Functional Group Imaging by Chemical Force Microscopy

C. Daniel Frisbie, Lawrence F. Rozsnyai, Aleksandr Noy, Mark S. Wrighton, Charles M. Lieber*

Mapping the spatial arrangement of chemical functional groups and their interactions is of significant importance to problems ranging from lubrication and adhesion to recognition in biological systems. A force microscope has been used to measure the adhesive and friction forces between molecularly modified probe tips and organic monolayers terminating in a lithographically defined pattern of distinct functional groups. The adhesive interactions between simple CH_3/CH_3, CH_3/COOH, and COOH/COOH functional groups correlate directly with friction images of sample surfaces patterned with these groups. Thus, by monitoring the friction between a specifically functionalized tip and sample, one can produce friction images that display predictable contrast and correspond to the spatial distribution of functional groups on the sample surface. Applications of this chemically sensitive imaging technique are discussed.

Lubrication in mechanical devices and recognition in biological systems are examples of two important scientific problems in which the spatial arrangement and interactions between chemical functional groups play an essential role (*1*). Techniques that directly probe the interactions between molecules or molecular assemblies with high spatial resolution could thus provide a means for significantly enhancing the understanding of these areas at the molecular level. Several methods are now available for the measurement of forces between macromolecules and molecular assemblies, including the surface forces apparatus (SFA) (*1–3*), optical tweezers (*4*), and atomic force microscopy (AFM) (*5–10*). The SFA has been used to measure adhesive and frictional forces between macroscopic assemblies of molecules (*3*), whereas optical tweezers have been used to probe interactions between individual macromolecules (*4*); however, neither technique can be used to map the spatial arrangement of functional groups that give rise to the observed interactions. In principle, AFM could be used to measure interactions between different functional groups and map their spatial arrangement, but recent AFM studies have focused only on measuring the forces between ligand-receptor pairs attached to the tip and sample surface (*11, 12*).

We report AFM studies that address both the interaction and the spatial mapping of chemically distinct functional groups. Our investigations focus on adhesive and friction force measurements of organic monolayers that have been lithographically patterned to produce a two-dimensional geometrical distribution of distinct functional groups. By using probe tips that have been functionalized with either hydrophobic or hydrophilic molecules, we show that the adhesive interactions between simple hydrophobic-hydrophobic, hydrophobic-hydrophilic, and hydrophilic-hydrophilic molecules can be measured reproducibly. Importantly, the differences in these adhesive interactions correlate directly with the friction images of the patterned sample surface, which demonstrates that the spatial distribution of hydrophilic (COOH) and hydrophobic (CH_3) functional groups can be predictably mapped with functionalized tips. Potential applications and limitations of this approach, which we call chemical force microscopy, are discussed.

Conventional repulsive-mode AFM images are obtained by recording the vertical deflection of a cantilever–probe tip assembly (often Si_3N_4) while rastering a sample in contact with the tip. Images of organic and biological materials produced by this means reflect the topography of these materials (*9*) but do not provide information about the chemical nature of different groups at these surfaces. It is also possible, by monitoring the lateral forces on the cantilever, to record an image of the friction forces between the tip and sample (*7*). Recent experiments involving the friction mapping of organic mono- and multilayer films have shown that friction differences are observed between distinct regions in these samples (*13, 14*), although the mechanism of contrast in these images may not be directly related to a chemical interaction between the tip and sample (*13*). We believe that the chemical sensitivity of AFM can be rationally enhanced by modifying the probe tip with specific functional groups. In conjunction with this idea, we hypothesized that the magnitude of the friction force on the probe tip is directly correlated with the magnitude of the adhesive force between the tip and the sample. On the molecular level, the fundamental relation between adhesion and friction is unclear, although a recent report has addressed this issue experimentally (*3*). Our premise nevertheless provides a simple approach to the implementation of chemically sensitive mapping by AFM; that is, by modifying probe tips with complimentary or noncomplimentary functional groups, one should be able to predict the friction contrast in images of surfaces patterned with different functional groups.

