Thin Film π-SQUIDs Offer Potential for Applications

Researchers at Augsburg University and IBM T.J. Watson Research Center have designed an all high-T_c thin-film dc superconducting quantum interference device (dc SQUID). The Josephson junctions consist of one standard junction and one junction with a π-phase shift (created by the junction and SQUID loop). In their article published in the February 7 issue of *Applied Physics Letters*, the researchers refer to this device as π-SQUID. In comparing properties of a standard high-T_c SQUID with π-SQUID, the researchers determined that the latter technology is extendible to the design of circuits that make use of a larger number of π-type Josephson junctions.

The researchers concentrated on a symmetric design of the π-SQUID, choosing a grain boundary angle to be as close to 45° as possible. The design was based on two ~9-μm-wide, symmetric 45° ± 1° [001]-tilt grain boundaries formed by a ~100-nm-thick, c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ film grown by pulsed laser deposition at 760°C in 0.25 mbar of O_2 on a $SrTiO_3$ tetracrystal. The researchers aimed for an inductance $L \cong 20$ pH, corresponding to the screening parameter $\beta_L \cong 10^{-1}$ at 77 K. As reported in the article, the maximum values reached by the critical current of the π-SQUID as a function of applied magnetic field were ~15 μA at 4.2 K and ~0.5 μA at 77 K as compared to ~200 μA and 14 μA for the standard SQUID.

The researchers conclude that the device has important potential for applications and should be further studied. They report that the ground states of the π-SQUID are characterized by two states of comparable energy, differing only by which is the π-junction, and that switching time between the ground states is short because "the π-SQUIDs allow coupling into logically interconnected systems."

Review Articles

The January and upcoming April issue of *Reviews of Modern Physics* include several materials-related review articles. Articles in the January 72 (1) issue include: P.W. Terry, "Suppression of Turbulence and Transport by Shear Flow"; D.D. Ryutov, M.S. Derzon, and M.K. Matzen, "The Physics of Fast Z Pinches"; K. De'Bell, A.B. MacIsaac, and J.P. Whitehead, "Dipolar Effects in Magnetic Thin Films and Quasi-Two-Dimensional Systems"; and V.S. Pande, A. Yu. Grosberg, and T. Tanaka, "Heteropolymer Freezing and Design: Towards Physical Models of Protein Folding."

Articles scheduled for the April 72 (2) issue include: T. Brabec and F. Krausz, "Intense Few-Cycle Laser Fields: Frontiers of Nonlinear Optics"; G. Tanner, K. Richter, and J.-M. Rost, "Theory of Two-Electron Atoms: From the Ground State to Complete Fragmentation"; P.J. Mohr and B.N. Taylor, "CODATA Recommended Values of the Fundamental Physical Constants: 1998"; and H.J.W. Zandvliet, "Energetics of Si(001)." The April issue is also scheduled to contain the Nobel lectures by physics prize recipients G. t'Hooft and M. Veltman.

STM Studies Illustrate Chemical Bonding during Single Molecule Formation

To gain a better understanding of how to better control chemical reactions, Wilson Ho, Cornell University professor of physics, and graduate research assistant Hyojune Lee have demonstrated a technique for single molecule formation. The researchers used a scanning tunneling microscope (STM) to manipulate atoms of iron and molecules of carbon monoxide adsorbed on a silver surface in a vacuum.

The researchers first used the STM to scan a surface and locate iron atoms and carbon monoxide molecules. They then lowered the tip over a CO molecule and increased the voltage and current flow of the instrument to pick up the molecule. They then moved the molecule on the tip over an iron atom and reversed the current flow, causing the molecule to bond to the atom and form an iron carbonyl Fe(CO) molecule.

