

tion, ultrasoft pseudopotentials, supercells, and plane waves. In particular, supercells or "superstructures" of Si-SiO₂-Si with 7–8 planes of Si layers separating the SiO₂ layers were used. The researchers concluded that H⁺ is the only charged state in the supercell because all positively charged defects were more stable than their neutral states by ~3 eV when their Fermi energy approached the top of the Si valence band. The researchers found that as an H⁺ atom approaches the interface, it is repelled by other H⁺ atoms, and either is immediately trapped inside a suboxide bond or SiO₂ protrusion, or migrates laterally throughout the supercell with energy barriers of 0.3–0.5 eV, with the barriers for leaving the cell being much larger. The research team also calculated how the reaction between H⁺ and Si-H defects occurs mechanistically. As H⁺ comes within 1.6 Å of the Si-H bond, a H⁺-H-Si bridge forms, followed by release of H₂ and the formation of a positive defect (D⁺). This was shown with electron-density plots. These plots, according to the research team, show the depassivation process as H⁺ approaches the Si-H bond, bridge formation, and subsequent defect formation. Total energies released from this reaction were 1.3 eV,

but the cost for the reaction was 1.6 eV. According to the report, this reaction was also found to be reversible with annealing in H₂ to show an energy barrier of 1.6 eV.

MATHEW M. MAYE

Large Ordered Arrays of Si Nanocrystals Achieved by Controlled Template Nucleation

The process of self-ordering nucleation of nanocrystals was previously demonstrated by using strained layers in non-lattice-matched systems and by chemically employing two-dimensional (2D) polymer matrices. A research group headed by Philippe Fauchet and Leonid Tsybeskov at the University of Rochester and Q. Xie from Semiconductor Product Sector in Mesa, Ariz. have demonstrated a way of managing silicon nucleation by facilitating the long-range ordering of uniformly sized and shaped nanocrystals through a controlled template. As reported in the November issue of *Nano Letters*, the research team used inverse-pyramid-shaped holes with submicrometer 2D periodicity to control the in-plane properties of the crystals. The *a*-Si/SiO₂ superlattices were deposited by sputtering and crystallized by high-temperature rapid

thermal annealing (RTA) on this template.

Using maskless interferometric lithography and reactive-ion etching, a periodic array of holes was transferred to an underlying oxide layer. Anisotropic KOH etching on exposed (100) Si was used to form an inverted pyramid due to a high etch ratio of (100) surfaces over (111) planes. Etching was carried out at 70°C for 3 min using a dilute (25%) KOH solution, yielding holes shaped like inverted pyramids with atomically smooth (111) walls. A 10-period *a*-Si/SiO₂ superlattice was grown on the predefined template by sputtering in the presence of alternate Ar/Ar + O₂ plasma. Using a Si target, the researchers made films with a final thickness of 50 Å for the *a*-Si layers and 30 Å for the SiO₂ layers. They said that transmission electron micrographs revealed the continuity of the film through the transition from the wafer surface to the sidewall, although gradual thinning along the pyramid's walls was also observed.

The nucleation process was carried out at 900°C for 30 s, using an RTA oven, a typical initiation step for the crystallization of amorphous silicon. According to the researchers, isolated, regularly sized and shaped silicon nanoclusters formed at or

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near the tips of the pyramids. They attributed the location of the nucleation sites to the unique strain gradients as a direct result of the template geometry. They said that superlattice instability and compressive strain, due to dissimilar coefficients of thermal expansion, could also favor nucleation. This feature, the researchers suggest, could be used in the fabrication of large arrays of individually addressable silicon quantum dots. The researchers were able to show that Si nanocrystals could be placed in specific locations on a Si wafer by using standard Si processing techniques.

CALIN MICLAUS

Theoretical Study Predicts Amide Formation is Preferred on Armchair Single-Walled Carbon Nanotubes

Using a theoretical approach to study the reactivity of carboxylic groups toward amines in the direct amidation of single-walled carbon nanotubes (SWNTs) and its dependence on the nanotube structure, some aspects of the chemical derivatization of these nanotubes have become further understood and their application areas expanded. Application areas of nanotubes could be significantly expanded by chemical derivatization. As reported in the November issue of *Nano Letters*, researchers Vladimir Basiuk, Elena Basiuk, and José-Manuel Saniger-Blesa of the National Autonomous University of Mexico obtained theoretical evidence that the direct formation of amides proceeds preferentially on armchair SWNT tips as compared with zigzag SWNT tips, according to the scheme



where $\text{R}^1 = \text{H}$ or Alk, and $\text{R}^2 = \text{Alk}$.

The reaction mechanisms were studied using a two-level so-called ONIOM (own n -layered integrated molecular orbital and molecular mechanics) approach, where the molecular system being studied is divided into two layers that are treated with different model chemistries. The results are then automatically combined into the final predicted results. Monocarboxylated short fragments of (10,0) zigzag SWNTs and (5,5) armchair SWNTs were used to interact with methylamine as model reaction systems. The transition states of the molecular systems were also treated and followed using ONIOM refinement. The researchers reported that all geometric optimizations follow the default convergence criteria set in the Gaussian 98W program.