To demonstrate this concept, we have used AFM to investigate systems consisting of (i) cantilever-tips that have been covalently modified with self-assembled monolayers (SAMs) terminating in specific functional groups and (ii) organic SAM surfaces that contain a lithographically defined arrangement of two different functional groups (Fig. 1). Self-assembly is an attractive method for modifying the probe tips (*15*) and sample surfaces because it yields robust (that is, covalent) monolayer coatings (*16*). In the experiments described below, we focus on surfaces that have been patterned with both CH_3 (hydrophobic) and COOH (hydrophilic) groups and probe tips that have been functionalized with either CH_3- or COOH-terminated molecules. The approach can be readily generalized, however, for the study of other interactions, including those between charged groups or chemically reactive groups, or both, and the specific binding between substrates and enzymes or nucleic acid oligomers (*17*).

Force versus cantilever displacement curves recorded on CH_3 and COOH surfaces with CH_3- and COOH-terminated probe tips are shown in Fig. 2. In these measurements, we monitor the deflection of the cantilever as the sample approaches, contacts, and is then withdrawn from the probe tip (*6, 8*). The deflection is converted to a force with the cantilever spring constant (*18*). Hysteresis in the force-displacement curves corresponds to an adhesive interaction between the tip and sample. Qualitatively, the curves in Fig. 2 show that the adhesive interaction between the functional groups on the modified tip and sample exhibit the following trend: COOH/COOH $> CH_3/CH_3 >$ COOH/CH_3. Results obtained on a number of independent tip-sample combinations are summarized in Table 1. The trend in adhesive forces that we have determined for the modified tips and surfaces is consistent with our expectation that the interaction between hydrophilic groups, which can form hydrogen bonds, will be stronger than that between hydrophobic groups (*19*), whereas the cross-inter-

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C. D. Frisbie, A. Noy, C. M. Lieber, Department of Chemistry and Division of Applied Sciences, Harvard University, Cambridge, MA 02138, USA.
L. F. Rozsnyai and M. S. Wrighton, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

*To whom correspondence should be addressed.

