

### Pyroelectric LiNbO<sub>3</sub> Crystals Emit Self-Focusing Electron Beam

Pyroelectric crystals—crystals that become electrically charged on heating or cooling—emit self-focusing, spatially stable electron beams with energies of up to 170 keV when heated in the 100–200°C range and cooled to room temperature. According to researchers J.D. Brownridge of the State University of New York—Binghamton and S.M. Shafroth of the University of North Carolina—Chapel Hill, electron beams with focal lengths of 17–22 mm were achieved by varying the thickness of the crystal. Brownridge said that this finding, which was reported in the November 12 issue of *Applied Physics Letters*, “allows us to replace—in some cases—the radioactive sources that are now used to excite elements in x-ray fluorescence spectrometers.”

While pyroelectricity is a well-known phenomenon used to produce sensitive devices for infrared detection and photonics, the emission of a focused electron beam had been overlooked until now. This is probably because at atmospheric pressure, the negatively polarized surface produced by the heating/cooling sequence is quickly neutralized by bombardment with positive ions present in the atmosphere. By maintaining pressures as low as 0.5 mTorr during the process, the surface charge can be maintained for hours, permitting the electron-beam phenomenon to be observed. Surface electrical-field lines are slightly inclined toward the axis of the crystal, which accounts for the focusing phenomenon.

Samples were prepared by cutting the LiNbO<sub>3</sub> crystal perpendicular to its three-fold rotationally symmetric z axis. By resistively heating the +z base of the crystal, the opposite -z base becomes positively charged; upon cooling, the -z base switches to a negatively charged state. When a cylindrical sample 5 mm in diameter and 5 mm thick was heated to 115°C in a <10 mTorr nitrogen atmosphere, a spatially stable, focused electron beam was observed on a ZnS screen placed 17 mm away when the sample reached room temperature. By repeating the experiment with pressures ranging from 0.5 mTorr to 8 mTorr, the investigators found that the electron beam became brighter and more diffuse with increasing pressure; at 8 mTorr, the electron beam “blew up,” and its intensity dropped to zero.

A cylindrical sample of the crystal 4 mm in diameter and 10 mm thick produced an electron beam with a focal length of 22 mm and a spot size of 1 mm. A surface-barrier electron detector installed in place of the ZnS screen measured electron energies as

high as 170 keV at room temperature for a sample that had been heated to 160°C. The beam energy decreased nearly exponentially with time after reaching room temperature, but was still emitting 20-keV electrons after 5 h.

Brownridge and Shafroth said that several x-ray fluorescence spectrometers using pyroelectric crystals as electron sources are already in operation in their research group. As a radiation safety officer at Binghamton, Brownridge particularly likes the safety of these crystals over standard radioactive sources. “If a student took out one of these crystals and accidentally put it in his pocket,” he said, “it would not be a problem.”

TIM PALUCKA

### STM Enables Study of CO Oxidation Mechanisms on a Metal Surface

While studying the mechanism of CO oxidation on a Ag(110) surface, Professor W. Ho and graduate student J.R. Hahn from the University of California—Irvine determined the presence of a previously proposed O–CO–O intermediate species in the production of CO<sub>2</sub>. The formation of CO<sub>2</sub> by the catalytic oxidation of CO at metal surfaces is important as a model for heterogeneous catalysis. According to Ho, the researchers were able to obtain their results by combining imaging, manipulation, and spectroscopic capabilities: They monitored the interaction of CO molecules with O atoms by scanning tunneling microscopy (STM) and vibrational analysis of CO by inelastic electron tunneling spectroscopy with the STM (STM-IETS). Ho said that this combination “allowed for direct visualization of reaction pathways at the single-molecule level.”

As reported in the October 15 issue of *Physical Review Letters*, the researchers used a home-built variable-temperature STM to carry out the measurements. The Ag(110) substrate was cleaned by Ne-ion sputtering and annealed at 693 K. The STM tip was prepared from polycrystalline tungsten wire and cleaned by Ne-ion sputtering. The O<sub>2</sub> molecules (<0.01 monolayer) were adsorbed at 45 K by a capillary doser to ensure molecular chemisorption. The CO molecules (<0.001 monolayer) were adsorbed at 13 K. The O atoms were generated by dissociating O<sub>2</sub> molecules with tunneling electrons from the STM tip. All experiments were carried out at 13 K.

According to their report, the O–CO–O intermediate complex was formed by bringing a CO molecule in close proximity to a pair of nearest-neighbor O atoms. The complex was formed whether this transfer was accomplished by lateral movement of adsorbed CO across the surface or by a

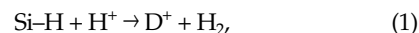
direct transfer of a CO molecule from the STM tip above the surface, they said. An electron pulse over the CO in this complex resulted in the production and desorption of a CO<sub>2</sub> molecule. STM-IETS data shows an increase in the vibrational energy of the CO molecule in the intermediate relative to adsorbed free CO. This data, they said, in conjunction with theoretical calculations, indicates that the interaction of the O atom with the CO molecule results in a weakening of the O–Ag bond and the formation of an O–CO bond. The spatial distribution of the CO vibrational intensity in the complex provides a direct view of its structure.

