

National Synchrotron Light Source ♦ Brookhaven National Laboratory

# Newsletter

November 2001

## Infrared Measurements of a High Dielectric Constant Titanate

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Microelectronics is driven by an almost insatiable appetite for smaller and faster devices. In memory devices based upon capacitive components, such as static and dynamic random access memories, the static dielectric constant  $\epsilon_0$  of a material will ultimately decide the degree of miniaturization. The dielectric constant of a material is related to the polarizability  $\alpha$ , in particular the dipole polarizability (an atomic property), which arises from structures with a permanent electric dipole that can change orientation in an applied electric field. These two quantities are linked through the Clausius-Mossotti relation. In metals the charge is delocalized and  $\epsilon_0 \ll 1$ . In insulators the charge is localized and  $\epsilon_0 > 1$ ; materials with a dielectric constant greater than that of silicon nitride ( $\epsilon_0 > 7$ ) are classified as high dielectric constant materials. In general, a value of  $\epsilon_0$  above 1000 is related to either a ferroelectric which exhibits a dipole moment in the absence of an external electric field, or a relaxor characterized by a ferroelectric response under high electric fields at lower temperature, but no macroscopic spontaneous polarization. However, both classes of materials show a peak of  $\epsilon_0$  as a function of temperature, which is undesirable for many applications. For instance, capacitors (with capacitance  $C = \epsilon_0 A/d$ ; two plates of area  $A$  separated by a distance  $d$ ) need to have static values to operate properly under a variety of conditions; if  $\epsilon_0$  has a strong temperature dependence then the device will not be robust and may fail. Recently, the perovskite-related body-centered cubic (BCC)

material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) revealed an extraordinarily high dielectric constant at room temperature of  $\sim 10^5$  [1,2], and was found to be practically constant between 100 and 600 K. Both properties are very important for device implementation [3,4]. However,  $\epsilon_0$  displays a 1000-fold reduction below 100 K without any detectable change of the long-range crystallographic structure when probed by high-resolution x-ray [2] and neutron powder diffraction [1]. This is in marked contrast to known ferroelectrics [5,6], which structurally distort due to a soft-mode condensation. The mysterious electronic

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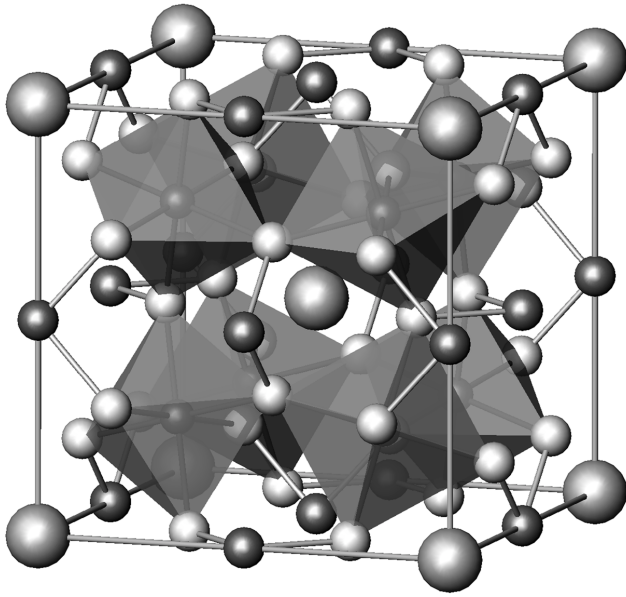


Figure 1. The unit cell of the cubic perovskite-related material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , shown as  $\text{TiO}_6$  octahedra with bridging Cu atoms bonded to the oxygens, and large Ca atoms at the corners and center of the unit cell, which are only weakly bonded.

properties and the absence of any obvious structural transition served as a natural motivation to look for changes in the infrared optical region using the NSLS infrared beamline U10A. The infrared region may be loosely defined as from  $\sim 10$  to 120 meV, or about 80 to 1000  $\text{cm}^{-1}$  (where 1 meV = 8  $\text{cm}^{-1}$ ); many phenomena in solid state physics have energetics in this region, i.e. lattice modes, semiconducting and superconducting energy gaps and other effects due to electronic correlations. We did indeed see changes in the infrared response of this material which have led us to propose a mechanism for the physical origin of the large value of  $\epsilon_0$ , and its 1000-fold drop below  $\sim 100$  K [7].

Single crystals of CCTO were grown by the traveling-solvent floating-zone method using an image furnace. The typical size of the grown single crystals was  $\sim 5$  mm in diameter and 20 mm in length. The  $\text{ACu}_3\text{Ti}_4\text{O}_{12}$  family of compounds has been known for some time, and their structures have been determined [8], as shown in **Figure 1**. A disc  $\sim 1$  mm thick was cut using a wire saw from the middle of the boule. The front of the disc was polished using successive laps to an optically flat, mirror-like surface. The temperature dependence of the real part of the complex dielectric function has been measured using a capacitive technique [2,9] at a number of different frequencies between 20 Hz and 1 MHz, as shown in **Figure 2**. The static dielectric constant is taken as  $\epsilon_0 = \epsilon_1(\omega \rightarrow 0)$ , where  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ . At 250 K,  $\epsilon_0 \sim 8 \times 10^4$  below 20 kHz;  $\epsilon_0$  decreases rapidly below  $\sim 100$  K.

The real part of the dielectric function as well as other optical constants may be determined from reflectance measurements. The reflectance is actually a complex

quantity, consisting of both reflected amplitude and a phase – in a typical experiment, only the amplitude is measured. However, if the reflectance is known over a very wide range, then the phase may be calculated using the Kramers-Kronig relation; once the reflectance and phase are known, then the complex optical properties can be calculated, in particular the real parts of the dielectric function and the conductivity. The temperature-dependent reflectance of CCTO was measured using an overfilling technique [10] over a wide frequency range ( $\sim 20$  to 16,000  $\text{cm}^{-1}$ ) and the optical properties determined from a Kramers-Kronig analysis. The temperature dependence of the real part of the complex conductivity  $\sigma_1(\omega)$  is shown in **Figure 3** in the low frequency region, and over a wider region at room temperature in the inset. In this insulating material [ $\sigma_{\text{dc}} \equiv \sigma_1(\omega \rightarrow 0) \approx 0$ ], the conductivity is dominated by the infrared-active lattice modes, all of which are shown in the inset. The degree to which the modes couple to the light depends on the strength of the induced dipole moment, which arises from the displacements of the ionic cores. The absorptions in the conductivity are modeled using simple Lorentzian oscillators with  $\epsilon(\omega) = \epsilon_\infty + \sum_j (S_j \omega_j^2) / (\omega_j^2 - \omega^2 - i\gamma_j \omega)$  where  $\omega_j$ ,  $\gamma_j$  and  $S_j$  are the frequency, width and oscillator strength of the  $j$ th vibration [the conductivity is related to the dielectric function by  $\sigma(\omega) = -i\omega\epsilon(\omega)/60$ ]. A general rule is that while the shape

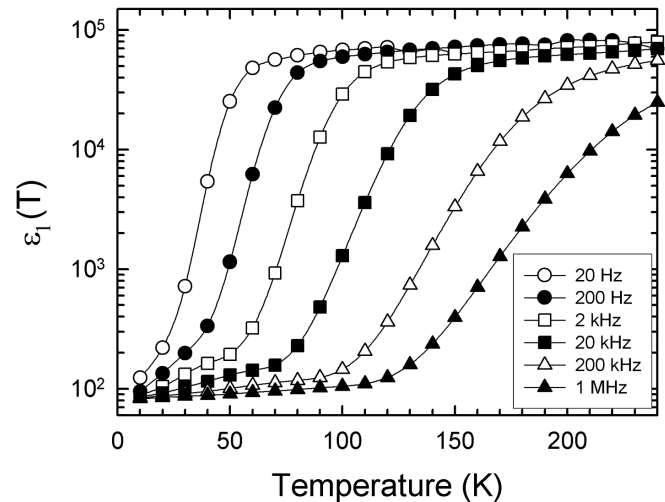


Figure 2. The temperature dependence of the real part of the dielectric response  $\epsilon_1$  of a single crystal of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  at different frequencies between 20 Hz and 1 MHz. At 250 K  $\epsilon_1 \sim 10^5$  below  $\sim 20$  kHz;  $\epsilon_1$  decreases dramatically below  $\sim 100$  K.

of the Lorentzian may narrow with decreasing temperature, the area under the curve is constant – this is referred to as the  $f$ -sum rule for oscillators [11]. However, it is apparent from an examination of **Figure 3** that the area under the lowest observed mode is not conserved at all, in fact it more than doubles, a clear violation of the  $f$ -sum rule. The increase in the oscillator strength of this mode is an indication of a larger induced dipole moment – the size of this increase (and others) may be related to the

redistribution of formal charges within the unit cell, but more specifically on the lighter elements, such as oxygen [12]. The increase in the formal charge on the oxygen atoms at low temperature suggests that the bonding in the oxygen sublattice is becoming increasingly ionic. At the same time, the phonon contribution to the static dielectric constant is just the sum of all of the oscillator strengths ( $S_j$ ), which yields  $\epsilon_0 \sim 100$ , in agreement with the low-temperature value, but far less than the value of  $\sim 10^5$  observed at room temperature. The disparity in the values of  $\epsilon_0$  indicates that there is a large absorption at radio frequencies (kHz), which is absent in the infrared (THz) region.