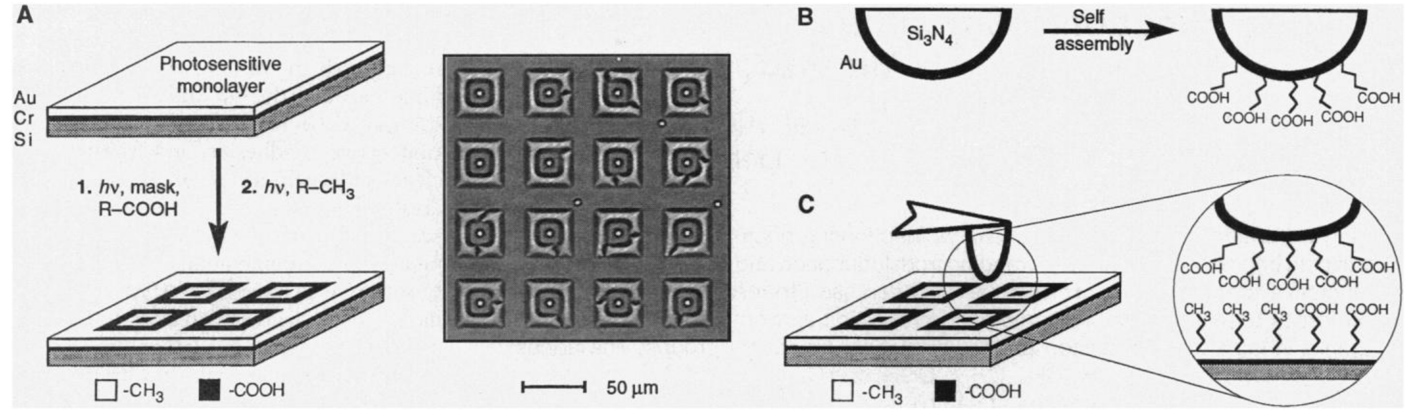

Fig. 1. (**A**) Schematic of the surface modification procedure (left) and a condensation image corresponding to a typical sample (right). Patterned sample surfaces containing lithographically defined hydrophilic and hydrophobic regions were prepared as previously described (*28*). Briefly, Au-coated Si(100) substrates were immersed in 1 mM methylcyclohexane solutions of di-11-(4-azidobenzoate)-1-undecyl disulfide to yield a photosensitive monolayer. Irradiation of these substrates with ultraviolet light (wavelength $\lambda > 260$ nm) through a mask and a thin film of ethyl 4-aminobutyrate yielded ethyl ester termination in the irradiated regions of the sample. The sample was irradiated a second time through a quartz plate and a thin film of dioctylamine to yield methyl termination in the previously unreacted areas of the sample. Lastly, the ethyl ester groups were converted to COOH groups by hydrolysis. We recorded the condensation image, which illustrates the spatial pattern of hydrophobic (CH_3)- and hydrophilic (COOH)-terminated regions in the sample, with an optical microscope while observing the condensation of water vapor onto the cooled sample surface (*29*). The water preferentially wets the COOH-terminated regions of the sample surface. (**B**) Modification of the cantilever-tip assembly with a specific functional group. Gold-coated Si_3N_4 cantilever-tip assemblies (*17*) were immersed in 1 mM ethanolic solutions of either octadecylmercaptan or 11-thioundecanoic acid for 2 hours to form covalently bound monolayers that were terminated with either CH_3 or COOH functional groups. The specific case of a tip terminating with COOH groups is shown. (**C**) Schematic views of the experiment. (**Inset**) Interactions between a tip terminating in COOH groups and a patterned sample terminating in both CH_3 and COOH groups.

action should be weakest. As shown in Table 1, the differences in the adhesive interactions between the same (COOH/COOH or CH_3/CH_3) or different (COOH/CH_3) functional groups are reproducibly larger than the uncertainty in these measurements, enabling the distinction of these functional groups simply on the basis of the magnitude of the measured adhesive force.

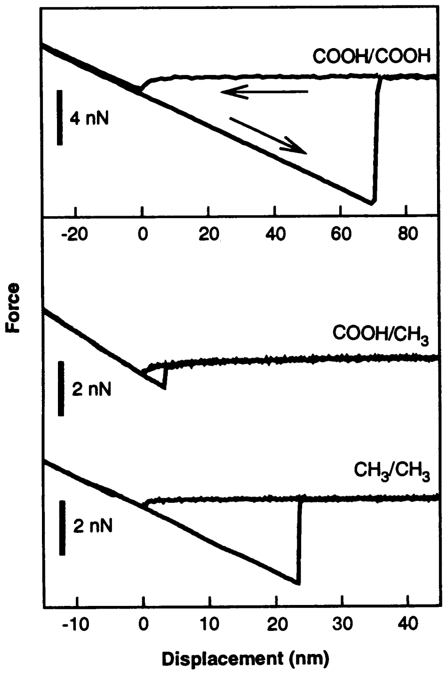

Fig. 2. Typical force versus displacement curves recorded between a COOH-terminated tip and sample, a CH_3-terminated tip and COOH-terminated sample, and a CH_3-terminated tip and sample in ethanol with a Nanoscope III lateral force micrscope.

