Planar wallpaper-Group Metamaterials Display Multiple Terahertz Resonances

Metamaterials—artificial structures with unusual properties—are aptly named (the Greek prefix "meta" means "beyond"). Although the recent upsurge in metamaterials research can be traced to several remarkable achievements, including the fabrication of materials with negative index of refraction, the demonstration of the "perfect lens" (capable of subwavelength focusing), and the demonstration of materials able to cloak themselves from interrogating light of a particular wavelength, the ultimate potential of metamaterials may lie in researchers' ability to fabricate materials with exact magnetic and electric responses. One obstacle to metamaterials applications is that their electromagnetic responses are narrow band, typically less than 5%. Using designs found in nature to overcome this impediment, C.M. Bingham of Boston College, H. Tao and R.D. Averitt of Boston University, and their co-researchers recently proposed, simulated, fabricated, and characterized two-dimensional metamaterials that are based on planar wallpaper groups and are composed of multiple sublattice elements, each exhibiting a distinct resonant frequency in the terahertz range. The new metamaterials displayed multifrequency response without significantly compromising the degree of the electromagnetic response.

As reported in the November 10, 2008 issue of *Optics Express* (DOI: 10.1364/OE.16.018565; p. 18565), the researchers designed two-dimensional metamaterials computationally by using a commercial simulation package. A standard lift-off process was used to fabricate the metamaterials onto a semi-insulating (SI) GaAs wafer (see Figure 1) coated with hexamethyldisilazane to assist adhesion of photoresist. The wafer was spin-coated with photoresist, which was processed and then removed from the areas intended for metalization. The metalization was composed of a 200-nm thick patterned layer of Au on an adhesion layer of 10 nm of Ti. The metamaterials' unit cells consisted of 1, 2, or 3 square or hexagonal primitive cells (the number of different primitive cells is given by n). The researchers selected specific sublattices with resonant responses of roughly 0.5 THz, 1 THz, and 1.25 THz, which coincide with the electromagnetic resonances of biotin, to investigate biodetector applications and electromagnetic mimicry. Metamaterials characterization was performed with Fourier transform infrared spectroscopy. The researchers achieved good agreement between experimental and simulated transmission for all