The frequency dependence of  $\epsilon_1$  in the radio frequency region has been mapped out for fixed temperatures, and is indicative of a single overdamped oscillator model ( $\gamma_0 \gg \omega_0$ ). The suggestion that the physical processes in this system are dominated by relaxation effects naturally favors the Debye model [13] for the relaxation time of a dipole  $P(t) = P_0 \exp(-t/\tau)$ , where  $P_0$  is the dipole moment and  $\tau$  is the characteristic relaxation time – the fits to the data are quite good and indicate that  $\tau$  is increasing exponentially with decreasing temperature,  $\tau = \tau_0 \exp(U/k_B T)$ . A linear regression of  $\log \tau$  vs  $1/T$  is shown in **Figure 4** yields  $U = 54$  meV and  $\tau_0 = 84$  ns.

Subramanian *et al.* [1] speculate that the high dielectric constant of this material is enhanced by its microstructure due to the creation of an effective circuit of parallel capacitors as found in boundary-layer dielectrics [14]. The recurring observation of twinned single crystals at very small length scales suggests this as a possible mechanism to create barrier layer capacitances at the twin boundaries and thereby enhancing  $\epsilon_0$ . However, it is surprising that, unlike in other stoichiometric titanates, a ferroelectric transition is not observed. Rather, the electric dipoles freeze via a relaxational process; at low temperatures one observes a relaxor-like slowing down of the dipole fluctuations as evidenced by the dramatic increase in  $\tau$  and a dramatic decrease in  $\epsilon_0$ . A clue to the large dielectric constant comes from its near temperature independence at high temperatures, which implies that the correlation length does not grow on cooling as in conventional ferroelectrics. Further, it is unusual that the changes in bonding within the oxygen sublattice do not distort the structure, as usually observed in perovskite compounds; the BCC structure persists down to low temperature. At present, these results suggest that the octahedral tilt in **Figure 1** is large enough to accom-

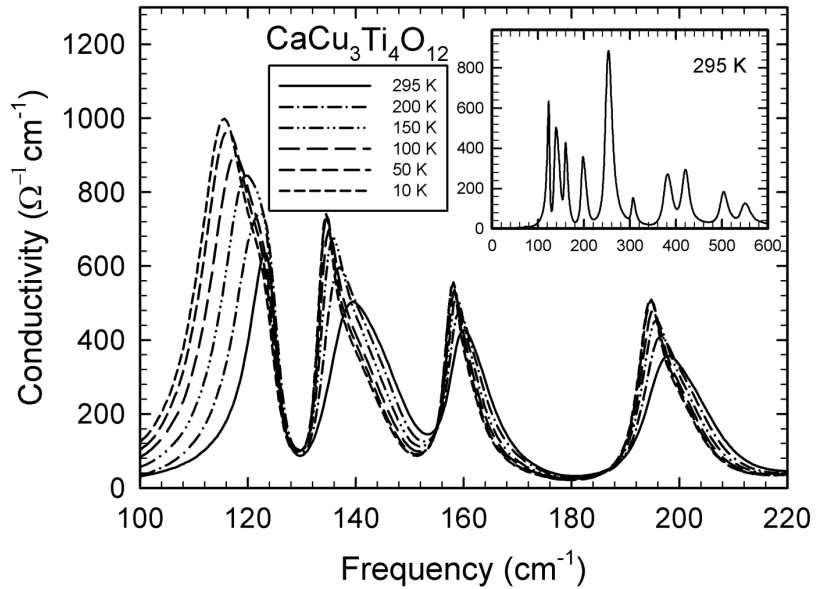


Figure 3. The temperature dependence of the real part of the optical conductivity of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  from 100 to 220  $\text{cm}^{-1}$ . The low-frequency mode shows a dramatic increase in intensity at low temperature; this increase violates the  $f$ -sum rule, and is an indication that there is a redistribution of charge within the unit cell. Inset: The optical conductivity at 295 K shown over a wide frequency range.

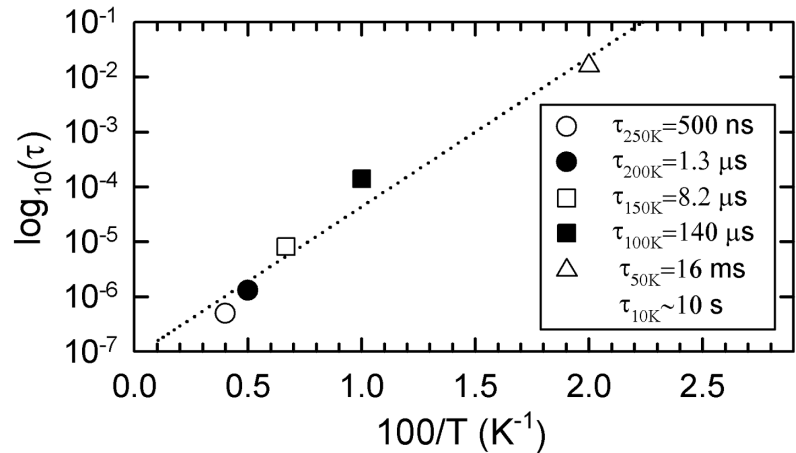


Figure 4. The log of the relaxation time  $\tau$  vs  $1/T$ , which shows activated behavior  $\tau = \tau_0 \exp(U/k_B T)$ ; a linear regression of the data (dotted lines) yields the values  $U = 54$  meV (630 K) and  $\tau_0 \sim 84$  ns. The legend also gives the estimated relaxation time at 10 K, which is not shown on the plot.

modate local distortions, thus effectively decoupling the ferroelectric order parameter and the crystal structure. Then, given the BCC structure, which prohibits ferroelectricity on symmetry grounds, the present results are consistent with a geometrical frustration of ferroelectric order [1].

We would like to acknowledge fruitful discussions with D. Buttrey, J.F. Scott, A.W. Sleight, M. Strongin, J.J. Tu, D. Vanderbilt, R. Werner, and P. Woodward. The work at Brookhaven supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

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## A User's Perspective

*Simon R. Barz*

*UEC Chair, WOP LLC*

I am sitting here in my office thinking about the tragedy that occurred on September 11th when terrorists conducted the worst ever attack against the US. I cannot imagine what it must be like for the families that are directly affected by this attack. If there are any users of the NSLS who have family or friends that suffered as a result of this horrendous act, then on behalf of the UEC, I would like to express my sincere sympathy to you during this most difficult time. And yet, I read and hear that life should go on, that we should not let these events dictate our lives, and so I move on to events of the UEC.

I would like to begin by thanking all those of you who wrote letters to the Senate and House Appropriations Committees in support of the overall funding for science, and specifically for the DOE-BES budget. I cannot over-emphasize how important, and the effect, that these letters have with our legislators. This is clearly going to be a very difficult year for discretionary spending, and for DOE funding particularly. Having said this, it is unclear to me how many people I am thanking: ten, twenty, a hundred? There are over 3,000 registered users of the facility, how many of you actually made the time to write? Please think about this the next time that a "call for action" is issued. On a brighter note, although I was personally unable to be at the laboratory during the recent visits by both Congressman Boehlert and Senator Clinton, I was very pleased to read that these visits occurred. As stated by Dr. Marburger these visits "should do us no harm in our future interactions with Congress." On behalf of the UEC I would like to thank all members of the laboratory, and particularly the NSLS, who helped out with these visits and made them the success that they were.

The BES-DOE review of the NSLS was held in early July. Thanks to all those who participated – and also for speaking out on those topics that concern you! As of today the committee has not issued their report. I am sure that you will hear comments as soon as they are available. On this note I would like to take this opportunity to remind you once again that as Users of the NSLS we all have obligations that we have to meet. When you get a request from the User Office for a list of publications, or list of invited talks, or whatever information is requested, please respond to the request. The statistics that are required by the DOE are generated from these requests, and it is this information that the DOE uses to rate the performance of the facility.