The ability to distinguish the interactions between these simple functional groups is significant because these interactions represent perhaps the most general type of forces that occur between molecules and molecular assemblies (*20*). We also find that these modified tips are stable; for example, by using a CH_3-terminated tip, we were able to switch repeatedly between COOH- and CH_3-terminated samples and obtain the expected differences in adhesive interaction between CH_3/COOH and CH_3/CH_3 groups at each switch (*21*). In contrast, measurements made with unmodified probe tips exhibit force-displacement curves that change significantly with time and vary from tip to tip. Finally, it is important to recognize that the measured forces correspond to interactions between a small number of discrete functional groups. We used the Johnson-Kendall-Roberts (JKR) model (*1*, *22*) to estimate that the contact area at pull-off is about 10 nm^2 and thus that the measured force results from the interaction between ~50 functional groups on the sample and tip (*23*). Our ability to probe such local interaction forces is consistent with other recent AFM studies (*11*, *12*, *24*), and it would be interesting to investigate whether the rupture of individual pairs of molecules could be observed as in two recent studies (*11*, *24*).

Our central result is the spatial mapping of friction forces between the functionalized tips and lithographically patterned samples. Topographic and lateral force images recorded with both CH_3 and COOH functionalized tips on surfaces terminated with CH_3 and COOH groups are shown in Fig. 3. In general, little or no evidence is seen for the pattern of CH_3 and COOH groups in maps of the surface topography (Fig. 3B). A relatively featureless topography is expected because the CH_3 and COOH regions of the sample are structurally quite similar. These chemically distinct regions are, however, clearly visible in images of the friction force. When a CH_3-terminated tip is used for imaging, the CH_3-terminated regions of the sample exhibit a larger friction than the COOH-terminated regions (Fig. 3C). When a COOH-terminated tip is used to image the same sample, the friction contrast is reversed; a low friction force is observed over the CH_3-terminated regions of the sample, and a high friction force is observed

Table 1. Summary of adhesive forces (in nanonewtons) measured between functionalized tips and samples. These data were obtained by averaging the results from at least 300 force versus displacement curves for each tip-sample combination.

Sample	Tip	
	COOH	CH_3
COOH	8.7 ± 3.2	0.85 ± 0.49
CH_3	0.71 ± 0.35	2.7 ± 0.92

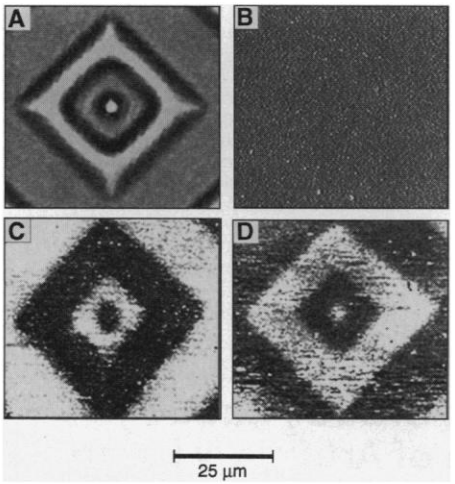

Fig. 3. (**A**) Optical condensation image of a patterned sample. The bright, raised areas in this image correspond to liquid H_2O that has condensed on the COOH-terminated regions of the sample. (**B**) Force microscope image of the sample topography of the same surface pattern as in (A) recorded with a probe tip terminated with CH_3 functional groups. As expected, there is little difference in the topography observable between the CH_3- and COOH-terminated regions of the sample. Similar topographic images were also recorded with COOH-terminated tips. (**C**) Image of the friction force recorded simultaneously with the topography in (B). The bright regions correspond to a high friction force, whereas the dark regions correspond to a lower friction force. In this image, which was recorded with a CH_3-terminated tip, high friction is observed over CH_3-terminated regions of the sample. (**D**) Image of the friction force recorded between a COOH-terminated tip and a similar region of the sample as in (A) through (C). In this image, high friction is observed over COOH-terminated regions of the sample. Images (B) through (D) were acquired under ethanol with an applied load of 4 nN and a scan rate of 3 Hz. Similar results have been obtained with scan rates between 1 and 10 Hz and applied loads from 3 to 10 nN.

over those regions terminated with COOH functional groups (Fig. 3D). These observed differences in image contrast agree with chemical intuition and our quantitative adhesion force data because higher friction is observed between similar functional groups (COOH/COOH or CH_3/CH_3) that interact more strongly with each other than dissimilar groups ($COOH/CH_3$). A minimum applied load of ~3 nN is necessary to observe friction images with good contrast, but this load is well below the recently reported threshold load for monolayer damage (*25*). In addition, image contrast with the modified tips is stable and reproducible, but images obtained with unmodified tips do not show reproducible variations in the friction force on the above modified surfaces.

