Mechanical Control of Spin States and Conductance Achieved in Cobalt Complex

Progress in the ability to fabricate controllable single-molecule electrical devices has enabled these devices to be used as scientific tools to perform detailed measurements of electron correlations on nanometer-length scales. Recently, D.C. Ralph of Cornell University; T.A. Costi of Forschungszentrum Jülich, Germany; P.S. Cornaglia of Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina; and their colleagues have studied the spin states in single molecules attached to gold electrodes and the Kondo effect by which the molecular spin can be screened by electrons, as a function of stretching the molecule. Electronic states depend on symmetry; for example, a complex composed of a transition metal and ligands breaks spherical symmetry and splits the metal's originally degenerate d orbitals. For spin $S > 1$, distortion of the ligand geometry causes additional splitting of the $(2S + 1)$-degenerate spin states, resulting in magnetic anisotropy.

The researchers modified the symmetry of a spin $S = 1$ Co complex by controllably stretching it, and simultaneously measuring the current flowing through it. They were able to use mechanical control of the Co complex to demonstrate the underscreened Kondo effect, where conduction electrons only partially screen the molecular spin, from $S = 1$ to $1/2$.

As reported in the June 11th issue of *Science* (DOI: 10.1126/science.1186874; p. 1370), the researchers used mechanically controllable break-junction devices to stretch individual $Co(tpy\text{-}SH)_2$ complexes (where tpy-SH is 4′-mercapto-2,2′:6′,2′′-terpyridine). The researchers measured differential conductance (dI/dV) as a function of increasing electrode separation at a temperature of 1.6 K.

Initially, the spectra displayed the typical signature of Kondo-assisted tunneling through the molecule—a single peak centered at $V = 0$. However, as the molecule was stretched beyond a certain device-dependent point, the peak split into two, in contrast to the spin $S = 1/2$ Kondo effect in C_{60} molecules, where no peak splitting was observed.

The researchers showed that the peak splitting observed for the Co complex is due to a higher spin $S = 1$ Kondo effect and degeneracy breaking within the triplet ground state caused by molecular distortion. The researchers said that their work makes possible "dramatically more detailed and precise comparisons with theory," and that it, "further demonstrates that mechanical control can be a realistic strategy for manipulating molecular spin states to supplement or replace the use of magnetic fields in proposed applications such as quantum manipulation or information storage."

STEVEN TROHALAKI

Defect-as-Qubit Paradigm Developed in New Materials Systems

Quantum computing is one of the most tantalizing promises of modern physics. Its actualization hinges on finding suitable materials systems for storing and manipulating bits of quantum information, known as qubits. An approach suggested in recent years is to use bound nitrogen-vacancy defect states in diamond, which enable manipulation and high-fidelity measurement of qubits at room temperature. Implementing these qubits in a quantum computer presents a formidable challenge, given the difficulty of growing and fabricating diamond, but researchers at the University of California at Santa Barbara have brought the science a step closer to technology by expanding the defect approach to other, more accessible host materials.

The nitrogen-vacancy defect in diamond ($N_CV_C^{-1}$) is a bound state of several electrons that can undergo certain spin transitions, allowing it to be pumped and probed optically in order to "read" and "write" the qubit. To identify similar systems in other materials, J.R. Weber, W.F. Koehl, J.B. Varley, A. Janotti, B.B. Buckley, C.G. Van de Walle, and D.D. Awschalom developed a list of criteria for both the defect centers and the host materials, simultaneously developing the paradigm of defects as qubits and providing a roadmap for exporting the diamond NV approach to other systems. As published in the May 11th issue of the *Proceedings of the National Academy of Sciences* (DOI: 10.1073/pnas.1003052107; p. 8513), their criteria address issues of initializing and reading the qubits, as well as ensuring long lifetimes and thermal stability.

