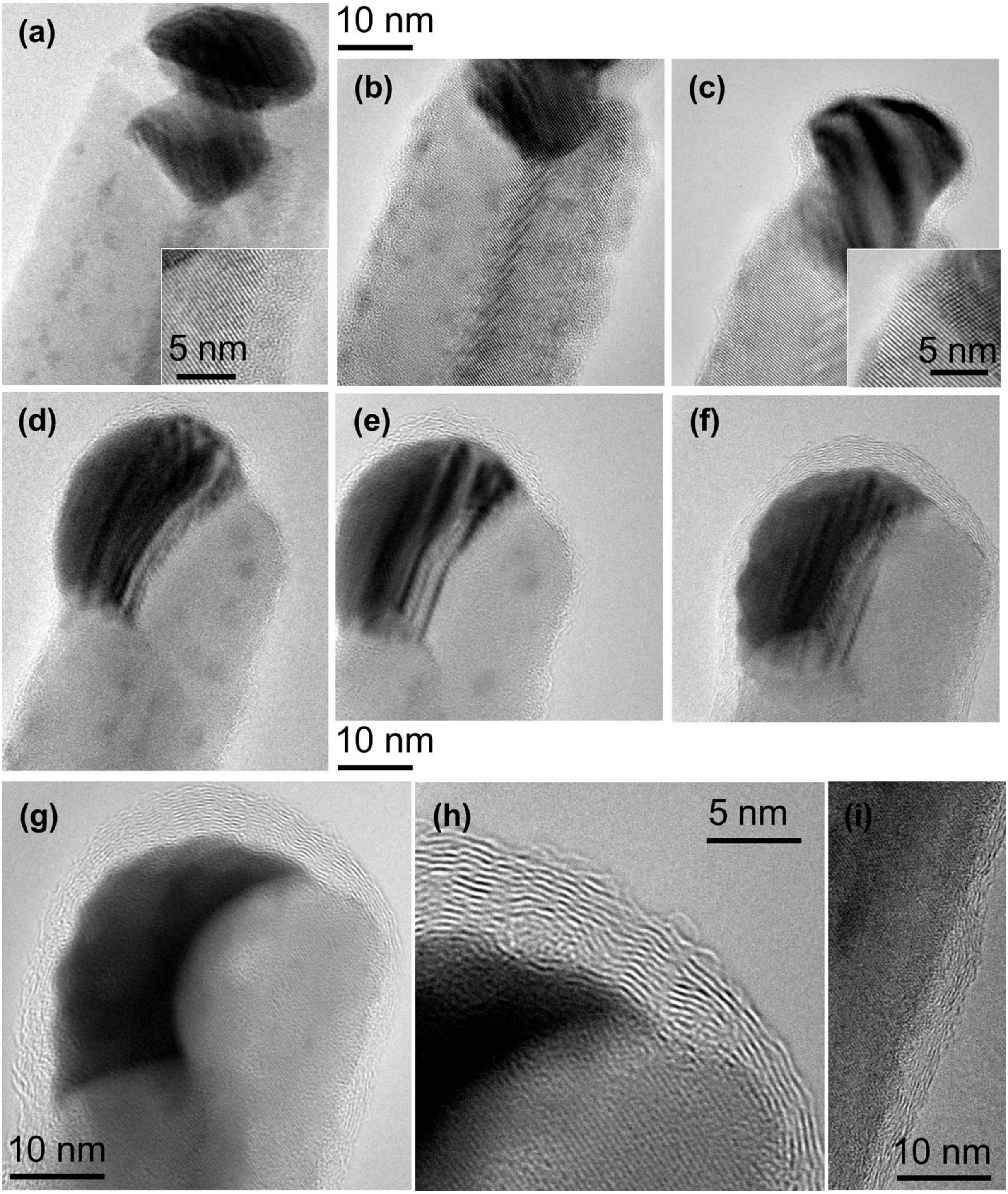

Figure 2. Sequence of TEM images showing the process of removal of the GeO_x surface layer (a–c) and the assembly of a C shell (d–g) around a Ge NW during in situ annealing at variable temperatures between room temperature and 350 °C. Sample temperatures: a) room temperature; b,c) 180 °C; d) 290 °C; e,f) 340 °C; g–i) 355 °C. At temperatures between 290 and 330 °C the Au/Ge nanoparticle at the tip moves to the left as some Ge is expelled from it (d). h,i) The graphitic shell close to the Au/Ge tip of the NW and on the Ge NW surface away from the tip, respectively.