The results demonstrate that it is possible to map in a predictable manner the spatial distribution of chemically distinct functional groups on a sample surface when functionalized tips are used. That is, sample regions that have strong interactions with the functionalized probe tip will exhibit large friction, and those with weak interactions will exhibit small friction (*26*). Chemical force microscopy is thus an appropriate description of this imaging technique because the image contrast is readily interpretable in terms of the chemical interactions between specific functional groups on the modified tips and those being mapped on the sample surface.

The lateral resolution of the images in Fig. 3 is estimated to be ~200 nm. However, we believe that the achievable resolution should be on the order of 10 nm, on the basis of our estimation of the contact area of the tip on the sample during imaging (*27*). Resolution in our present images is believed to be limited by the resolution inherent in our monolayer patterning procedure. Ultimately, the achievable lateral resolution could be improved beyond 10 nm with the use of sharper probe tips.

We have demonstrated the concept of chemical force microscopy for the specific case of functional groups exhibiting hydrophobic and hydrophilic character. It should also be possible to map the spatial distribution of other types of functionality such as charged or chemically reactive groups with this approach. The ability to map different chemical functionality on surfaces should be very useful in studies of adhesion and lubrication. In addition, we believe that more specific interactions, for example those between complimentary and noncomplimentary oligonucleotides and ligand-receptor pairs, could be readily mapped with high resolution. One could thus envision attaching a specific oligonucleotide or receptor to the probe tip and then mapping the friction force on a surface that contains an array of different nucleotide sequences or ligands to find those having the strongest interaction. Finally, in cases where the sample surface exhibits significant topographic variations, it should still be possible to image with functional group sensitivity by mapping the adhesive force between a specifically functionalized tip and the unknown sample (determined from force-displacement curves recorded simultaneously with the topographic map) as a function of lateral coordinates.

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18. The Si_3N_4 cantilevers with integrated tips (triangular, 200 µm long, from Digital Instruments) were coated with a 30 Å Cr adhesion layer followed by 1000 Å of Au with an Edwards (Wilmington, MA) Auto306 thermal evaporator. The cantilever force constants were determined by the end-mass resonance detection method [J. P. Cleveland, S. Manne, D. Bocek, P. K. Hansma, *Rev. Sci. Instrum.* **64**, 403 (1993)]. We measured the force constants of the uncoated and Au-coated levers to be 0.07 and 0.12 N/m, respectively.
19. The strength of a single hydrogen bond is on the order of 10 kJ/mol, whereas that of a van der Waals (hydrophobic) bond is about 1 kJ/mol.
20. AFM has been used previously to measure the adhesive interaction between hydrocarbon groups (*15*); however, measurements of the adhesive interaction between different types of functional groups (for example, CH_3/CH_3, CH_3/COOH, and COOH/COOH) have not to our knowledge been reported.
21. Additionally, analysis of the adhesive force as a function of time with a COOH-terminated tip showed that the average force dropped only 15% after 400 force-displacement curves. The CH_3-terminated tips appear to exhibit greater stability.
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23. The radius of the tip-sample contact area at separation a_s is

$$a_s = 1.67\left[\frac{\gamma R^2}{K}\right]^{1/3}$$

where γ is the work of adhesion per unit area of contact, R is the radius of curvature, and K is an elastic constant, which is calculated from the Poisson ratio and Young's modulus of Au. For the CH_3/CH_3 system, $\gamma = 5$ mN/m and $K = 64$ GPa. For our experimental geometry, we estimate $R = 115$ nm. Substituting these values into the above equation yields $a_s = 1.7$ nm, or a contact area of 9.0 nm^2. This area corresponds to ~50 surface-confined molecules [0.2 nm^2 per molecule (*16*)]. The force per CH_3/CH_3 interaction can be calculated by dividing our experimental value of ~3 nN (Table 1) by 50, which gives 6×10^{-11} N. This value is consistent with another, independent calculation of the force