The team then applied the criteria to defect systems in diamond and the 4H polytype of SiC. The researchers used density functional theory (DFT) to calculate defect stabilities, charge, and spin states, employing hybrid functionals to accurately determine bandgaps and constrained DFT to calculate defect excitation energies. An analysis of the results reveals that the required features, primarily the existence of a ground-state spin triplet, may be supported by certain N_CV_{Si} systems in SiC, as well as by isolated vacancies such as V_{Si}^{-2}. Taking these results as a starting point, the researchers extend their discussion to analogous defect centers in other semiconductors. Their work paves the way for a broad expansion of the defect-as-qubit paradigm and brings quantum computing one step closer to reality.

ALISON HATT

High Quality Photoactive Cubic-Phase Copper Selenide Nanodiscs Show Promise for Photovoltaics

Copper selenide is a promising candidate for active components in solar cells because it contains cheap and abundant elements and has a bandgap in an optimal range to absorb energy from the solar spectrum. Colloidal nanomaterials may enable inexpensive, large area fabrication through solution processing. However, current copper selenide nanoparticle syntheses often use phosphine-based precursors which, in addition to being toxic and oxygen sensitive, tend to result in polydisperse size and shape of nanomaterial reaction products. Recently, J. Choi, N. Kang, H.Y. Yang, and S.U. Son from Sungkyunkwan University, Suwon, Korea, and H.J. Kim from the Korea Basic Science Institute, Daejeon, Korea, report a solution-based approach to obtaining high-quality cubic phase copper selenide nanodiscs of uniform size and shape as published in the June 22nd issue of *Chemistry of Materials* (DOI: 10.1021/cm100902f; p. 3586).

The researchers generated a new, air stable selenium precursor, 1,3 dimethylimidazoline-2-selenone using *N*-heterocyclic carbene (NHC) chemistry. Nanoparticle synthesis using this precursor was optimized for solvent content, reactant concentration, and temperature. The nanodiscs obtained in their optimal process were characterized by transmission electron microscopy, energy-dispersive spectroscopy, x-ray powder diffraction, and x-ray photoelectron spectroscopy. The discs are cubic phase $Cu_{2-x}Se$ with diameters of 17 (±1) nm and thicknesses of 2.6 (±1) nm, making these among the smallest $Cu_{2-x}Se$ nanomaterials yet synthesized.

According to the researchers, cubic phase two-dimensional nanomaterials are uncommon, though a significant number occur in wet chemical syntheses. It is thought that these phases are the result of growth kinetics being controlled by ligand interactions with certain crystal planes of the materials as they grow in solution. The researchers said that the NHC products generated after selenium is removed from the precursor molecule play a significant role in forming the disc-shaped materials, particularly by coordinating copper species on one particular plane forcing continued growth to occur preferentially in the radial direction rather than equally in all directions. Changing the selenium precursor concentration relative to the copper source altered the particle shapes, which varied from a mixture of discs and tetragonal particles to irregular morphology. Using selenium powder instead of the NHC-based precursor formed irregular particles.

$Cu_{2-x}Se$ is a *p*-type semiconductor with a 1.0–1.4 eV indirect bandgap, a range suitable for use as an absorbing layer in photovoltaic devices. Based on UV-vis absorption, the researchers calculate the nanodisc bandgap to be 1.55 eV, an increase attributed to the quantum confinement effect. Photoconductivity measurements as a function of electrical bias on thin films of nanodiscs contacted by silver electrodes on glass substrates show an approximately sixfold increase in current under illumination compared with dark current. This is taken as evidence that the nanodiscs synthesized in this work may be incorporated into solar cells through solution-based processing.

Alia P. Schoen

White Light Illumination Produces Tunable Color from Silicon Nanostructures

Silicon is widely used in the microelectronics industry due to its electronic characteristics. On the other hand, the use of Si for optical applications requiring emission of light has been limited by the fact that silicon has an indirect bandgap, which results in poor light emission. Researchers have somewhat overcome these limitations by leveraging the impressive nanofabrication capabilities that exist for Si to produce structures capable of light emission, optical cloaking, waveguiding, and sensing.