The formation of an intermediate complex was not observed if the CO was brought in close proximity to O atoms that were farther apart than nearest neighbors. In such cases, the researchers said, CO<sub>2</sub> production could only be induced if the CO was released from the STM tip above an O atom. No reaction was observed when the STM tip with an adsorbed CO molecule was simply brought in contact with the adsorbed O atoms. The production of CO<sub>2</sub> was not observed between CO and molecular O<sub>2</sub>.

GREG KHITROV

### Theoretical Calculations Predict that H<sup>+</sup> Causes Direct Depassivation of Si–H Bonds

One question facing the microelectronics industry deals with the control of the surface/interface properties of silicon. In particular, the study of Si–SiO<sub>2</sub> interfaces and how the introduction of a proton increases the quality of such interfaces is important. H is essential to passivate dangling bonds in order to produce high quality interfaces. A computational study was recently reported on this topic by researchers at Vanderbilt University in Nashville, Tenn. and Oak Ridge National Laboratory. In the October 15 edition of *Physical Review Letters*, these researchers introduced results demonstrating the interaction of protons with a (001) Si–SiO<sub>2</sub> interface. The researchers found that the depassivation of dangling Si bonds was due not to the dynamics of Si electrons and space charge regions, but instead to the ability of H<sup>+</sup> to easily diffuse throughout the interfacial plane and that important depassivation of Si–H bonds occurs by the reaction



where D is a dangling bond. After this process, the positively charged dangling bonds freely interact with Si electrons. The researchers used calculations based upon density-functional theory (DFT), local-density approximations for exchange correla-

tion, ultrasoft pseudopotentials, supercells, and plane waves. In particular, supercells or "superstructures" of Si-SiO<sub>2</sub>-Si with 7–8 planes of Si layers separating the SiO<sub>2</sub> layers were used. The researchers concluded that H<sup>+</sup> is the only charged state in the supercell because all positively charged defects were more stable than their neutral states by ~3 eV when their Fermi energy approached the top of the Si valence band. The researchers found that as an H<sup>+</sup> atom approaches the interface, it is repelled by other H<sup>+</sup> atoms, and either is immediately trapped inside a suboxide bond or SiO<sub>2</sub> protrusion, or migrates laterally throughout the supercell with energy barriers of 0.3–0.5 eV, with the barriers for leaving the cell being much larger. The research team also calculated how the reaction between H<sup>+</sup> and Si-H defects occurs mechanistically. As H<sup>+</sup> comes within 1.6 Å of the Si-H bond, a H<sup>+</sup>-H-Si bridge forms, followed by release of H<sub>2</sub> and the formation of a positive defect (D<sup>+</sup>). This was shown with electron-density plots. These plots, according to the research team, show the depassivation process as H<sup>+</sup> approaches the Si-H bond, bridge formation, and subsequent defect formation. Total energies released from this reaction were 1.3 eV,

but the cost for the reaction was 1.6 eV. According to the report, this reaction was also found to be reversible with annealing in H<sub>2</sub> to show an energy barrier of 1.6 eV.

MATHEW M. MAYE

### Large Ordered Arrays of Si Nanocrystals Achieved by Controlled Template Nucleation

The process of self-ordering nucleation of nanocrystals was previously demonstrated by using strained layers in non-lattice-matched systems and by chemically employing two-dimensional (2D) polymer matrices. A research group headed by Philippe Fauchet and Leonid Tsybeskov at the University of Rochester and Q. Xie from Semiconductor Product Sector in Mesa, Ariz. have demonstrated a way of managing silicon nucleation by facilitating the long-range ordering of uniformly sized and shaped nanocrystals through a controlled template. As reported in the November issue of *Nano Letters*, the research team used inverse-pyramid-shaped holes with submicrometer 2D periodicity to control the in-plane properties of the crystals. The *a*-Si/SiO<sub>2</sub> superlattices were deposited by sputtering and crystallized by high-temperature rapid

thermal annealing (RTA) on this template.

Using maskless interferometric photolithography and reactive-ion etching, a periodic array of holes was transferred to an underlying oxide layer. Anisotropic KOH etching on exposed (100) Si was used to form an inverted pyramid due to a high etch ratio of (100) surfaces over (111) planes. Etching was carried out at 70°C for 3 min using a dilute (25%) KOH solution, yielding holes shaped like inverted pyramids with atomically smooth (111) walls. A 10-period *a*-Si/SiO<sub>2</sub> superlattice was grown on the predefined template by sputtering in the presence of alternate Ar/Ar + O<sub>2</sub> plasma. Using a Si target, the researchers made films with a final thickness of 50 Å for the *a*-Si layers and 30 Å for the SiO<sub>2</sub> layers. They said that transmission electron micrographs revealed the continuity of the film through the transition from the wafer surface to the sidewall, although gradual thinning along the pyramid's walls was also observed.

The nucleation process was carried out at 900°C for 30 s, using an RTA oven, a typical initiation step for the crystallization of amorphous silicon. According to the researchers, isolated, regularly sized and shaped silicon nanoclusters formed at or

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