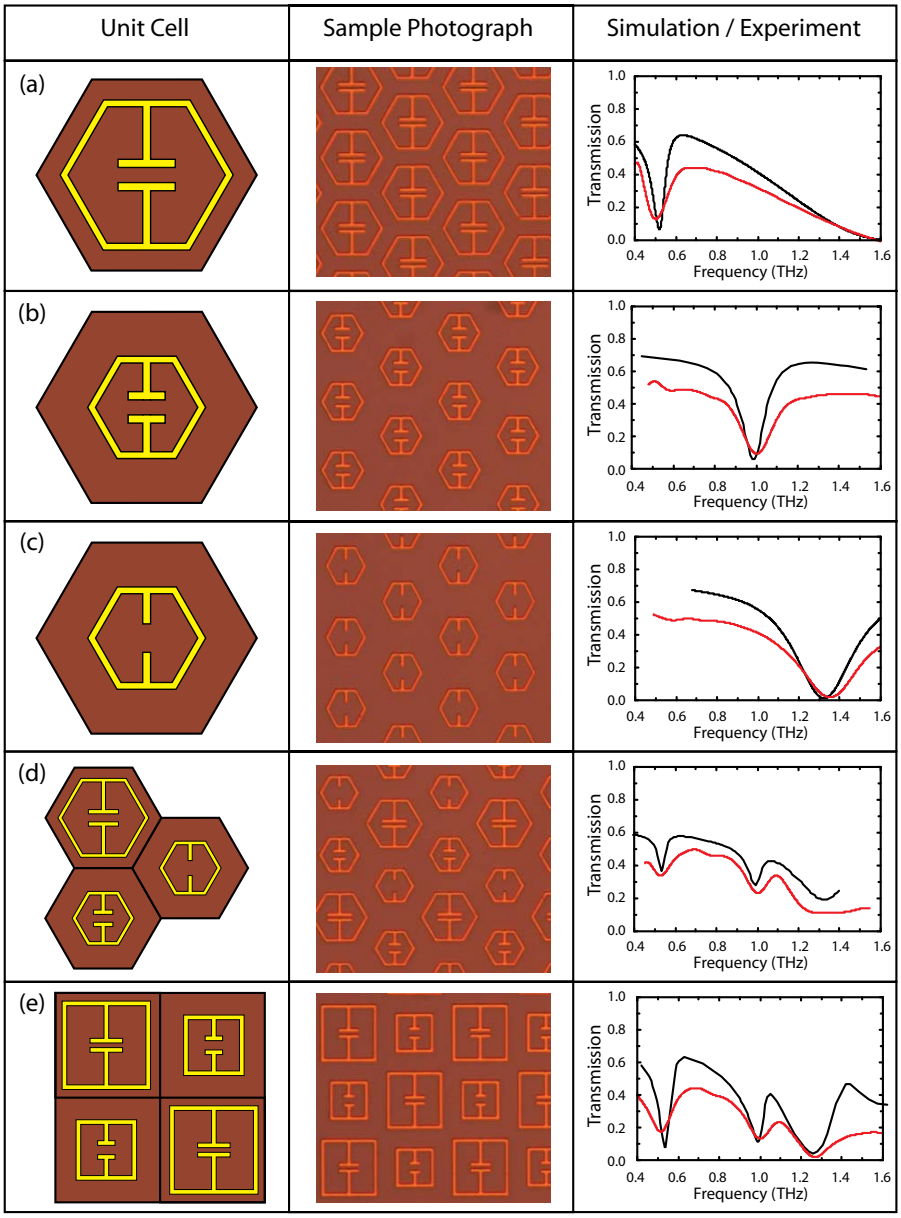

Figure 1. Simulation and experimental results of two-dimensional metamaterials composed of a 200-nm thick patterned layer of Au on a SI-GaAs wafer. The left column shows the unit cell models, the center column shows images taken of the fabricated samples, and the right column shows plots of simulated (black curve) and experimental (red curve) data. Reprinted with permission from *Optics Express* **16** (23) (2008) p. 18565. ©2008 by the Optical Society of America.

metamaterials. The hexagonal metamaterial with $n = 3$ (Figure 1, d) displays the same three resonant frequencies observed in the three different $n = 1$ metamaterials (Figure 1, a–c), demonstrating that the combined metamaterial behaves as if it was a single-element structure over a specific frequency range.

The researchers also demonstrated the engineering versatility of their approach by designing an $n = 2$ metamaterial (composed of square primitive cells in a checkerboard pattern, see Figure 1, e) that displays the same electromagnetic response as the hexagonal metamaterial with $n = 3$.

The researchers discussed several applications for their new metamaterials, including an identification method that involves detecting the sub- or superharmonic modes created upon excitation. The researchers said that "nonlinearities associated with overlapping resonant metamate-

rials and molecular responses, through engineering metamaterials to a bio or chemical hazard of interest, will provide an interesting approach beyond simple dielectric induced resonance shifts."

STEVEN TROHALAKI

Nonlinear Optical Mixing Enables Silicon-Chip-Based Ultrafast Oscilloscope with Sub-Picosecond Resolution

As high-speed optical communications and ultrafast science have pushed the envelope on the meaning of "fast," they have created a corresponding need for ultrafast measurement technologies. Techniques based on nonlinear optical mixing and repeated averaging can achieve very high time resolutions, but are not useful for measuring single, nonperiodic, or asynchronous optical events. Now A.L. Gaeta, M.A. Foster, and colleagues at Cornell University have developed a device that may lead to a new class of ultrafast oscilloscopes based on nonlinear optical mixing in silicon. Their device has a resolution of 220 fs and a record length of 100 ps, and is fully compatible with complementary metal oxide semiconductor (CMOS) technology. They reported their results in the November 6, 2008 issue of *Nature* (DOI: 10.1038/nature07430; p. 81).

The research team's device uses the technique of time-to-frequency conversion, in which a quadratically varying phase shift is added to the optical signal to be measured. This phase shift causes the signal to evolve so that at a later period its amplitude in time is a scaled replica of its original frequency spectrum, and its frequency spectrum is a scaled replica of its original amplitude in time. The group accomplishes this phase shift addition by injecting the optical signal (centered at 1580 nm wavelength) into a 1.5-cm length nanoscale silicon-on-insulator waveguide (with a cross-sectional area of 300 nm by 750 nm) along with a suitably prepared pump signal wave. Four-wave mixing in the waveguide leads to a quadratic phase shift (or linear frequency shift) that is equivalent to 1 nm of wavelength shift for every 5.2 ps shift in time. After the waveguide and an appropriate signal propagation time, the signal spectrum is measured by an optical spectrometer, and the spectrum is scaled to obtain the original signal amplitude in time.

To characterize the device, the researchers first measured several 342-fs optical pulses with varying delays, determining that the device's record length is 100 ps and its inherent resolution is 220 fs. These limits are likely caused by high-order dispersion in the optical fibers carrying the signal and the performance of the spectrometer, and not by the four-wave mixing in the silicon waveguide. The researchers next measured several more complicated signals, and compared the results with measurements of the same signals using an average of many conventional cross-correlation measurements. The results clearly demonstrate the accuracy of the device and its ability to maintain a long (100 ps) record with high time resolution in a single shot.