Recently, L. Cao and colleagues from the Geballe Laboratory for Advanced Materials at Stanford University have exploited the resonant light scattering properties of Si nanostructures to produce silicon nanowires (SiNWs) and nanoparticles (SiNPs) with engineered color. In the July 14th issue of *Nano Letters* (DOI: 10.1021/nl1013794; p. 2649), the team described the white light illumination (polarized and unpolarized) of SiNWs under grazing incidence using a confocal, darkfield optical microscope. The group led by M.L. Brongersma grew SiNWs using a gold colloid-catalyzed chemical vapor deposition process which allowed for accurate diameter control and precise elucidation of the relationship between NW size and resonant light scattering. The researchers observed a continuous change in SiNW color across the entire visible spectrum under randomly polarized white light illumination, with color shifting linearly from blue to red with increasing wire diameter. Similarly, they observed size-dependent color in large-scale, sub-wavelength SiNW and SiNP arrays (Figure 1) which were generated with carefully selected physical dimensions using standard polycrystalline Si thin-film deposition, lithographic patterning, and dry etching.

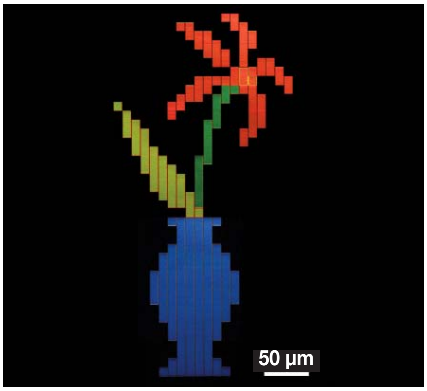

Figure 1. Darkfield optical image of a large-scale patterned Si nanowire (SiNW) array. The array was fabricated using standard polycrystalline silicon thin-film deposition, lithographic patterning, and dry etching. The pattern consists of four types of arrays with distinct NW widths: 170 nm (blue), 200 nm (green), 240 nm (yellow), and 300 nm (red). The NW lengths (10 µm) were chosen to be much longer than the width. Their height was set by the deposited film thickness of 180 nm. The interspacing between NWs was 130 nm. Credit Pengyu Fan

The Stanford team noted that color also varied with the polarization state of the illumination source and related this polarization dependence, as well as the size dependence, to the well-known Lorentz-Mie theory of light scattering. They also described the sensitivity of SiNW light scattering to their surrounding dielectric environment, which is related to the "leaky" nature of NW modes whose fields extend outside of the NWs. The ability to engineer color in Si nanostructures by strategic selection of size, dielectric environment, and illumination conditions greatly increases its potential application for information, display, camouflage, ornamental, and biotechnologies.

"Si is expected to further solidify its dominance in an increasing number of high-volume technologies," said Cao, when considering these new findings in conjunction with Si's excellent electrical, mechanical, and biochemical properties. "This puts this material in a new light."

Samesha R. Barnes

Stagnation Mechanism Revealed in Simulations of Grain-Boundary Roughening in Nickel at High Temperatures

Grain growth in polycrystalline materials almost always stops well before the equilibrium state of single crystal is reached. Conventional mechanisms for grain-growth stagnation include solute segregation to grain boundaries and pinning of grain boundaries by second phase particles. However, grain-growth stagnation is also observed in materials where such mechanisms are not applicable, as in high purity materials, and materials with high solute diffusivity. In order to expand understanding of the mechanisms hindering grain growth, E.A. Holm and S.M. Foiles from Sandia National Laboratories applied computational models to simulate grain growth in pure nickel. Their results suggested an alternative mechanism, which they described in the May 28th issue of *Science* (DOI: 10.1126/science.1187833; p. 1138).

The researchers used a synthetic-driving force molecular dynamics method (MD) to calculate grain boundary mobility for a