The researchers then added another CO molecule to the Fe(CO), forming a molecule of $Fe(CO)_2$. In subsequent images of the surface, the Fe(CO) molecule appears to have a small lobe on one side, indicating that the CO structure is not attached in a straight up-and-down fashion to the iron atom but is tilted slightly to one side. The $Fe(CO)_2$ molecule appears to have two lobes, indicating that the two CO structures are tilted in opposite directions in a "rabbit-ears" shape. Since there is no way to determine exactly what the angle of the tilt is from their measurements, that would be left to theoretical calculations, the researchers said in their article published in the November 26, 1999, issue of *Science*.

Lee said, "By the image change we can predict that a new molecule has been formed, but we need absolute confirmation." To measure the vibrational energy of bonds in the molecules, the researchers hold the STM tip at a constant height above a bond and vary the voltage. At certain voltages they will see peaks where energy is absorbed by the bond. These peaks create a vibrational spectrum by which the type of bond can be identified. To confirm the presence of a bond between carbon monoxide and iron, the researchers compared the vibrational spectrum of the molecules they had created with the spectra of CO molecules bonded to the silver surface.

In the course of their work, Ho and Lee discovered serendipitously that when a CO molecule was attached to the tip of the STM, the resolution of the instrument increased, enabling the researchers to see the lattice of silver atoms on the working surface. This made it possible to see the bonding sites on the surface for the different chemical species, they said.

Gated Probe for STM Developed to Study Nanostructures

In order to better control and change electronic states with the use of a gate electrode when using scanning tunneling microscopy (STM), researchers at Delft University of Technology in the Netherlands have demonstrated the operation of scanning gate probes by performing single-electron tunneling spectroscopy on 20-nm gold clusters for different gate voltages. L. Gurevich, L. Canali, and L.P. Kouwenhoven of the Department of Applied Physics report in the January 17 issue of *Applied Physics Letters* their design of the tunneling tip and the gate electrode on a silicon nitride cantilever.

Using low-pressure chemical vapor deposition, the researchers covered a Si (100) wafer on both sides with a multilayer of SiN_x-SiO_2-SiN_x, 100 nm per layer, from which a thin membrane formed on the top side of the wafer. The researchers fabricated the Pt tip on the sharp end of the silicon chip, and etched out of the wafer the sharp freestanding cantilever. They then underetched the oxide part of the SiN_x-SiO_2-SiN_x multilayer in order to prevent unwanted electrical contacts between the final top and bottom electrodes. They evaporated the platinum gate electrode on the back side of the chip. The two metal electrodes making up the probes are separated by about 200 nm. The probe can be installed in standard STM heads where, as an additional electrode, it does not make contact with the sample and can be used as a gate.

The researchers found that the probe functioned correctly as they tested it on 20-nm Au clusters. They conclude that the scanning gates can be applied to a large spectrum of nanostructures both at room and low temperatures.

Thin, Flexible, Lightweight $Cu(In,Ga)Se_2$ Solar Cells Developed on Polymer Substrate

Researchers at the Thin Film Physics Group, Institute of Quantum Electronics, Swiss Federal Institute of Technology (ETHZ) in Zurich, Switzerland, have developed a process to make high-efficiency thin-film solar cells on lightweight and flexible polymer films. The total thickness of the solar cell, including polymer substrate, is less than 25 μm. A polycrystalline thin layer of $Cu(In,Ga)Se_2$ compound semiconductor is used for the absorption of solar light and generation of electrical current.

Conventionally, $Cu(In,Ga)Se_2$ (CIGS) solar cells are grown on soda-lime glass substrates at a temperature of about 550°C. However, glass is a heavy and rigid substrate. According to the researchers, lightweight and flexible polymer substrates are essential for many emerging terrestrial and space applications where a high specific power (W/kg) is required. CIGS solar cells/modules on lightweight and flexible substrates such as polymer sheets can yield more than 1.5 kW/kg specific power.