to the assembly of C sheets around the Au nanoparticles observed previously.[13] Figure 2e, f, and g ($T = 340\,^{\circ}\mathrm{C}$) shows that the continued buildup and organization of this C shell occurs both on the Au/Ge catalyst particle and on the surface of the Ge NW. The shell formation starts with the assembly of small curved segments (Fig. 2e) that gradually build up several layers covering the whole NW, and eventually straighten and organize into stacks of extended curved graphene sheets

(Fig. 2g and h). From the high-resolution image in Figure 2h the spacing of the graphene layers is determined to be ca. 0.3–0.4 nm, consistent with the *c*-axis spacing in graphite. From Figure 2i, which was obtained far from the NW tip and Au/Ge catalyst particle, it appears that at this stage the entire Ge wire is embedded in a C shell consisting of several graphene layers. The observed assembly process indeed leads to the complete encapsulation of the entire Ge NWs in ordered multilayer C shells. One example of an encapsulated NW is shown in Figure 3, showing an overview of the wire (Fig. 3a) as well as high-magnification images of the core/shell interface at different positions along the NW (Fig. 3b–d). An ordered graphene C shell continuously covers the entire NW surface. The number of layers, that is, the thickness of the shell, is largest at the Au-rich tip, where it builds up more than 20 graphene layers (~ 8.8 ± 0.3 nm) for the NW shown in Figure 3. Away from the tip, we consistently observe a slightly reduced shell thickness, which is, however, rather uniform along the entire length of the wire. For the NW shown in Figure 3, we measure (6.9 ± 0.3 nm).

Our in situ annealing experiments, combined with previous observations of the assembly of C shells around Au nanoparticles,[13] strongly suggest that the small Au islands detected on the wire surface play a key role in the assembly of ordered C shells around the Ge NWs. We have performed a number of complementary experiments that confirm this assertion. Extensive in situ annealing in the transmission electron microscope of metal-free Ge nanoparticles on C supports does not result in encapsulation, that is, in the absence of Au Ge does not catalyze the assembly of ordered graphene fragments or layers. Under similar experimental conditions, we find that in samples consisting of mixtures of Ge and Au nanoparticles, Au particles are encapsulated in C shells while the Ge particles are not. These findings strongly suggest that Au at the surface of our Ge NWs is instrumental in their encapsulation in a C shell. The observations of Figure 2 show that, analogous to