The UEC met in the morning of July 23 and conducted a town meeting that afternoon. As usual there were many issues discussed. The UEC voted to revise its charter. Among other things the charter, as it currently exists, is outdated, contains sexist language, and contains many inconsistencies and grammatical errors. A subcommittee of the UEC was established to review the existing charter and propose wording for a revised charter. This is something that you will all be hearing about in the coming months as a vote by the Users is required for a passage of a new charter.

Another interesting topic of discussion was the specialized needs of the protein crystallography community regarding rapid access to beam time. Clearly there is a need for more rapid access for these experiments than currently exists. Once again a subcommittee of the UEC was formed to discuss these specialized needs and make a recommendation back to the UEC at their next meeting. It is interesting to note that this is obviously not only

a NSLS problem. In a recent issue of the ALS news there was the following: "The ALS is considering a major overhaul of its procedure for reviewing and allocating beamtime for protein crystallography proposals. The present system is cumbersome and, in some cases, more than a year can elapse between submission of a proposal and receipt of beamtime. To get this interval down to a few months, a new rapid-access procedure is being developed. The new procedure would allow the submission of independent investigator proposals at any time rather than just twice a year. Once a month, the new proposals would be peer reviewed and scored, and those scoring highest would be allocated beamtime over the next few months. Proposals not receiving beamtime would remain active for three months." If anyone has any comments or suggestions regarding the current NSLS proposal system for protein crystallography proposals please provide your input to me at the e-mail address at the end of this article.

The plans for the 2002 NSLS Users' meeting are going full steam ahead. Please contact the meeting organizer, Leemor Joshua-Torr, if you have any suggestions for workshops or for the meeting itself. The dates for the meeting are May 20-23, 2002.

As one of my personal goals as UEC chair I would like to expand the educational aspects of the NSLS. As a

start, the proposal that is under preliminary planning on is a 3-4 day course in "Experimental Aspects of X-ray Absorption Spectroscopy." This course would be primarily targeted at graduate students wishing to learn all aspects of XAFS: from how to prepare a good sample, to tricks in collecting good data, to analyzing and interpreting the results. The course would include classroom time, time at the beamline, and time to work up the data. At this stage I would appreciate your comments on this idea, or indeed suggestions for other courses/educational aspects that the NSLS could be involved with.

Finally I would like to publicly congratulate Dr. Marburger on his nomination to the position of Assistant to the President for Science and Technology Policy. I realize that this is not a done deal, and may not be for several months, given the recent events. However, I believe that it is great news for the Users, for BNL, and for all of science, to be represented at the highest level by Dr. Marburger.

I would like to close by saying that the UEC exists to provide an independent forum for the interests of you, the User of the NSLS. Please do not hesitate to contact me if you have any concerns, questions, or ideas about all aspects of the NSLS. We can't act on your concerns if we don't know about them. Please send comments to me at [srbare@uop.com](mailto:srbare@uop.com).



## Facility Report

*Gerry Van Derlaske*  
*NSLS Building Manager*

All of us have been shocked, moved, and affected by the terrible attacks upon our homeland on September 11, 2001. Security measures have been stepped up as a proactive response to increase our safety and awareness of possible future antagonistic actions. Please remember to wear your ID badge at all times when on site, and refrain from parking your vehicle within 30 yards of the NSLS Facility. Routine Security Patrols have also increased, and you may encounter a heightened BNL Police presence within the NSLS Facility via foot patrols. Your full cooperation and adherence to these measures during this time is greatly appreciated.

Two long awaited projects have recently been completed. The installation of a new, 250 square foot addition to the existing RF Penthouse; and construction of equipment storage cages in Bldg. 820A.

The addition to the RF Penthouse will effectively reduce downtime by providing immediate local access to spare parts necessary for repairs during downtime periods. Integral to this area will be a fully equipped technician workbench station to help expedite such repairs. Future plans include housing additional RF upgrades.

Bldg. 820A has been acquired as a new NSLS warehousing storage facility. We will be eliminating the portable storage trailers and sea shipping containers located on the east side of Bldg. 727. Excessing these trailers will occur after the transfer of presently stored equipment found in these units to new storage areas in Bldg. 820A. This warehouse is a high bay facility, confined within a controlled environment, complete with overhead crane and separate, lockable storage cages for individual technical groups of the NSLS Department. These factors combine to make this warehouse a welcomed addition to the NSLS Complex.

The Laboratory has instituted a new, enhanced bicycle lending program for our Collaborators, Guests, and Students. This project will be overseen by the BNL Quality of Life / Guest Services. The NSLS has purchased 5 (five) bicycles that are available on a first come, first serve basis. A \$275.00 deposit fee will be held as collateral for the duration of time a bicycle is signed out to a particular person or group. Upon return and receipt of the bicycle in good condition, your deposit will be refunded. Please contact Michelle Herman at [mherman@bnl.gov](mailto:mherman@bnl.gov) or ext. 8481 for more information about this new program.

# NSLS Annual Users' Meeting and Workshops

## May 20-23, 2002

*Leemor Joshua-Tor*

*User Meeting Chair, Cold Spring Harbor Laboratory*

The 2002 National Synchrotron Light Source Annual Users' Meeting and associated Workshops will provide a scientific forum for the presentation and discussion of recent developments in many diverse areas of science where synchrotron radiation has been used to further the field. New research opportunities and significant accomplishments will be presented in both invited talks and contributed posters.

### Workshops

The program of one-day workshops will focus on specific scientific topics and techniques of interest to the synchrotron community. The following one-day workshops are currently planned:

- In-situ Materials Growth  
*K. Ludwig and C.-C. Kao*
- Catalysis Research using Synchrotron Radiation  
*Simon Bare*
- X-Ray Sources for Studies of Ultrafast Processes  
*J. Sutherland*
- IR and X-ray Micro-analysis and Imaging  
*L. Miller and T. Lanzirotti*
- EXAFS Study of Low-Dimensional Systems,  
*V. Harris*

Other tentative workshops are:

- High Throughput Methods in Structural Biology  
*H. Robinson*
- Environmental Molecular Sciences  
*D. Hunter*
- Advanced Detector Development Forum  
*P. Siddons*

### Poster Session

A poster session will be held concurrently during Monday's opening Reception and Tuesday's Annual Meeting in Berkner Hall. All Users are encouraged and invited to present posters highlighting research activities conducted over the past year at NSLS. This is an excellent opportunity to showcase the caliber and diverse nature of the research performed at NSLS. Graduate students or postdoctoral associates submitting posters, and who are also registered for the Users' Meeting, are eligible to win one of three cash prizes that will be awarded for the best posters in three scientific categories. Representatives of the NSLS UEC will judge the posters. Detailed information will be available in the Registration Booklet and at our meeting web site linked from <http://nslsweb.nsls.bnl.gov/nsls/users/meeting/>. The deadline to submit an application for poster session submission is April 29, 2002.

### Planning Committee Members

Leemor Joshua-Tor, CSHL	Chair
Lonny Berman, NSLS	Program Chair
Anatoly Frenkel, Yeshiva U.	Workshops
Lisa Miller, NSLS	Posters
Caroline Kisker, SUNY	Publicity
Dan Fischer, NIST	Sponsorship
Lydia Rogers, NSLS	Meeting Coordinator
Nancye Wright, NSLS	Vendors
Mary Anne Corwin, NSLS	NSLS User Administrator

### Equipment Exhibit

The ever-popular instrumentation and equipment exhibit will be held beginning on Monday evening at 5:30 p.m. in Berkner Hall with a reception for all registered meeting/workshop attendees. A variety of vendors will be on-hand to showcase their latest instruments and equipment. All vendors interested in participating should contact Nancye Wright as soon as possible.

### Social Functions

A reception will be held for all meeting/workshop attendees on Monday evening in Berkner Hall. Both the equipment exhibit and poster session will be on display for viewing during this reception. A varied selection of hot and cold hors d'oeuvres will be served along with complimentary refreshments. A conference banquet will be held Tuesday evening, May 21. The location is yet to be finalized.

### Registration

Registration for the 2002 Users' Meeting including information about housing and transportation can be found at <http://nslsweb.nsls.bnl.gov/nsls/users/meeting>.

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**Reminder...Pre-Register for Every Visit:** All non-badged NSLS Users and those with expired appointments are required to pre-register with NSLS User Administration prior to each visit so that BNL gate security personnel is notified of your arrival. To access the online pre-registration form, go to URL: <http://nslsweb.nsls.bnl.gov/nsls/dbforms/user-regis.asp>. Please provide this information at least 7 days prior to your arrival at BNL.