As described in *Progress in Photovoltaics: Res. Apl.* 7 (1999), the polycrystalline solar cell is a multilayer stack of ZnO/CdS/CIGS/Mo/polyimide. A physical vapor deposition method is used to grow a 2-μm-thick CIGS absorber layer at a substrate temperature of about 450°C. The efficiency to convert solar light into electricity was independently measured at the Fraunhofer Institute of Solar Energy Systems (FhG/ISE), Freiburg, Germany, an authorized center for certification in Europe. The efficiency was measured at 12.8% under AM1.5 global illumination, where AM is air mass and AM1.5 is a measure for the light illumination level for earth (AM0 represents solar light intensity in space). Further optimization is expected to yield efficiency of more than 15%. The researchers used 5 cm × 5 cm substrates with solar cells of 4 mm × 3 mm on the substrate.

According to co-author Ayodhya N. Tiwari, leader of the Photovoltaic Materials and Devices Group at the Thin Film Physics Group, the technology needs to be upscaled for industrial manufacturing. Tiwari said that such thin, flexible, and lightweight solar cells are interesting for satellites, building facades, solar cars and boats, easily transportable power sources in remote and rural areas for emergency applications, and in many consumer electronic applications such as smart cards.

Repeatable Molecular Computer Switch Fabricated

Using chemical processes rather than silicon-based photolithography, researchers at Rice University and Yale University have created a molecular computer switch with the ability to be turned on and off repeatedly.

The switch works by applying voltage to a 30-nm-wide self-assembled array of molecules, allowing current to flow in only one direction within the device. The current only flows at a particular voltage, and if that voltage is increased or decreased, it turns off again, making the switch reversible. The gate can be recycled repeatedly, which is in contrast to an earlier demonstration of a molecular gate.

In addition, the difference in the amount of current that flows in the on/off state, known as the peak-to-valley ratio, is 1000:1. The typical silicon device response

is 50:1. The response from off to on when the voltage is applied indicates the increased reliability of the signal.

The active electronic compound, 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiol, was designed and synthesized at Rice. The measurements of the amount of current passing through a single molecule, taken at Yale, occurred at a temperature of approximately 60 K.

The researchers said that since publication of their findings in the November 19 issue of *Science*, they have observed the reversible switch behavior in a similar molecule at room temperature, with a current peak-to-valley ratio of 1.5:1, which is still sufficient for numerous electronic applications. Potential applications include logic gates and a variety of computing components such as high-frequency oscillators, mixers, and multipliers.

Stable Metal-Organic Framework Developed from Zinc Oxide and Terephthalic Acid

A team of chemists working at Arizona State University has designed and synthesized a stable example of a class of materials expected to be of special use as catalysts. The new material, formed from zinc oxide and terephthalic acid, is a porous material and belongs to a class of materials known as "metal-organic frameworks." Though metal-organic frameworks have been studied by chemists for some time, this is the first such material developed that is stable in the absence of other molecules. Arizona State chemist Michael O'Keeffe said, "The problem has been that the frameworks made previously have been unstable. If you remove material from the central pores, they begin to collapse. The trick is to find something that's stable."

As reported in the November 18, 1999, issue of *Nature*, the new material, which has a double bond linking the organic acid to the zinc oxide, is exceptionally stable. The material retains its integrity at temperatures of up to 300°C. "You can pump out the material and leave it completely empty and it's still stable," said O'Keeffe. "It's even stable in a vacuum. All sorts of molecules can now be put in and out of its structure. It's a molecular sieve that can handle quite large molecules."