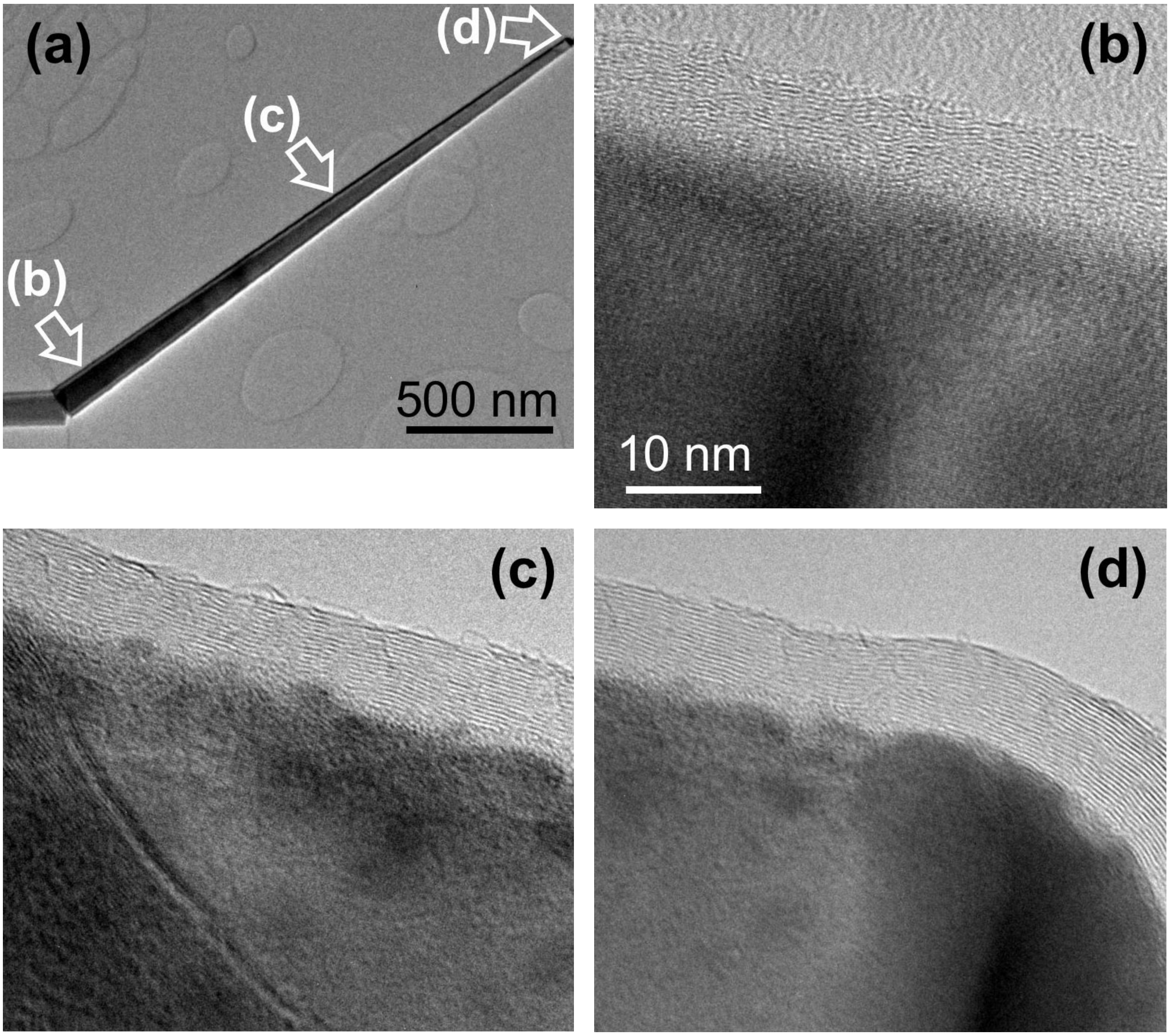

Figure 3. TEM images of a Ge NW completely embedded in a multilayer C shell. a) Overview image showing the entire NW; b–d) higher magnification images showing the Ge core and C shell, taken at different positions along the NW indicated by arrows in (a).

the encapsulation mechanism of Au nanoparticles, Ge NWs whose surface is decorated with small Au islands initiate the formation of small fragments of C sheets, which then become progressively more ordered and organize into well-defined curved graphene sheets.[20] The difference in shell thickness between the Au-rich tip and the Au-decorated Ge wire suggests that C sheet assembly is slightly less efficient on small Ge-supported Au clusters than on larger Au or Au-rich nanoparticles, which may offer a higher density of required active sites per unit surface area. Differences in the chemical reactivity of Au and Ge surfaces are likely responsible for the observed assembly of graphene sheets on Au/Ge, and its absence on Ge surfaces without Au decoration. Other transition metals, such as Ni or Co, are commonly used as catalysts for C-nanotube growth. One of their key roles in this process is their strong binding of C atoms at low-coordination sites, for example, step edges,[21] which is due to the overlap between C adsorbate states and metal d-states. Although bulk Au is a noble metal, its reactivity and chemisorption energy for different adsorbates was shown to increase significantly for larger bond length and reduced coordination, as found in nanoclusters.[22] C atoms or small sp^2-bonded graphene embryos chemisorb and are anchored at such binding sites, and grow into graphene sheets by further attachment of diffusing C.[21,23] Separate in situ TEM experiments on Au nanoparticles, showing that graphene sheets readily form at non-faceted Au particles with a high density of low-coordination sites, but do not form on particles with extended facets,[13] corroborate this scenario based on the overlap of adsorbate states with Au d-states at low-coordinated sites. For covalent semiconductors, such as Ge, the chemical reactivity is dominated by s–p hybridized states near the Fermi energy, which would not enable such a process. Our findings suggest that the graphene C encapsulation could be performed generally on Ge NWs synthesized on Au/Ge catalyst particles. Indeed, one previous observation of the formation of Ge/C core/shell structures on Au-catalyzed Ge wires[24] very likely involved traces of Au on the wire surface as well.