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## X-Ray Ring Status

*Jeff Rothman*  
*X-Ray Ring Manager*

The X-Ray ring has been running well since the spring shutdown. During that shutdown the major job was installing a circulator on RF system 2. The device isolates the IMAC power amplifier from the RF cavity. This allows the power amplifier to see a constant 50-ohm load regardless of beam current. During the past four months the circulator has performed very well and greatly simplified tuning and maintenance of the power amplifier. Previous upgrades to the IMAC amplifier have decreased power dissipation and greatly improved stability. The improvements included upgrading the contacts inside the amplifier tuning cavity and improving the cooling. These modifications have been adopted by the manufacturer and will be incorporated into future commercial products.

A series of active interlock beam dumps occurred in July. This was due to the orbit in the X1 area being too close to the active interlock trip points. Moving the orbit 500 $\mu$ M further from the trip point solved the problem. The orbit in the X13 straight section is also near an active interlock trip point. Operators have periodically corrected the values in the ramp file to prevent the beam from dumping in this area during the ramp process.

The trim magnets continue to run near maximum as a result of the upgrade to 2.8GeV. The situation has not affected users significantly but requires constant monitoring by the machine operators. If a trim magnet is used in a feedback system and that trim saturates, the feedback system will likely oscillate. This may affect the orbit all around the ring. Operators must be careful during the initial orbit correction process not to drive the trims too hard. Once beam is turned over to the users the operator must periodically check the trim drive levels.

The process of upgrading the trims is now under way. The power supply group has received the first shipment of new trim power supplies and the mechanical group is now modifying the trim magnets during maintenance periods. The trim magnets have been assigned a priority according to the impact they will have on users. Trims used in both local and global feedback systems have top priority, followed by trims used only in local feedback systems. Trims not involved in feedback have a low priority unless they directly affect beamline operations.

## VUV Ring Status

*Stephen Kramer*  
*VUV Ring Manager*

The VUV ring came back into operation following the extensive May shutdown, on time and in good shape. The leaking ceramic gap was replaced, with the new cool-

ing channels in place. This should insure less thermal distortion in this vacuum chamber section and less likelihood that the leak will redevelop. In this same period of the ring, a strip line kicker for the longitudinal damping system was also replaced. This kicker had a bad connector that prevented it from being used to help reduce the phase noise on the beam. The ring came back into operation on schedule in June and the vacuum continued to improve throughout the month. The vacuum has been restored to the levels that existed prior to the leak in this gap, however the lifetime continues to be low at low currents. This has had little impact on the integrated current since the lifetime remains high at the higher currents.

During the May shutdown, the new amplifier for the harmonic RF system wasn't replaced, since the manufacturer could not deliver it in time. The new amplifier is a solid state system that will simplify maintenance of this system, as well as replacing the tube amplifier, for which replacement parts can no longer be readily obtained. Due to the lack of manpower and the extensive amount of work being planned on the X-ray ring for the winter 2001 shutdown, it is unlikely that this amplifier will be replaced before the spring 2002 shutdown. Therefore the winter 2001-2002 shutdown will be as short as possible for the VUV ring and beam should be operational shortly after the New Year.

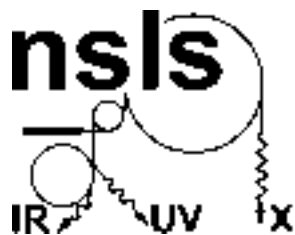
U3B, U10IR and U12IR beam lines have been used to study the high frequency (microwave) impedance of the beam chamber. Direct evidence of the beam induced wake fields produced in the bellow shields of the ring have been measured. The microwave signals from the beam have been shown to provide a sensitive measure of the RF phase noise on the beam.

### Saturday Shopping Shuttle 8:30 am - 12 noon

The Saturday Shopping Shuttle is a courtesy shuttle which operates continuously to and from the Southport Shopping Mall as follows:

8:30 am	Fleming House - Bldg. 180
8:35 am	Curie House - Bldg. 258
8:45 am	Childrens Outdoor Shelter (Lollipop House)
8:50 am	Efficiency Apts. 41-42
<hr/>	
12:00 noon	Depart Waldbaums' Supermarket for final return to BNL.

The vehicle is provided by "Sunrise Coach Lines"



# X-Ray Ring Long Range Schedule

X-RAY SCHEDULE - January 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
		<b>1 Holiday</b>	<b>2</b> 00-2400 Cond.	<b>3</b> 00-2400 Cond.	<b>4</b> 00-2400 Cond.	<b>5</b> 00-2400 Cond.
<b>6</b> 00-2400 Cond.	<b>7</b> 00-2400 Cond.	<b>8</b> 00-2400 Cond.	<b>9</b> 00-2400 Cond.	<b>10</b> 00-2400 Cond.	<b>11</b> 00-2400 Cond.	<b>12</b> 00-2400 Cond./Ops.
<b>13</b> 00-2400 Cond./Ops.	<b>14</b> 00-2400 Cond./Ops.	<b>15</b> 00-2400 Cond./Ops.	<b>16</b> 00-2400 Ops.	<b>17</b> 00-2400 Ops.	<b>18</b> 00-2400 Ops.	<b>19</b> 00-2400 Ops.
<b>20</b> 00-2400 Ops.	<b>21 Holiday</b>	<b>22</b> 00-0800 Template 08-2400 Ops.	<b>23</b> 00-2400 Ops.	<b>24</b> 00-2400 Ops.	<b>25</b> 00-2400 Ops.	<b>26</b> 00-2400 Ops.
<b>27</b> 00-1200 Ops. 12-2400 Studies	<b>28</b> 00-0600 Studies 06-1200 Intlk. 12-2400 Studies	<b>29</b> 00-1200 Studies 12-2400 Ops.	<b>30</b> 00-2400 Ops.	<b>31</b> 00-2400 Ops.		

X-RAY SCHEDULE - February 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
					<b>1</b> 00-2400 Ops.	<b>2</b> 00-2400 Ops.
<b>3</b> 00-2400 Ops.	<b>4</b> 00-1200 Ops. 12-2400 Studies	<b>5</b> 00-2400 Studies	<b>6</b> 00-1200 Studies 12-2400 Ops.	<b>7</b> 00-2400 Ops.	<b>8</b> 00-2400 Ops.	<b>9</b> 00-2400 Ops.
<b>10</b> 00-2400 Ops.	<b>11</b> 00-1200 Ops. 12-2400 Studies	<b>12</b> 00-0800 Studies 08-2400 Maint.	<b>13</b> 00-2400 Maint.	<b>14</b> 00-1200 Studies 12-2400 Ops.	<b>15</b> 00-2400 Ops.	<b>16</b> 00-2400 Ops.
<b>17</b> 00-2400 Ops.	<b>18 Holiday</b>	<b>19</b> 00-0800 Template 08-2400 Ops.	<b>20</b> 00-2400 Ops.	<b>21</b> 00-2400 Ops.	<b>22</b> 00-2400 Ops.	<b>23</b> 00-2400 Ops.
<b>24</b> 00-1200 Ops. 12-2400 Studies	<b>25</b> 00-0600 Studies 06-1200 Intlk. 1200-2400 Studies	<b>26</b> 00-1200 Studies 12-2400 Ops.	<b>27</b> 00-2400 Ops.	<b>28</b> 00-2400 Ops.		

X-RAY SCHEDULE - March 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
					<b>1</b> 00-2400 Ops.	<b>2</b> 00-2400 Ops.
<b>3</b> 00-2400 Ops.	<b>4</b> 00-1200 Ops. 12-2400 Studies	<b>5</b> 00-2400 Studies	<b>6</b> 00-1200 Studies 12-2400 Ops.	<b>7</b> 00-2400 Ops.	<b>8</b> 00-2400 Ops.	<b>9</b> 00-2400 Ops.
<b>10</b> 00-2400 Ops.	<b>11</b> 00-1200 Ops. 12-2400 Studies	<b>12</b> 00-0800 Studies 08-2400 Maint.	<b>13</b> 00-2400 Maint.	<b>14</b> 00-1200 Studies 12-2400 Ops.	<b>15</b> 00-2400 Ops.	<b>16</b> 00-2400 Ops.
<b>17</b> 00-2400 Ops.	<b>18</b> 00-2400 Ops.	<b>19</b> 00-0800 Template 08-2400 Ops.	<b>20</b> 00-2400 Ops.	<b>21</b> 00-2400 Ops.	<b>22</b> 00-2400 Ops.	<b>23</b> 00-2400 Ops.
<b>24</b> 00-1200 Ops. 12-2400 Studies	<b>25</b> 00-0600 Studies 06-12 Intlk. 12-2400 Studies	<b>26</b> 00-1200 Studies 12-2400 Ops.	<b>27</b> 00-2400 Ops.	<b>28</b> 00-2400 Ops.	<b>29</b> 00-2400 Ops.	<b>30</b> 00-2400 Ops.
<b>31</b> 00-2400 Ops.						