According to the researchers, the use of dispersion-flattened fiber or dispersion-engineered waveguides may enable sub-100-fs resolution, and the technique can be used with other CMOS-compatible waveguiding materials such as SiN or SiON. Additionally, the individual components of the device are all the subject of extensive current research in photonics, suggesting that it may soon be possible to integrate the entire device on a chip. If that is correct, both telecommunications engineers and ultrafast scientists may one day think of bulky, super-picosecond oscilloscopes as a thing of the past.

COLIN MCCORMICK

Spin-Echo Technique in Nitrogen-Vacancy Diamond Impurities Enables Nanoscale Magnetic Sensing

The ability to detect extremely weak magnetic fields at short distances would enable important applications in a wide range of fields, from probing individual nuclear spins in complex biological molecules to storing and controlling quantum information encoded in electronic or nuclear spins. In pursuit of this ability, researchers M.D. Lukin and A. Yacoby of Harvard University, R.L. Walsworth of Harvard and the Harvard-Smithsonian Center for Astrophysics, J.S. Hodges of Harvard and the Massachusetts Institute of Technology, J.M. Taylor of the Massachusetts Institute of Technology, M.V.G. Dutt of the University of Pittsburgh, and their colleagues have demonstrated the use of coherent control of an individual electronic spin in nitrogen-vacancy diamond impurities to detect magnetic fields at the nano-Tesla level. In combination with diamond nanocrystals, this technique may lead to a new class of sensitive, extremely short-range magnetic sensors.

Electronic spin in nitrogen-vacancy (NV) impurities in diamond has been extensively studied as a candidate quantum bit because of its relative isolation from environmental effects that would cause quantum decoherence. Since ^{12}C has no nuclear magnetic moment, the primary source of local magnetic field for NV impurities comes from the nuclear spin of the small number (roughly 1% isotopic abundance) of ^{13}C atoms in the diamond lattice. As reported in October 2, 2008 issue of *Nature* (DOI: 10.1038/nature07279; p. 644) used a standard spin-echo technique to manipulate the electronic spin of a single NV impurity in a bulk, ultrapure diamond sample. By matching the length of the spin-echo sequence to the period of the Larmor precession of the ^{13}C nuclei caused by an external dc magnetic field, the researchers were able to decouple the NV electronic spin from the nuclear magnetic field, and obtain strong spin-echo signals at times exceeding 0.5 ms. They then imposed a weak (~100 nT) ac magnetic field on the sample, and observed a sinusoidal variation of the decoupled spin-echo signal as a function of the ac field strength, caused by the accumulation of additional magnetic-precession phase from the time-varying Zeeman shift of the NV electronic spin during the spin-echo sequence. The system achieved a resolution of a few nano-Teslas for a 3.2-kHz ac magnetic field after 100 s of averaging, limited by the photon shot noise in the optical readout of the spin-echo signal.

The researchers also conducted a similar experiment using NV impurities in 30-nm-diameter diamond nanocrystals. These samples contained more spin impurities, leading to a shorter spin-coherence time (4–10 μs), and the technique displayed a sensitivity of 0.5 $\mu T\ Hz^{-1/2}$ for a field at 380 kHz. A higher sample purity and higher efficiency optical detection would likely improve this sensitivity significantly. In related work, a group at Stuttgart and Texas A&M Universities led by F. Jelezko, P. Hemmer, and J. Wrachtrup has used diamond nanocrystals to create a scanning magnetic-field sensor. In combination, these results may soon enable an extremely short-range (~10 nm), high-sensitivity (~1 nT) magnetic field sensor, with important applications in fields ranging from molecular biology to quantum information.

COLIN MCCORMICK

Silicon Nitride Membrane Dynamic Masking Allows Improved Shapes of Near-Field Optical Apertures Fabricated by FIB

Plasmonic devices structured on the scale of tens of nanometers for applications in optical interconnects, data storage, near-field lithography, and bio-sensors are often produced by directly milling the metal surface with a focused ion beam (FIB) (direct metal milling, DMM). However, obtaining high-quality structures by using this technique is difficult, as the ion beam's

Gaussian profile produces rounded edges on apertures with small sizes and the structure becomes contaminated with gallium ions. To overcome these problems, J.B. Leen, P. Hansen, Y.-T. Cheng, and L. Hesselink from Stanford University have proposed a method of fabricating apertures by milling the metal through a silicon nitride membrane that allows long milling times that polish the metal sidewalls, and reduces the gallium contamination to negligible lateral depths, protecting in this way the metal layer from damaging gallium ions and beam tails. As reported in the December 1, 2008 issue of *Optics Letters* (DOI: 10.1364/OL.33.002827; p. 2827), the researchers compared C-apertures of various sizes fabricated with their new method of through-the-membrane milling (TMM) with apertures fabricated with conventional DMM, and simulated them by using realistic finite difference time domain (FDTD) modeling that includes rounding, gallium contamination, and metal surface roughness.