The controlled, Au-induced encapsulation of our Ge NWs suggests the possibility of judiciously assembling a protective C shell to passivate the surface and prevent oxidation of the wires in ambient air. To demonstrate the oxidation resistance achieved by multilayer graphene shells, we imaged embedded Ge NWs before and after prolonged exposure to air. TEM images comparing the wires and shells before and after 48 h exposure to ambient conditions are shown in Figure 4. No oxide layer is formed on the Ge surface, and the layer structure and thickness of the C shell remain completely unchanged. The only difference observed is the buildup of an amorphous layer, likely consisting of hydrocarbons adsorbed in ambient, at the outer surface of the C shell.

Our observations demonstrate a rational route toward the encapsulation of crystalline Ge NWs in protective C shells, exploiting traces of Au on the wire surface left behind from the NW growth on a Au/Ge catalyst nanoparticle. Au may be an ideal material, since it does not form stable compounds with Ge but is, at least in the form of nanoclusters, still sufficiently reactive to promote the formation of graphene C sheets. The resulting C shell provides efficient protection of the Ge surface against oxidation in ambient air, which highlights a potential beneficial effect of residual Au atoms at the NW surface, in contrast to their well-known detrimental effect on the electronic properties when dispersed in the bulk. More generally, our results suggest the possibility of using metal surface decoration, accidental (as for Ge) or deliberate, to trigger the encapsulation of a wide variety of NW materials in C shells to build a protective layer against ambient influences or construct functional semiconductor/C core/shell NW structures.

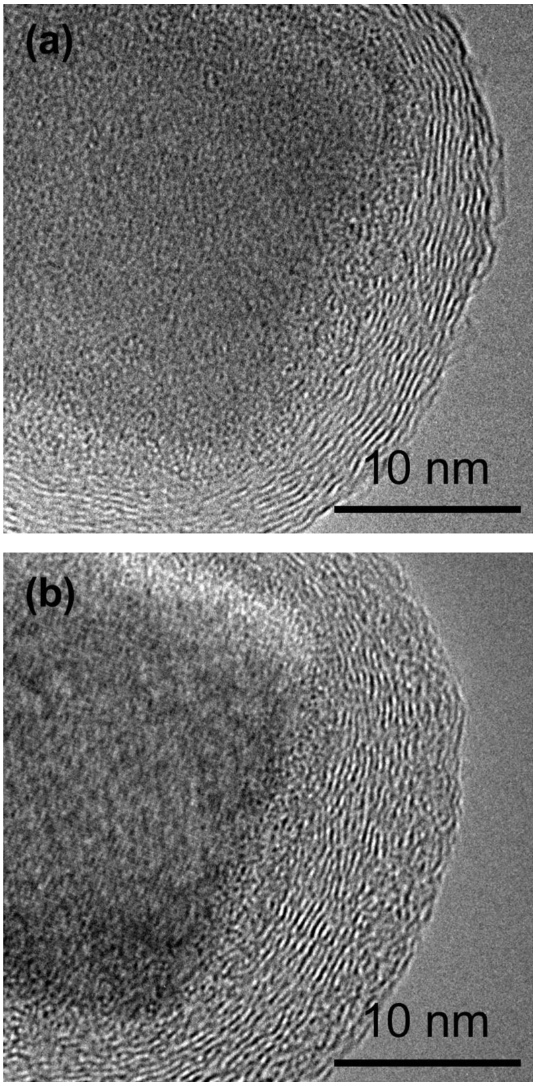

Figure 4. TEM images of a Ge NW base embedded in a C shell a) before and b) after 48 h in air.

Experimental

The Ge NWs were synthesized prior to the in situ studies by CVD from GeH_4 in a ultra-high vacuum reactor with a base pressure of 2×10^{-10} Torr (1 Torr ~133 Pa). The synthesis was carried out over a Au catalyst (10 nm Au nanoparticles commercially purchased from British BioCell International) on a Si substrate at ca. 320 °C. They were then transferred through air and dispersed on amorphous C films supported by standard Cu grids for variable-temperature TEM imaging.

The variable temperature in situ experiments were carried out in a JEOL JEM 3000F field-emission transmission electron microscope equipped with a Gatan 652 high-temperature sample holder. They covered the temperature range between room temperature and 400 °C at pressures below 2×10^{-5} Pa, and at low electron-irradiation intensities to prevent any uncontrolled electron-beam-induced structural changes.

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