X-RAY SCHEDULE - April 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
	<b>1</b> 00-1200 Ops. 12-2400 Studies	<b>2</b> 00-2400 Studies	<b>3</b> 00-1200 Studies 12-2400 Ops.	<b>4</b> 00-2400 Ops.	<b>5</b> 00-2400 Ops.	<b>6</b> 00-2400 Ops.
<b>7</b> 00-2400 Ops.	<b>8</b> 00-1200 Ops. 12-2400 Studies	<b>9</b> 00-0800 Studies 08-2400 Maint.	<b>10</b> 00-2400 Maint.	<b>11</b> 00-1200 Studies 12-2400 Ops.	<b>12</b> 00-2400 Ops.	<b>13</b> 00-2400 Ops.
<b>14</b> 00-1200 Ops. 12-2400 Studies	<b>15</b> 00-0600 Studies 06-1200 Intlk. 12-2400 Studies	<b>16</b> 00-1200 Studies 12-2400 Ops.	<b>17</b> 00-2400 Ops.	<b>18</b> 00-2400 Ops.	<b>19</b> 00-2400 Ops.	<b>20</b> 00-2400 Ops.
<b>21</b> 00-2400 Ops.	<b>22</b> 00-2400 Ops.	<b>23</b> 00-0800 Template 08-2400 Ops.	<b>24</b> 00-2400 Ops.	<b>25</b> 00-2400 Ops.	<b>26</b> 00-2400 Ops.	<b>27</b> 00-2400 Ops.
<b>28</b> 00-2400 Ops.	<b>29</b> 00-1200 Ops. 12-2400 Studies	<b>30</b> 00-2400 Studies				





# VUV Ring Long Range Schedule

VUV SCHEDULE - January 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
		<b>1 Holiday</b> 00-2400 Maint.	<b>2</b> 00-2400 Cond.	<b>3</b> 00-2400 Cond.	<b>4</b> 00-2400 Cond. and/or Ops.	<b>5</b> 00-2400 Cond. and/or Ops.
<b>6</b> 00-2400 Cond. and/or Ops.	<b>7</b> 00-2400 Ops.	<b>8</b> 00-2400 Ops.	<b>9</b> 00-2400 Cond. and/or Ops.	<b>10</b> 00-2400 Cond. and/or Ops.	<b>11</b> 00-2400 Cond. and/or Ops.	<b>12</b> 00-2400 Ops.
<b>13</b> 00-2400 Ops.	<b>14</b> 00-2400 Ops.	<b>15</b> 00-0800 Ops. 08-2400 Studies	<b>16</b> 00-2400 Studies	<b>17</b> 00-2400 Ops.	<b>18</b> 00-2400 Ops.	<b>19</b> 00-2400 Ops.
<b>20</b> 00-2400 Ops.	<b>21 Holiday</b> 00-2400 Ops.	<b>22</b> 00-2400 Ops.	<b>23</b> 00-2400 Ops.	<b>24</b> 00-2400 Ops.	<b>25</b> 00-1800 Ops. 18-2400 Studies	<b>26</b> 00-2400 Ops.
<b>27</b> 00-2400 Ops.	<b>28</b> 00-2400 Ops.	<b>29</b> 00-0800 Ops. 08-2400 Studies	<b>30</b> 00-2400 Studies	<b>31</b> 00-2400 Ops.		

VUV SCHEDULE - February 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
					<b>1</b> 00-2400 Ops.	<b>2</b> 00-2400 Ops.
<b>3</b> 00-2400 Ops.	<b>4</b> 00-2400 Ops.	<b>5</b> 00-2400 Ops.	<b>6</b> 00-2400 Ops.	<b>7</b> 00-2400 Ops.	<b>8</b> 00-2400 Ops.	<b>9</b> 00-2400 Ops.
<b>10</b> 00-2400 Ops.	<b>11</b> 00-2400 Ops.	<b>12</b> 00-0800 Ops. 08-2400 Studies	<b>13</b> 00-2400 Maint.	<b>14</b> 00-2400 Maint.	<b>15</b> 00-1800 Ops. 18-2400 Timing	<b>16</b> 00-2400 Ops.
<b>17</b> 00-2400 Ops.	<b>18 Holiday</b> 00-1800 Ops. 18-2400 Timing	<b>19</b> 00-2400 Ops.	<b>20</b> 00-2400 Ops.	<b>21</b> 00-2400 Ops.	<b>22</b> 00-1800 Ops. 18-2400 Studies	<b>23</b> 00-2400 Ops.
<b>24</b> 00-2400 Ops.	<b>25</b> 00-2400 Ops.	<b>26</b> 00-0800 Ops. 08-2400 Studies	<b>27</b> 00-2400 Studies	<b>28</b> 00-2400 Ops.		

VUV SCHEDULE - March 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
					<b>1</b> 00-2400 Ops.	<b>2</b> 00-2400 Ops.
<b>3</b> 00-2400 Ops.	<b>4</b> 00-2400 Ops.	<b>5</b> 00-2400 Ops.	<b>6</b> 00-2400 Ops.	<b>7</b> 00-2400 Ops.	<b>8</b> 00-1800 Ops. 18-2400 Studies	<b>9</b> 00-2400 Ops.
<b>10</b> 00-2400 Ops.	<b>11</b> 00-2400 Ops.	<b>12</b> 00-0800 Ops. 08-2400 Studies	<b>13</b> 00-2400 Maint.	<b>14</b> 00-2400 Maint.	<b>15</b> 00-1800 Ops. 18-2400 Timing	<b>16</b> 00-2400 Ops.
<b>17</b> 00-2400 Ops.	<b>18</b> 00-1800 Ops. 18-2400 Timing	<b>19</b> 00-2400 Ops.	<b>20</b> 00-2400 Ops.	<b>21</b> 00-2400 Ops.	<b>22</b> 00-1800 Ops. 18-2400 Studies	<b>23</b> 00-2400 Ops.
<b>24</b> 00-2400 Ops.	<b>25</b> 00-2400 Ops.	<b>26</b> 00-0800 Ops. 08-2400 Studies	<b>27</b> 00-2400 Studies	<b>28</b> 00-2400 Ops.	<b>29</b> 00-2400 Ops.	<b>30</b> 00-2400 Ops.
<b>31</b> 00-2400 Ops.						

VUV SCHEDULE - April 2002						
Sun	Mon	Tue	Wed	Thu	Fri	Sat
	<b>1</b> 00-2400 Ops.	<b>2</b> 00-2400 Ops.	<b>3</b> 00-2400 Ops.	<b>4</b> 00-2400 Ops.	<b>5</b> 00-1800 Ops. 18-2400 Studies	<b>6</b> 00-2400 Ops.
<b>7</b> 00-2400 Ops.	<b>8</b> 00-2400 Ops.	<b>9</b> 00-0800 Ops. 08-2400 Studies	<b>10</b> 00-2400 Maint.	<b>11</b> 00-2400 Maint.	<b>12</b> 00-1800 Ops. 18-2400 Timing	<b>13</b> 00-2400 Ops.
<b>14</b> 00-2400 Ops.	<b>15</b> 00-1800 Ops. 18-2400 Timing	<b>16</b> 00-2400 Ops.	<b>17</b> 00-2400 Ops.	<b>18</b> 00-2400 Ops.	<b>19</b> 00-2400 Ops.	<b>20</b> 00-2400 Ops.
<b>21</b> 00-2400 Ops.	<b>22</b> 00-2400 Ops.	<b>23</b> 00-0800 Ops. 08-2400 Studies	<b>24</b> 00-2400 Ops.	<b>25</b> 00-2400 Ops.	<b>26</b> 00-2400 Ops.	<b>27</b> 00-2400 Ops.
<b>28</b> 00-2400 Ops.	<b>29</b> 00-2400 Ops.	<b>30</b> 00-2400 Studies				