According to the report, analysis of total optimized geometries for the reaction complexes shows that there is a weak hydro-

gen bond between the amino and carboxylic groups in the armchair SWNTs, whereas the corresponding distance in the zigzag nanotubes is far too long to consider it a H bond. The transition states in both models do not differ significantly in geometry, but the energy of the armchair reaction complex is 10.5 kcal mol⁻¹ higher than that of its zigzag counterpart, implying, the researchers said, that there is a stronger methylamine adsorption on the zigzag SWNTs. Also, the armchair amidation products achieve a lower energy compared with the zigzag SWNT tips; therefore, the latter reaction is less energetically favorable, according to the researchers.

While the results of two-level ONIOM calculations suggest that the direct amidation of carboxylic groups on the armchair SWNT tips is energetically preferable to the zigzag nanotube tips, Basiuk said, "Further detailed studies are desirable to verify whether this can be generalized for other aliphatic amines...It is too premature to discuss practical implications of the data obtained."

KINSON C. KAM

Ferroelectric Domain Inversion Demonstrated in BaMgF₄

In their study of BaMgF₄ (BMF) as a material for ultraviolet generation, researchers from the Massachusetts Institute of Technology, AC Materials (Winter Park, Fla.), and the National Institute of Standards and Technology have demonstrated ferroelectric domain inversion. It also has transparency to <140 nm, and is resistant to solarization. BMF, along with β -BaB₂O₄, LiB₃O₅, and CsLiB₆O₁₀, displays short-wavelength transparency and the potential for UV and vacuum-UV frequency conversion.

To achieve frequency conversion in materials, phase-matching has to be obtained first. One option researchers have is to create materials with a large birefringence, which is not applicable in the case of BMF. Another possibility is to use ferroelectric domain inversion techniques to produce a quasi-matched structure. The advantage of quasi-phase matching (QPM) is that the output wavelength is a function of the period of the structure and is independent of the material's parameters.

According to the researchers' report in the November 1 issue of *Optics Letters*, BMF single-domain crystals, in the shape of an elongated sphere (with the longest dimension of 3 cm along the growth direction and a maximum diameter of 2 cm), were grown using the Czochralski technique. Based on the transmission spectra, the BMF crystals were transparent to wavelengths of ≤ 140 nm. Refractive indices

of interest were measured and correlated with the values given by the Sellmeier fit. The results were then used to calculate the grating periods for QPM interactions. Periodically poled BMF was fabricated from a 500- μm -thick crystal, lithographically patterned with a 19.2- μm grating. A charge of 5.4 μC was delivered in 19 pulses at voltages from 16 kV/mm to 20 kV/mm. The domains were imaged with an environmental scanning microscope. According to the researchers, this experiment demonstrated short-wavelength transmission, domain inversion, and solarization resistance in BMF.

IULIA MUNTELE

Narrow-Band Čerenkov Radiation Generated in a Silicon Foil

By firing 5-MeV electrons at a 10- μm -thick silicon foil, researchers in the Netherlands have succeeded in generating narrow-band Čerenkov radiation at 99.7 eV, proving that soft x-rays (in the range of 100 eV to several keV) can be produced using small accelerators and moderate electron energies. The emission of Čerenkov radiation occurs when the velocity of a charged particle exceeds the phase velocity of light (c/n), where c is the velocity of light and n is the refractive index of the medium. This requires $n > 1$, but at ultraviolet and shorter wavelengths, n is generally less than 1. However, there are narrow regions of resonant anomalous dispersion at atomic absorption edges for which $n > 1$ at soft x-ray wavelengths. Previous demonstrations of this radiation phenomenon used electrons with energies of at least 75 MeV; this demonstration used moderate-energy electrons, as reported in the October 29 issue of *Applied Physics Letters*.

W. Knulst and co-workers at the Eindhoven University of Technology, and J. Verhoeven of the FOM Institute for Atomic and Molecular Physics in Amsterdam, used a multilayered mirror consisting of 101 alternating layers of Mo and Si coupled with a photodiode to detect the Čerenkov radiation. Electrons accelerated to 5 MeV passed through the 10- μm foil of undoped single-crystal silicon and were bent by a 90° dipole magnet into an electron dump. The Čerenkov radiation from the silicon L edge was emitted in a cylindrical cone around the original electron trajectory in the forward direction. For a silicon foil and 5-MeV electrons, the angle of maximum emission of radiation was calculated to be 10.6°, so the detector geometry was arranged to measure the yield at emission angles of 5° and 10° ($\pm 0.5^\circ$). A yield of 1×10^{-3} photon/electron was obtained, which is in reasonable