Microanalysis shows a cubic crystal consisting of $Zn_4O(BDC)_3 \cdot (DMF)_8(C_6H_5Cl)$ (where DMF is dimethylformamide), called MOF-5. The structure can be derived from a cubic six-connected net. First the researchers replace the nodes of the net by clusters of secondary building units. A Zn_4O tetrahedron is formed when the single O atom at the core of the cluster bonds to four Zn atoms. A $Zn_4(O)(CO_2)_6$ cluster is then formed as each edge of each Zn tetrahedron is capped by a $-CO_2$ group. The links of the net are replaced by finite rods, called struts, of BDC molecules (i.e., $O_2-C-C_6H_4-C-O_2$). According to the report, the BDC struts provide an extended network with a three-dimensional intersecting channel system with 12.94-Å spacing between the centers of adjacent clusters. The researchers report that 55–61% of the space is accessible to guest species. They calculated pore volumes of 0.61–0.54 cm^3cm^{-3}, whereas zeolites, which typically have higher molar masses than $Zn_4O(BDC)_3$, exhibit pore volumes of 0.18 cm^3cm^{-3} (for analcime) to 0.47 cm^3cm^{-3} (for zeolite A).

Lithographically Induced Self-Assembly Allows Fabrication of Ultrasmall Plastic Structures

Professor of electrical engineering Stephen Chou and his research team at Princeton University have created ultrasmall plastic structures with a method Chou dubbed "lithographically-induced self-assembly" (LISA). While working on a nanofabrication process called imprinting, also invented by Chou, the researchers accidentally found a pattern that self-assembled. In the process of imprinting, a pattern, or mask, is pressed into a soft plastic polymer. The researchers were pressing a mask into polymer when dust prevented the two pieces from coming together. Afterwards, when they examined the polymer, they found that it contained a pattern of pillars even though the mask never touched it. Not only had the pillars grown by themselves, they had arranged themselves into an ordered array. The pillars are a little more than half a micron in height and width.

Chou said that the LISA method complements the imprinting technique. Imprinting has become a valuable tool because the arduous photolithography process only needs to be done once in making the mask—after that, nanostructures can be stamped out. As a result, the cost is reduced more than a thousandfold and opportunities arise for mass-produced products. According to Chou, LISA is even simpler: A carefully engineered mask is not necessary. The mask merely defines the outline of the pillar array.

Despite many follow-up experiments, Chou is not certain of the physics at work in making the pillars rise up toward the mask. In general, he believes they arise from the interplay between the electrostatic attraction of the mask and the hydrodynamic instability of the polymer.

In a presentation at the International Symposium on Cluster and Nanostructure Interfaces in October 1999, Chou described the possible application of LISA in the development of organic light-emitting devices and in the design of ultrasmall circuits.

Stress Theory Helps Predict Volcanic Eruptions

Youxue Zhang, a professor of geological sciences at the University of Michigan, drew from stress theory to help understand how to predict volcanic eruptions. Scientists have known that a process called fragmentation determines when a volcano will erupt, but they have not understood the process well enough to predict the critical moment when it will occur.

In a letter published in the December 9, 1999, issue of *Nature*, Zhang describes how he used brittle-failure theory to understand fragmentation. During fragmentation, he said, multitudes of bubbles in the magma break up at the same time, releasing gas that was trapped inside. The bubble breakup can be viewed as a type of brittle failure, similar to what happens when glass shatters. Materials science shows that brittle failure occurs when stress on a material exceeds the material's tensile strength.

Zhang said that as the bubbles in the magma grow, stresses build. When the stress at the inner walls of the bubbles is greater than the strength of the magma, fragmentation occurs.

Using what they know about bubble growth in magma, Zhang and his students can calculate the likelihood of fragmentation for a given sample, based on the magma's composition, initial water content, and temperature. Zhang said the best way to measure these quantities before eruption would be to measure melt inclusions in crystals that formed in the magma chamber and then came out during a precursor eruption.

He said, "The melt inclusions are small pots of melt (magma) that was encased in a crystal, and hence keeps its initial water content, which is the most important parameter for whether a pyroclastic flow would form. Only certain crystals such as quartz can maintain the integrity of melt inclusions and hence this does not always work."

Furthermore, dangers are involved in sampling the erupted products because the volcano is often still very active, he said. Zhang anticipates that robotic and remote sampling methods may be developed in the future to reduce the danger. □