*Focus On . . .*

## Electrical Design and Mechanical Design

*Slobodan Pjerov*

*Design/Drafting Group Mechanical Supervisor*

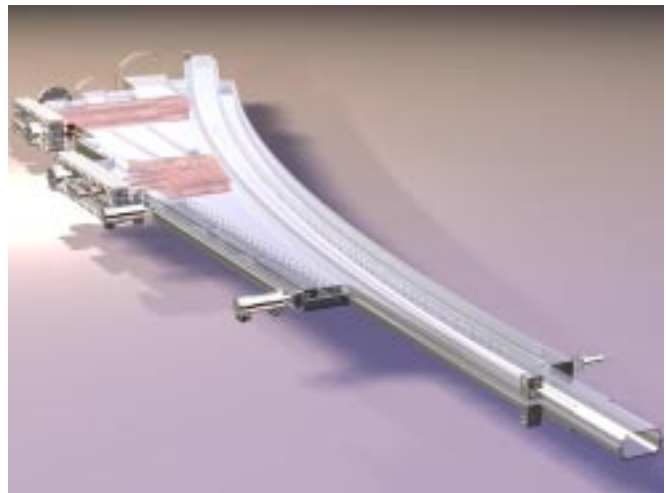
The electrical and mechanical design groups provide the crucial link between concept and hardware, giving life and breath to the complex devices that make up the National Synchrotron Light Source. Often working with a minimal set of specifications, the members of the both design groups, using state-of-the-art 2D and 3D CAD systems, and utilizing their collective years of experience in accelerator component design and electrical design, create outline, detail, and assembly drawings to provide a complete and accurate technical description of all of the components of the NSLS accelerator, as well as support equipment, tools and infrastructure.

The technical documentation provided by the design groups is the language in which technology is communicated, whether it is 2D and 3D renderings for presentations, layout and outline drawings for conceptual studies or detail and assembly drawings for component construction. As a whole, these documents communicate fully the information required to translate the most esoteric and complicated scientific and engineering concepts, calculations and data into the drawings, which are the vocabulary of the machinist and technician. It is the mission of the design group to assure that this communication is accomplished fully, so that the best of ideas become reality at the Light Source.

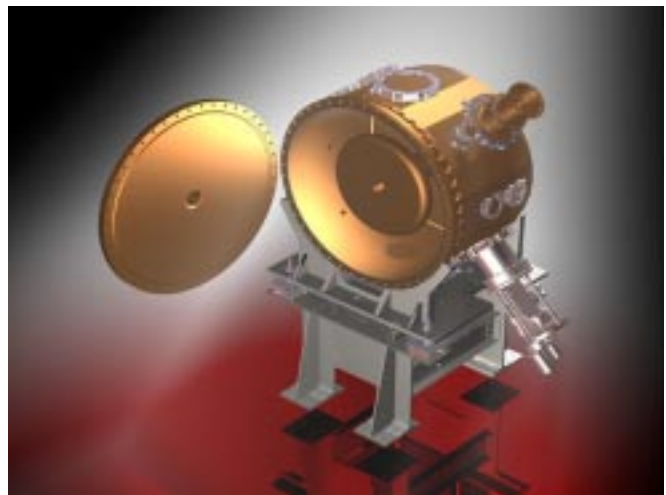
To accomplish this mission, the electrical and mechanical design groups as a whole must have a working knowledge of all the technical disciplines at play in the Light Source, from relativistic particle physics to the electronics and mechanics of screw fasteners. The group must also be abreast of all current capabilities for fabrication and assembly processes, as well as suppliers of materials and components.

The design process is often a collaborative effort between the design groups, scientists, engineers and technicians, often requiring many iterations and tradeoff studies to find the right balance of performance, reliability, maintainability, cost and timing. Taking the concepts provided by the scientists, working closely with the engineers and technicians to iteratively analyze and design the physical requirements of these designs, the design

groups ultimately provide the accurate technical documentation that governs the fabrication, assembly and installation of the devices so designed. Collectively, these devices become the accelerators, detectors, beamlines and supporting equipment, which comprise the world-class research facility that is the NSLS.



*Vacuum Chamber*



*RF Cavity*



*Electrical and Mechanical Design Group: Front from left: Marc Pfeffer, Richard Gambella, Thomas Kim, Charlotte Wrigley, and Sal Pjerov. Back from left: Walter Stoeber, Al Almasy, John Bohenek, Florin Staicu, Yoong Koh. Missing from photo: Peter Gross, Madeline Hughes, Steve Palo, and Chris Stelmach.*



## **“Suspicious” Object Found in Front of NSLS Building**

*W. Robert Casey, NSLS Associate Chairman for ESH/Q*

*Nicholas J. Gmir, NSLS ESE&H Coordinator*

A “suspicious” object was left on the bench near the front entrance to NSLS Bldg. 725 the night of Sept. 27, 2001. The object was a small stainless steel dewar about 18" high and 6" in diameter. The dewar had a commercial label. A name was written on the side of the dewar, but the person could not be found at the NSLS.

The dewar was first reported to the NSLS Control Room about midnight by a user who saw it when leaving the building. The Control Room staff called the BNL Police and several hours were spent talking to personnel in Bldg. 725 trying to identify the contents and owner of the dewar. During this time, the area was cordoned off and no entry or exit was permitted through the front entrance. The dewar was checked with an explosive detector and found clean. NSLS ESH personnel were also involved at this time.

Additional support was requested about 4:00 AM from the Suffolk County Police Bureau. An x-ray of the dewar taken at its location indicated that it was empty. As a precaution, it was decided to remove the dewar to a more isolated area where it could be examined by personnel wearing protective clothing. When the dewar was finally opened by BNL fire-fighters around 7:00 AM, it was found to be empty.

The owners were identified by about 8:30 AM when they returned to the NSLS after spending the night in the dorms. Much to their discomfort, they spent time discussing the events with BNL Police and NSLS personnel. The dewar had been used to store liquid nitrogen for their experiment and had been inadvertently left on the bench outside when they were taking equipment back to their car at the end of their run.

### Recommended Actions

- Do not leave equipment or other objects in places where their use or purpose may be misunderstood. Everyone, particularly Police and Emergency Services personnel, will react to them strongly, especially at times of heightened alert.
- Keep your equipment well labeled so that others will know whom to contact if there are questions.
- Users should always call the Control Room for lock out at the end of a run. This is an NSLS requirement, and in this case the owners of the dewar would have been identified more quickly, since the search was for departing users.

# Synchrotron Studies of Oligomer and Polymer Assemblies on Elastomeric Substrates

*Jan Genzer and Kirill Efimenko*  
*North Carolina State University*

Tuning the surface characteristics of materials, including lubrication or wetting, has become of paramount interest in many everyday applications. For example, in some situations surfaces are required to be completely wettable, such as the surfaces of metals before paint deposition, in other applications one needs to prevent the surfaces from being wettable. Examples of the latter include non-stick layers, marine antifouling coatings, surfaces of car windshields or frying pans, etc.

Deposition of self-assembled monolayers (SAMs) composed of end-functionalized alkanes is a widely used method of tuning the surface wettability. For example, the surface of silica or gold can be decorated with SAMs made of silane-based or thiol-based molecules, respec-

tively. While simple to perform, this methodology usually produces surfaces, which contain numerous structural defects. When exposed to polar liquids, such as water, these defect-containing SAMs usually surface reconstruct as the water molecules penetrate through the imperfections in the SAMs. These non-desirable surface reconstruction effects can likely be minimized (or even completely prevented from occurring) by increasing the packing density of the SAMs through increasing the density of the grafting points at the surface. However, tailoring the grafting density of the SAM chains is not an easy task because as mentioned earlier, SAMs are formed through self-assembly processes that are governed by the chemical and structural nature of the SAM molecules the means of their attachment to the substrate.

We have recently developed a method for controlling the grafting densities of molecules on surfaces. Specifically, we demonstrated that the combination of the self-assembly with mechanical manipulation of the grafted molecules on surfaces provides means of fabricating MAMs ("mechanically assembled monolayers"). In order to provide a proof of concept, we have created MAMs by assembling semifluorinated (SF) alkanes and showed that these produce superhydrophobic surfaces with superior long-lasting barrier properties.<sup>3</sup> The method for fabricating superhydrophobic MAMs is schematically shown in the upper portion of Figure 1. First, a pristine poly(dimethyl siloxane) (PDMS) network film was prepared. After chemically removing any non-cross-linked oligomers, the film was cut into small strips ( $\approx 1 \times 5 \text{ cm}^2$ ) and mechanically uniaxially stretched by a certain length,  $\Delta x$ . Subsequent exposure to ultraviolet/ozone (UVO) treatment produced hydrophilic PDMS surfaces (PDMS-UVO) composed mainly of hydroxyl groups. The SF chlorosilane molecules,  $\text{F}(\text{CF}_2)_8(\text{CH}_2)_2\text{SiCl}_3$  (F8H2), were deposited from vapor onto this stretched substrate to form an organized SAM. Finally, the strain was released from the PDMS-UVO film, which returned to its original size, causing the grafted F8H2 molecules to form a densely packed MAM. To remove weakly physisorbed F8H2 molecules the samples were thoroughly washed in warm ( $\approx 60^\circ\text{C}$ ) deionized (DI) water for 1 minute and dried with nitrogen.

