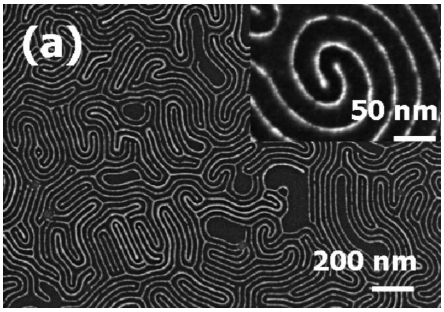
Making (and Breaking) the Mold for Metallic Nanowires

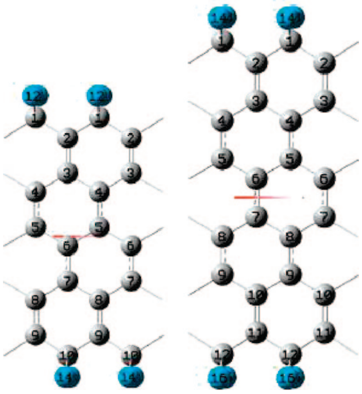
■ Metallic nanowires continue to be a popular research topic due to their unique properties and range of potential applications. A limiting factor in using these nanostructures in future applications is the ability to assemble, pattern, and align large, high-density areas of the nanowires on technologically relevant supports in an economically feasible way. One approach is to use a template made of a self-assembling block copolymer. Researchers have already exploited block copolymers to fabricate metallic nanoclusters by embedding metal ions within one phase of the template block copolymer and then reducing these ions to nanoparticles through plasma, chemical reducing agents, hydrogen gas exposure, or thermal decomposition.

Using a similar technique, Chai and Buriak (p 489) created patterned and aligned metallic nanowires using self-assembling block copolymer domains oriented parallel to a silicon surface. The patterned block copolymer templates were immersed in solutions containing anionic metallic salts. Through electrostatic interaction, the metal ions adsorbed to the positively charged phase of the block copolymer. The block copolymer template was subsequently removed *via* oxygen plasma exposure, resulting in metallic nanowires in precisely defined patterns. The researchers demonstrated the versatility of this method by using different metal ion solutions and produced nanowires of gold, palladium, platinum, copper, nickel, cobalt, and iron. Using the same technique with topographically defined silicon substrates, the researchers fabricated nanowires in various types of patterns with long-range order. The researchers suggest that varying processing parameters, including deposition time, metal ion concentration, and molecular weight of the block copolymer, could produce nanowires of different properties suitable for a variety of applications.



Zigzag Nanoribbons: Electrifying Potential

■ A few early studies have generated considerable interest in zigzag graphene nanoribbons due to the peculiar magnetic states found at their edges. To realize the full potential of graphene nanoribbons, researchers have focused on understanding their unique electronic properties from both experimental and theoretical perspectives. Research in this area has suggested that the band gap varies inversely with width for graphene nanoribbons in which all carbon atoms are sp^2 type.

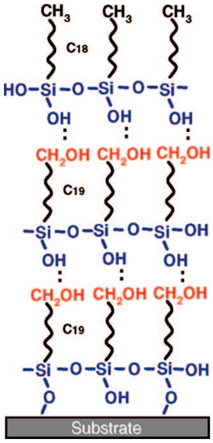


Looking to expand on this knowledge, Kudin (p 516) performed a first principles study of the electronic properties of ribbons with saturated edges, created by adding either two hydrogen or two fluorine atoms. In contrast to previously studied nanoribbons, carbon atoms along the edges of these structures are sp^3 type. Kudin calculated band gaps and formation energies for nanoribbons ranging in width from 2 to 13 zigzag carbon chains. Calculations showed that the band gap varies from 2 to 7 eV as a function of decreasing nanoribbon width for spin-restricted solutions. The nature of the substituent also shifted the energy levels, with fluorine-functionalized nanoribbons experiencing a downward shift of ~3 eV. Calculated Raman spectra showed a distinctive shift toward higher vibrational frequencies for graphene nanoribbons having saturated edges. Kudin suggests that this blue shift could offer a way to identify ribbons with sp^3 carbon regardless of the environment in which they are embedded. These results demonstrate the potential for tuning the electronic properties of graphene nanoribbons on the basis of the chemical nature at the edges and the width of the ribbon itself.

Peeling Back the Layers in Organosilane Films

■ Self-assembling multilayers with unique chemical and architectural nature are involved in numerous applications, and organosilanes are ideal candidates for these supramolecular systems. Films made of multilayer organosilanes have previously been used as nonlinear optical elements in electro-optic devices, for fabricating alignment films in liquid crystal displays, and for crafting durable molecular printboards for supramolecular patterning on silicon oxide substrates. Though these materials have proved their utility, few details are known about their structural features, internal bonding, and how these aspects change with chemical modifications.

To address these questions, Wen *et al.* (p 579) performed a thorough analysis on an 8-layer organosilane film both before and after modifying it by *in situ* wet chemical oxidation to change the terminal alcohol group into a carboxylic acid. Using several different characterization techniques—Fourier transform infrared spectroscopy, synchrotron X-ray scattering, X-ray photoelectron spectroscopy, and contact angle measurements—the researchers painted a detailed picture of the multilayer characteristics. The data from all the techniques consistently show that the chemical modification does not cause any major structural changes other than in the topmost layer, which lost ~25% of its molecules during the reaction. Though some covalent bonding exists between layers of the unreacted molecule, findings showed that the reacted film is practically free of interlayer covalent bonds. The authors suggest that insight into how chemical transformations affect these multilayers could eventually help in the construction of families of structurally related but functionally different film assemblies.



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