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

$$\text{SWNT-COOH} + \text{HNR}^1\text{R}^2 \rightarrow \text{SWNT-CO-NR}^1\text{R}^2 + \text{H}_2\text{O}, \quad (1)$$

where R^1 = H or Alk, and R^2 = 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 hydrogen 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 $BaMgF_4$

In their study of $BaMgF_4$ (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-BaB_2O_4, LiB_3O_5, and $CsLiB_6O_{10}$, 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° (±0.5°). A yield of 1×10^{-3} photon/electron was obtained, which is in reasonable

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agreement with theoretical values.

According to the researchers, the ability to generate soft x-rays from moderate-energy electron sources makes tabletop sources of soft x-rays feasible, with possible applications in extreme-ultraviolet laboratory lithography, x-ray microscopy in the water window (284–543 eV), and x-ray fluorescence analysis of low-atomic-number elements.

TIM PALUCKA

STM Induces Luminescence from Metallic Quantum Wells

The tunneling current of a scanning tunneling microscope (STM) has been shown to induce light emission from the metallic quantum well system Na on Cu(111). Using photoluminescence induced by an STM, researchers from the Christian-Albrechts-Universität zu Kiel in Germany have examined the role of confinement on the electronic structure of ultrathin Na overlayers on Cu(111) substrates. The research team has determined that the tunneling spectra and tunneling junction fluorescence from quantum-well states arise from confinement created by the vacuum barrier on one side of the Na overlayer and the local bandgap of the Cu(111) substrate on the other.

As reported in the October 22 issue of *Physical Review Letters*, 0.6–2.0 monolayers (ML) of Na were prepared on Cu(111) in an ultrahigh-vacuum (UHV) STM apparatus with a lens system coupling light output from the tunneling junction to a grating spectrometer with a liquid-nitrogen-cooled CCD detection camera. The research team recorded, at positive sample voltages, tunneling spectra of the differential conductance. Measurements were taken at 4.6 K.

The researchers reported that tunneling spectroscopy from a 0.6-ML Na sample showed features at sample biases of ~0.4 V, ~2.0 V, and ~2.9 V that correspond to three distinct quantum-well states. Their fluorescence measurements showed emission for low sample biases of less than ~2.0 V, with the emission maximum exhibiting a strong blue-shift for more positive biases. The research team attributes the high-energy cutoff of this peak to radiative decay of coupled plasmons excited by inelastic tunneling from the STM tip to the lowest unoccupied quantum-well state at ~0.4 V. A second emission for sample biases greater than 2.1 V showed a weak dependence on sample bias. The research team said this emission matches the energy separation of sample biases at ~2.0 V and ~0.4 V, indicating that fluorescence occurs from a transition between these two states.

At a coverage of 2 ML, the researchers found radiative transitions between the quantum-well states and fluorescence due to radiative decay of a coupled plasmon of the tip and sample excited by inelastic tunneling from an initial state in the STM tip to quantum-well states at ~0.15 V, ~2.2 V, or ~3.3 V. At this coverage, the energies of the quantum-well states are shifted, causing the cutoff, transition, and threshold energies to be altered from the 0.6-ML samples.

"Our work shows that sample related electronic transitions can be resolved spectroscopically in STM-induced light emission, not only from semiconductors but from metals," said researcher Germar Hoffman.

According to the researchers, this technique benefits from the lateral spatial resolution of the STM, which does not average over macroscopic areas like other methods. Hoffman said, "This spatial resolution is essential in getting reliable numbers which are not affected by impurities and other defects."

CHRISTOPHER MATRANGA

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