The researchers milled C-apertures in a 75-nm thick silicon nitride membrane onto which a 100-nm thick layer of gold and a 6-nm chrome sticking layer were sputtered. Apertures were produced by milling for ~3 s from the metal side (DMM) or for ~30 s from the nitride side (TMM), using a FIB operating at 30 keV and 1 pA beam current. The researchers observed that the tongue of the DMM aperture was heavily eroded by the tails of the FIB, and gallium contamination could be easily seen in and around the aperture, making it nearly useless for applications in optical data storage. On the other hand, TMM apertures were well formed, with the metal surface untouched by damaging gallium ions.

Simulation showed that the TMM aperture's near-field spot was 2.2 times smaller and 63 times more intense than the DMM aperture and that the primary effects of extending the aperture channel into the silicon nitride are to shift the resonant aperture size to larger values and to increase transmission by about 100%, both due to the lower refractive index at the aperture entrance.

The researchers verified the simulation by measuring far-field optical transmission and observed a strong resonance of the TMM apertures, 8.8 times more intense than that of the DMM aperture transmission peak, which implied a good agreement with simulations.

The researchers have simulated, fabricated, and tested a new method of creating high-quality near-IR regime near-field apertures in thin metal films and they said that the preservation of fine features at the metal surface and the protection from gallium contamination that the TMM technique provides is useful in the fabrication of several optical near-field structures including bow-tie and fractal apertures, periodic arrays, and gratings.

JOAN J. CARVAJAL

Nanoporous Carbon Membranes Characterized for Biological Use

Nanoporous membranes may serve as interfaces between implantable biosensors, immunoisolation devices, or drug delivery devices in biological environments. Once implanted within the body, medical device function may be inhibited by the adsorption of cells and proteins in a process known as biofouling. Currently, hydrogels, phospholipids, and other organic materials have been used to modify the tissue-medical device interface and reduce adsorption. An ideal tissue-medical device interface would be thin and highly porous in order to allow the medical device to quickly detect changes in the surrounding environment. Now researchers have proposed the use of diamond-like carbon-coated (DLC) nanoporous alumina for a biosensor membrane.

As reported in the August 8, 2008 issue of *Biomedical Materials* (DOI: 10.1088/1748-6041/3/3/034107), R.J. Narayan of the University of North Carolina (UNC), Chapel Hill; N.A. Monteiro-Riviere of UNC and North Carolina State University; R. Crombez of Eastern Michigan University; and their colleagues have analyzed coated alumina membranes for morphology, mechanical strength, and biocompatibility of DLC carbon-coated alumina membranes. To prepare the membranes, researchers used the ultraviolet pulsed laser deposition technique to deposit thin films of diamond-like carbon, gold, and titanium on nanoporous alumina membranes (pore size = 100 nm) at 25°C for 2 min. The surface properties were characterized using a Nanoscope IIIa scanning probe microscope and the mechanical properties were determined using the Nano-indenter XP system. Cell viability was determined by incubating the membranes in a human epidermal keratinocyte culture and evaluating mitochondrial activity.

Imaging revealed a smooth surface containing a high number of pores that were also monodisperse in appearance on the DLC membranes. Additionally, by changing the parameters of the deposition process, such as electric field strength and processing temperature, the size of the pore can be altered. A comparison of the uncoated alumina membranes and the DLC membranes showed that the DLC membranes had a lower hardness value and Young's modulus, attributed to the larger pore sizes of the DLC membrane. The 24-h MTT assay demonstrated the human epidermal keratinocyte cell viability was highest in the uncoated membranes; and that the viability of the DLC-coated membrane was significantly higher than that of the gold- and titanium-coated membranes. The researchers said that the diamond-like carbon-coated membranes have potential use in a large number of medical applications.