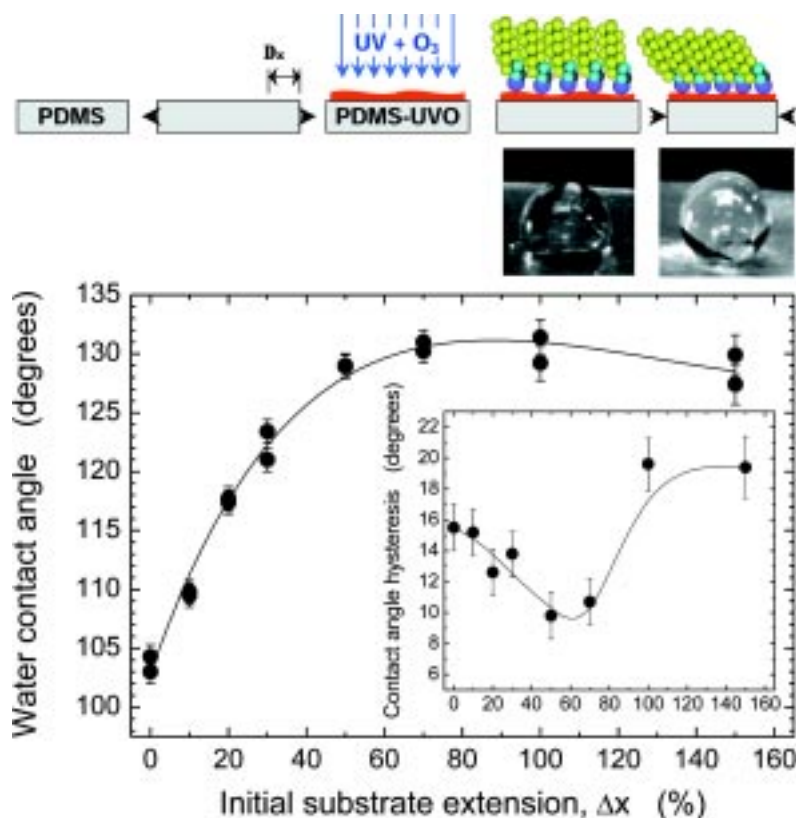


Figure 1: The upper panel show schematic illustrating the technological steps leading to the production of MAMs ("mechanically assembled monolayers"). The lower part denotes the dependence of DI water contact angle,  $\theta_w$ , on F8H2-MAM samples on the degree of stretching of the PDMS substrate before the UVO treatment,  $\Delta x$ . The inset shows the corresponding contact angle hysteresis (defined as the difference between the advancing and receding DI water contact angles). The lines are meant to guide the eye. Also shown are photographs of a DI water droplet spreading on the F8H2-SAM and F8H2-MAM ( $\Delta x = 70\%$ ) surfaces.

The bottom part of Figure 1 shows the dependence of the advancing contact angle of DI water,  $\theta_w$ , of F8H2-MAM on the PDMS substrate extension,  $\Delta x$ . The results in Figure 1 show that as  $\Delta x$  increases,  $\theta_w$  increases (hydrophobicity of the surfaces increases) and reaches a maximum at  $\Delta x \approx 70\%$  and then decreases slightly for  $\Delta x > 70\%$ . The inset to Figure 1 shows the corresponding DI water contact hysteresis values (the difference between the advancing and receding DI water contact angles). The hysteresis decreases with increasing  $\Delta x$ , reaches a minimum at around  $\Delta x \approx 60\%$ , and then increases for  $\Delta x > 70\%$ . The results in Figure 1 provide first round information about the packing of F8H2 in the F8H2-MAMs. As  $\Delta x$  increases from 0%, the number of the F8H2 groups per unit area increases, which in turn results in closer chain packing within the MAM. At  $\Delta x \approx 60-70\%$ , the molecules are already densely packed. With  $\Delta x > 70\%$ , the molecules in the MAM must begin to corrugate as a layer. The latter behavior gives rise to an enhanced molecular roughness and causes the contact angle hysteresis to increase.

Experiments aiming at investigating the stability of the MAMs – in particular the resistance of the F8H2-MAMs to surface reconstruction – revealed that these possess long-lasting superhydrophobic properties that do not deteriorate even after prolonged exposure to DI water. Specifically, while  $\theta_w$  on the F8H2-MAM fabricated on the unstretched substrate dropped almost immediately after a short DI water exposure (hours), indicating that the F8H2 chains surface reconstructed, the wettability of the F8H2-MAM samples immersed for 7 days in DI water and stored for 6 months in a Petri dish under ambient laboratory conditions decreased only by  $\approx 5^\circ$ .

We used carbon K-edge near edge x-ray absorption fine structure (NEXAFS) spectroscopy to study the molecular orientation of the MAMs surfaces. NEXAFS involves the resonant x-ray excitation of a K or L shell electron to an unoccupied low-lying antibonding molecular orbital of  $\sigma$  symmetry,  $\sigma^*$  (and  $\pi$  symmetry,  $\pi^*$ ). The initial state K shell excitation gives element specificity, while the final-state unoccupied molecular orbitals provides bonding or chemical selectivity. Because of the fixed geometry and governing of the  $1s \rightarrow \sigma^*$  (and  $1s \rightarrow \pi^*$ ) excitations by dipole selection rules, the resonance intensities vary as a function of the direction of the electric vector  $\mathbf{E}$  of the incident polarized X-ray relative to the symmetry of the molecule. The NEXAFS experiments were carried out on the U7A NIST/Dow Materials Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at

Brookhaven National Laboratory (NSLS BNL). The set up at NSLS BNL is capable of measuring both the partial electron yield (PEY) NEXAFS and the fluorescence yield (FY) NEXAFS spectra. By simultaneously detecting both the PEY and FY NEXAFS signals, whose probing depths are  $\approx 2$  and  $\approx 100$  nm, respectively, the orientation of the molecules on the surface and in the interior of the sample can be resolved.

No measurable fluorine signal could be detected in the FY NEXAFS spectra of the SF-MAMs suggesting that the UVO treatment and subsequent MAMs deposition did not modify the interior of the PDMS. On the other hand, the PEY NEXAFS data revealed a strong peak at 292.0 eV, corresponding to the  $1s \rightarrow \sigma_{CF}^*$ .<sup>5</sup> PEY NEXAFS spectra were taken in the direction parallel and perpendicular to the stretching direction; in all cases the PEY NEXAFS spectra were collected at the normal ( $\theta = 90^\circ$ ) and grazing ( $\theta = 20^\circ$ ) incidence geometries, where  $\theta$  is the angle between the sample normal and the polarization vector of the x-ray beam. A detailed analysis of the NEXAFS data performed using models presented elsewhere<sup>5</sup> provided information about the average tilt angles of the fluorocarbon helix,  $\langle \tau_{F\text{-helix}} \rangle$ . Figure 2 shows the values of the average tilt angles of the fluorocarbon helix,  $\langle \tau_{F\text{-helix}} \rangle$ , that were determined from PEY NEXAFS spectra collected from F8H2-MAMs with  $\Delta x = 0\%$  (squares) and  $\Delta x = 70\%$

