very large spin polarization." In their related work published in *Advanced Materials* (15, 2003), the researchers showed that proton microbeam makes it possible to create magnetic spots on the graphite with diameters of only a few micrometers.

Andrei A. Eliseev

## CdS Nanoparticles on Si Self-Organize into Luminescent Nanorings

Realization of nanometer-sized devices is dependent on the physical properties of nanostructures. A group of researchers from NTT, the Royal Institution of Great Britain, the University of Wales, and Yokohama National University has achieved a self-organization process of cadmium sulfide nanoparticles that results in the formation of luminescent nanometer-sized ring structures on a silicon wafer.

As reported in the September 16, 2003, issue of *Advanced Materials*, nanoparticles of CdS, 10 nm in size, were synthesized by the reaction between cadmium acetate and thioacetamide. This method enables control of the size and shape of the CdS nanoparticles. Planar silicon wafers of (111) orientation with a thin oxide layer (<1 nm) were used as the substrate. Nanoparticles were introduced onto the silicon wafer by dip coating from ethanol suspension, aided by an ultrasonic bath, at room temperature. On annealing of these Si substrates, in an ultrahigh-vacuum chamber at 800-850°C, the CdS nanoparticles formed circular structures on the silicon surface. The nanorings, consisting of particles from 20 nm to 100 nm, ranged in size from 100 nm to 1000 nm. Information about particle size was obtained by atomic force microscopy. Mapping of tunneling electron luminescence from these nanoring structures showed a oneto-one correspondence between the topography and light emission. The resolution of this mapping technique enabled the observation of luminescence from individual nanoparticles (about 10–20 nm in size). The researchers said that the decomposition of the silicon oxide layer, followed by a drying phenomenon, leads to the formation of these luminescent nanorings.

The researchers said that "this material could be a potential candidate for developing optical components on silicon, if ultimate control of these structures can be achieved."

MAXIM NIKIFOROV

## InGaP/GaAs HBTs Operate as Light-Emitting Transistor

The concept of wide-bandgap semiconductor emitters for minority carrier injection efficiency has been known since the work of Shockley in 1948 and Kroemer in 1953. This concept has been used to achieve high minority carrier injection efficiency in bipolar transistors, of which InP heterojunction bipolar transistors (HBTs) are the fastest, with operating speeds exceeding 450 GHz. In this approach, base-current recombination has been regarded as a source of undesired waste heat. However, as reported in the January 5 issue of *Applied Physics Letters*, M. Feng,

N. Holonyak Jr., and W. Hafez of the Department of Electrical and Computer Engineering at the University of Illinois at Urbana-Champaign have directly observed radiative recombination in the graded base layer of an InGaP/GaAs HBT. The researchers were able to change the spontaneous light-emission intensity by varying the base current from 0 mA to 5 mA. They demonstrated that the modulation of the light emission was in phase with the base current modulated in transistor operation at 1 MHz.

The scientists used metalorganic chemical vapor deposition to grow the InGaP/ GaAs HBT test structure consisting of a 3500 Å *n*-type GaAs collector, a 600 Å carbon-doped and compositionally graded p-type InGaAs base with 1.4% In, an 800 Å *n*-type InGaP emitter, and a 1000 Å *n*-type InGaAs emitter contact cap. The tested HBT device consists of electron-beamdefined Ti/Pt/Au emitter contacts fabricated by using self-aligned emitter etch and base metal deposition. The researchers employed a bisbenzocyclobutene (BCB) based etch-back process for back-end fabrication to render the electrode and contact formation on the top of the transistor.

The researchers observed no light emission for zero base current, while at 1 mA, they observed the first weak light emission that increased in strength when the base current was increased to 5 mA. The output emission wavelength of 885 nm is consistent with the energy bandgap of the compositionally graded InGaAs base of the HBT. The researchers also performed tests of output light modulation at 1 MHz



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and at 100 kHz electrical modulation, which demonstrated that the output signal tracked the input signal at transistor speed.

With a three-terminal HBT as a light source, a wide range of applications is possible for integrated circuits that would use both electrical and optical signals, including the interconnection of optical and electrical signals for display technologies and communication purposes. In addition, it could make this transistor the fundamental element in optoelectronics as well as in electronics. This work might be the start of an era in which photons are transported around a chip in the same fashion as electrons, according to the researchers.

ALFRED A. ZINN

## Tailored Contrast Agent for Nuclear Spin Tomography Optimized

Nuclear spin tomography (or magnetic resonance imaging, MRI) has developed into an important medical diagnostic procedure. Although MRI is often used in a non-invasive manner, the contrast between tissues of different types is sometimes too low for effective diagnosis. Consequently, materials are often used to increase the sensitivity or specificity of an image. A research team from the University of Texas at Dallas, Macrocyclics Inc., and the University of Texas Southwestern Medical Center has demonstrated optimization of contrast agents based upon complexes of the rare-earth metal gadolinium, as reported in the December 2003 issue of Angewandte Chemie International Edition.

Nuclear spin tomography uses the "spin" of hydrogen atom nuclei. The spins align themselves in a strong magnetic field, but a pulsed radio wave causes them to "flip" in the opposite direction. After the pulse, the hydrogen atoms release electromagnetic waves as they fall back to their ground spin state. The amplitude and duration of this signal depend on the concentration of hydrogen and the relaxation times, which differ for different tissue types, but may not differ enough for unambiguous analysis. Contrast agents, which influence the relaxation times of the protons in water molecules, are used to increase the contrast. Gadolinium ions have seven unpaired electrons, which induce a strong alternating electromagnetic field that "shakes" the spins of neighboring water molecules, causing them to return to their ground state more quickly than usual. However, gadolinium ions have toxic effects, and they need to be well protected within a complex. A. Dean Sherry of the University of Texas at Dallas and his team are using 1,4,7,10-tetra-azacyclododecane-1,4,7,10-tetra-acetic acid complex with a

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carbon-nitrogen ring with arms to contain the ion. The gadolinium ion is held fast by four nitrogen atoms from the ring and four oxygen atoms from the arms, and sits within these ligands. On the "open" side, there is room for one water molecule. In order for the contrast agent to function optimally, the water molecule must disappear as quickly as possible after "relaxing" so as to make room for another. The turnover time depends on the structure of the complex.

Each set of four nitrogen and four oxygen atoms in the complex makes a square. This results in two possible configurations, an antiprism and a twisted antiprism, which differ in the degree of rotation of the two squares relative to each other. These can be interconverted by a "flip" of the ring and a rotation of the arms. To determine whether the two forms hold onto water molecules for different lengths of time, Mark Woods of the University of Texas at Dallas attached "stoppers" to the ring and each arm in order to prevent flipping and rotation. By selecting the stereochemical configuration of the side-chain arms, both forms could be obtained. The researchers found that water molecules spent considerably less time in the twisted antiprism configuration than in the antiprism configuration. The rate of water exchange in the twisted antiprism was 15 ns, close to the theoretical optimum value of 30 ns. This represents an important step toward a targeted design for nuclear spin contrast agents, according to the research team.  $\square$ 