TARA D. WASHINGTON

News of MRS Members/Materials Researchers

Alexander E. Farrell

Alexander E. Farrell, associate professor at the University of California, Berkeley, passed away in April 2008. Alex came to the Energy and Resources Group at UC–Berkeley after managing the Electricity-Industry Center at Carnegie Mellon University—a research and outreach center focused both on innovation and genuine academia–industry partnership in the energy field. Prior to that, Alex had been a postdoctoral fellow in the Science and Technology Policy program at the J.F. Kennedy School at Harvard University, and he did his doctoral work on energy at the University of Pennsylvania. Prior to that, Alex served in the nuclear submarine fleet in the U.S. Navy, after receiving his undergraduate education at the U.S. Naval Academy. All of these periods of time, and experiences, were very much apparent in, and part of, who Alex was as a person. Alex continued to collaborate with—and remained close friends and business partners with—several of the post-doctoral fellows from his time at Harvard. Similarly, the collaborations and friendships from Alex's time at Carnegie Mellon were some of the closest bonds I have ever seen between professional colleagues. Alex lived and breathed the science and technology policy methods, approaches, and, in fact, the overall ethos of the CMU community.

Alex and I began to collaborate day

one of his time at Berkeley, and we spoke several times each day. Because Alex rose and began work so early in the morning, and I was on the opposite schedule, we often joked that our "duty cycle" permitted us to keep a project moving forward literally 24 hours per day. Alex focused on transportation issues, and very rapidly became a key player in the state, regional, and international discussions on a wide range of transportation and energy issues. His projects extended from assessments of the energy and climate impacts of biofuels—publishing a paper that became a "cottage industry" in itself, with thousands of academic and media requests, and a remarkable team of students including Rich Plevin, Andy Jones, Brian Turner, and others, who have continued in the Alex tradition of careful and detailed analytical assessment of fuels.

At the same time, Alex and his doctoral student Adam Brandt were developing an assessment of the environmental impacts of unconventional forms of oil—those derived from tar sands, shale rock, and other sources—many of which come with a far larger "environmental footprint" than does gasoline. Their subsequent article became a "best seller" in a new journal, *Environmental Research Letters*, which is notable for the open access format that Alex favored. The Farrell and Brandt paper appeared in the inaugural issue. In fact, Alex has been the most frequent contributor to *Environmental Research Letters*.

These efforts led to a defining project in Alex's career—collaboration, analysis, and education and collaboration with industry, elected officials, and the non-governmental sector efforts around the design of a Low Carbon Fuel Standard (LCFS). The LCFS sets a fleet-wide maximum greenhouse gas impact for transportation—measured on a life-cycle basis—and has been globally influential in re-thinking how we assess and regulate vehicle pollution. We worked together on this project—along with our students, and Professor Dan Sperling of the University of California, Davis and his students and colleagues, along with a number of non-governmental groups. The project was vetted frequently during the process of developing the two major reports with individuals from industry, government agencies, and colleagues in Europe who where working on various national and European Union commissions. Alex and Dan Sperling took the lead on this, but Alex and I chatted at least once each and every day about the issues—both high-level and minute—that arose in this work.

Governor Schwarzenegger signed Executive Order S-1-07 enacting the LCFS in January 2007.

Throughout his career, Alex continued to expand the range of technologies and practices he studied. The day he died, Alex was working on a detailed assessment of battery issues for work on plug-in hybrid vehicles. This work was published: D. Lemoine, D.M. Kammen, and A.E. Farrell, "An Innovation and Policy Agenda for Commercially Competitive Plug-In Hybrid Electric Vehicles," *Environmental Research Letters* **3** (2008) p. 1.

Publications on other significant work highlighted earlier are S.R. Arons, A.R. Brandt, M. Delucchi, A. Eggert, A.E. Farrell, B.K. Haya, J. Hughes, B. Jenkins, A.D. Jones, D.M. Kammen, C.R. Knittel, D.M. Lemoine, E.W. Martin, M. Melaina, J.M. Ogden, R. Plevin, D. Sperling, B.T. Turner, R.B. Williams, and C. Yang, "A Low-Carbon Fuel Standard for California Part 1: Technical Analysis," (Office of the Governor/Air Resources Board, 2007); A.R. Brandt, A. Eggert, A.E. Farrell, B.K. Haya, J. Hughes, B. Jenkins, A.D. Jones, D.M. Kammen, C.R. Knittel, M. Melaina, M. O'Hare, R. Plevin, and D. Sperling, "A Low-Carbon Fuel Standard for California Part 2: Policy Analysis" (Office of the Governor/Air Resources Board, 2007); A.E. Farrell and A. Brandt, (2006) "Risks of the Oil Transition," *Environmental Research Letters* **1** (2006) p. 1; and A.E. Farrell, R.J. Plevin, B.T. Turner, A.D. Jones, M. O'Hare, and D.M. Kammen, "Ethanol Can Contribute to Energy and Environmental Goals," *Science* **311** (2006) p. 506.

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