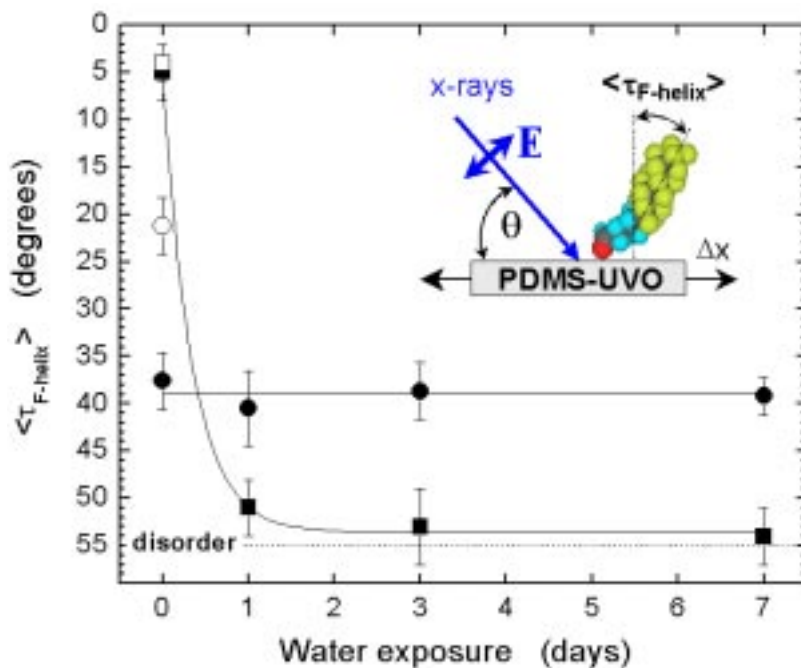


Figure 2: The dependence of the average tilt angle of the fluorinated helix,  $\langle \tau_{F\text{-helix}} \rangle$ , in F8H2-MAMs on the exposure time of the F8H2-MAM to DI water. The squares and circles denote  $\langle \tau_{F\text{-helix}} \rangle$  in F8H2-MAM ( $\Delta x = 0\%$ ) and F8H2-MAM ( $\Delta x = 70\%$ ) samples, respectively. The solid and open symbols represent  $\langle \tau_{F\text{-helix}} \rangle$  measured along and perpendicular to, respectively, the stretching direction. The dashed line marks the value of  $\langle \tau_{F\text{-helix}} \rangle$  corresponding to a completely disoriented MAM. The solid lines are meant to guide the eye. The inset shows schematically the setup geometry.

(circles). The data shows that  $\langle \tau_{F\text{-helix}} \rangle$  measured along and perpendicular to the stretching direction on the F8H2-MAM sample prepared on unstretched PDMS-UVO substrate, was  $\approx 5^\circ$  and  $\approx 4^\circ$ , respectively. Thus, the FyH2 molecules are oriented almost perpendicular to the PDMS-UVO substrate, which is in accord with the orientation of F8H2-SAM deposited on a  $\text{SiO}_x$  substrate.<sup>5</sup> The analysis of the PEY NEXAFS spectra from F8H2-MAM with  $\Delta x = 70\%$  revealed that  $\langle \tau_{F\text{-helix}} \rangle$  measured along the stretching direction is  $\approx 38^\circ$  and  $\langle \tau_{F\text{-helix}} \rangle$  collected perpendicular to the stretching direction was  $\approx 21^\circ$ . The NEXAFS experiments thus showed clearly that as  $\Delta x$  increased, the F8H2 chains tilted away from the sample normal in the stretching direction. The fact that  $\langle \tau_{F\text{-helix}} \rangle$  increased from  $\approx 4^\circ$  to  $\approx 21^\circ$  as  $\Delta x$  increased from 0% to 70% can be attributed to the slight compression of the sample perpendicular to the uniaxial stretch.

NEXAFS has proven invaluable for providing molecular-level information on chain mobility in the SF-MAMs exposed to DI water. As mentioned earlier, the F8H2-MAMs prepared on unstretched PDMS-UVO substrates ( $\Delta x = 0\%$ ) stand almost perpendicular to the sample surface. However, the data in Figure 2 shows that when exposed to DI water, the chain orientation starts to disappear very rapidly and after about 1 day of DI water exposure, the F8H2-MAMs with  $\Delta x = 0\%$  disorient completely. The behavior of the F8H2-MAMs prepared on PDMS-UVO substrates with  $\Delta x = 70\%$  is very different. Specifically, the NEXAFS data reveal that  $\langle \tau_{F\text{-helix}} \rangle$  on samples exposed to DI water for up to 7 days is virtually indistinguishable from that measured on the same specimen before the DI water exposure. These results thus provide further evidence that the F8H2 molecules in MAMs with  $\Delta x = 70\%$  are closely packed and mechanically interlocked; this interlocking hinders the chain's tendency to move and reconstruct on the MAM surface. We attribute this unusual behavior to the extremely high packing densities of the MAMs – values that can only be achieved using this novel assembling method.

Very recently, we have extended the MAM technology to produce: i) polymer brushes with variable grafting densities using MAPA (“mechanically assisted polymer assembly”) by performing the polymerization directly on the pre-stretched PDMS substrate, and ii) molecular gradients with tailorable surface properties. In both these projects, NEXAFS has proven invaluable in characterizing the chemistry and in the case of the molecular gradients also the molecular orientation of the anchored oligomers.

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9. We note that the tilt angle determined from NEXAFS represents an average value. There is no straightforward way to discriminate between the case of all chains homogeneously tilted by the same angle and the case of a disordered system with a broad distribution of tilt angles. Hence, we express our results on the orientation of the SF moieties in terms of the average tilt angle of the fluorocarbon part of the single SF groups,  $\langle \tau_{F\text{-helix}} \rangle$ .
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ESOL for Children English classes are offered free of charge by USB's AmeriCorps Community Outreach Program (COPE) and the Volunteers for Community Service (VCS).

For information, contact: Genie Portillo, Volunteer Services Coordinator 631-632-6812 or email [vcsamericorps@notes.cc.sunysb.edu](mailto:vcsamericorps@notes.cc.sunysb.edu)

# Call for NSLS General User Proposals

For Beam Time in Cycle  
May - August 2002

Deadline is:  
Thursday, January 31, 2002

## Prior to Submitting a Proposal

You must contact the beamline personnel responsible for the beamline(s) selected in order to verify technical feasibility on the beamline(s) and discuss any special arrangements for equipment. Your chance of getting beam time is improved by being able to use more than one beamline.

## Preparing Your Proposal

The same form is used for both new proposals and beam time requests against existing proposals. Follow the instructions on the information sheet and complete and submit all the required sections. Type or print all information legibly. MAIL OR FAX ONE COPY of the proposal form and any attachments to the NSLS User Administration Office. Only one copy is required - do not mail a hard copy if you have already faxed one.

## Macromolecular Crystallography (PX) Requirements

**New Proposals:** The proposal represents a two-year program. Provide an overall plan for your research according to the instructions on the proposal form. If you can, estimate the number of crystals you plan to measure over the two years. If you require the use of an insertion device beamline like X25, be sure to indicate your need for the enhanced performance. New proposals must also include your plans for the upcoming cycle for which you are requesting time (below).

**Beam Time Requests:** Be specific about what you plan to study in the upcoming cycle. Submit PX Forms only for the crystals you plan to study in that cycle. Answer all the questions, use the back of the form if you need more space. Be clear about what crystals you already have, which you expect to have, and how you would use the beam time you requested if you were unable to obtain the planned crystals in time (i.e., other crystals described in your program).

## Proposal Deadline

The complete proposal package must be received by the User Administration Office on or before 5:00 p.m. Eastern Standard Time on the above date to be considered for beam time in this cycle. The fax machine is always extremely busy on the deadline date. Do not rely on faxing the proposal successfully on the deadline date. New proposals should be sent by mail or fax prior to the deadline. Beam time requests for active proposals will be accepted after the deadline, but will be allocated beam time only after requests received on time have been allocated. Late requests are not eligible for a rating upgrade if beam time could not be allocated to them.

Each proposal will receive a prompt preliminary review to verify that it is complete and legible. If there is a problem with the proposal, you will be contacted immediately. Submitting your proposal well in advance of the deadline date assures that the User Administration Office has time to reach you and that you will have enough time to correct any deficiencies.

## Proposal Forms and Additional Information

Blank proposal forms and instructions are available on the World Wide Web. From the home page at <http://www.nslsweb.nsls.bnl.gov>, go to User Information, then "Getting Beamtime." The PX form must now be completed online. A guide to the NSLS beamlines and more information about the General User Program can be found through our homepage, <http://www.nslsweb.nsls.bnl.gov> or by contacting G. Cisco or L. Rogers in the NSLS User Administration Office. Office hours are Monday through Friday, 8:00 a.m. to 5:00 p.m. Eastern Standard Time (EST). Contact information is on the back page of this Newsletter.

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## Safety Approval Form

Safety Approval Forms (SAFs) are required for every experiment. Your SAF must be submitted online **at least one week before** your scheduled beam time. Do not send in SAFs with your proposal. Be sure to include the birthdates of each experimenter so that the final SAF will provide accurate training information. Go to URL:

<http://130.199.76.52/safety/>

**NSLS User Administration Office  
Brookhaven National Laboratory  
NSLS Building 725B  
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### **Important Upcoming Dates**

November 8, 2001	UEC Meeting 1:00-3:00 NSLS Town Meeting
January 10, 2002	Deadline for submissions, March Newsletter
January 31, 2002	Deadline for General User Proposals (May-Aug. 2002)
May 20-23, 2002	NSLS Annual Users' Meeting and Workshops

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