between two CH_3 groups, which assumes the interaction can be treated with a Lennard-Jones potential (*27*).
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26. It has been suggested on the basis of SFA studies of different hydrocarbon-terminated layers that it is the hysteresis in adhesion that will correlate with friction (*3*). We believe that in comparisons of chemically distinct functional groups, which exhibit large differences in adhesive interaction, friction differences are directly related to the variations in the adhesive forces.
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30. The spherical tungsten particles used as end-masses were provided by J. P. Cleveland. C.M.L. acknowledges support by the Office of Naval Research and Air Force Office of Scientific Research. C.D.F. acknowledges the National Science Foundation (NSF) for a postdoctoral fellowship (CHE-9302409), and M.S.W. also thanks the NSF for financial support.

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Superconductivity in $SrCuO_2$-$BaCuO_2$ Superlattices: Formation of Artificially Layered Superconducting Materials

D. P. Norton, B. C. Chakoumakos, J. D. Budai, D. H. Lowndes, B. C. Sales, J. R. Thompson, D. K. Christen

Pulsed-laser deposition was used to synthesize artificially layered high-temperature superconductors. Thin-film compounds were formed when the constraint of epitaxy was used to stabilize $SrCuO_2$-$BaCuO_2$ superlattices in the infinite layer structure. Using this approach, two new structural families, $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ and $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$, have been synthesized; these families superconduct at temperatures as high as 70 kelvin.

Since the discovery of high-temperature superconductivity (HTSc) (*1*), intensive efforts have revealed numerous families of layered crystal structures containing copper oxide layers (*2*), with superconducting transition temperatures (T_c) as high as 135 K for the Hg-containing cuprates (*3*). Typically, bulk synthesis techniques have been the primary tool in the search for new HTSc materials. Recently, high-pressure synthesis methods have been used to make metastable cuprate phases (*4–7*). However, thin-film growth methods offer unique advantages for the atomic engineering of new HTSc materials because with this technique it is possible to form artificially layered crystal structures. Moreover, the surfaces of single-crystal substrates provide an atomic template that can be used to stabilize epitaxial films in metastable crystal structures.

Advances in the understanding of epitaxial thin-film growth of the cuprates have heightened interest in the possibility of creating artificially layered materials (*8–10*). The cuprate superconductors are ideal candidates for study because their crystal structures are composed of chemically distinct layer modules, the most important of which is the square CuO_2 layer. A prelude to this development has been the epitaxial stabilization of "infinite layer" $(Ca,Sr)CuO_2$ single-crystal thin films (*11–14*). The infinite layer $(Ca,Sr)CuO_2$ structure type, consisting of square CuO_2 layers alternately stacked with square layers of alkaline-earth atoms, is the simplest cuprate with the essential structural features for HTSc (*15*). Indeed, the infinite layer structure can be viewed as a fundamental building unit of all of the HTSc cuprates. Already, by the addition of infinite layer $(Ca,Sr)CuO_2$ modules, metastable thin-film structures of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ have been extended to $n > 3$ with the use of molecular beam epitaxy (MBE) and laser-MBE growth techniques (*16, 17*). In recent pioneering work, laser-MBE, in conjunction with reflection high-energy electron diffraction to monitor the film growth process, was used to grow the first artificially layered HTSc films, which were tentatively identified as 3 unit cells–1 unit cell $BaCuO_2$-$CaCuO_2$ infinite layer superlattices (*18*).

We report here the synthesis of two series of artificially layered HTSc compounds, grown as $SrCuO_2$-$BaCuO_2$ crystalline superlattice structures. Although earlier efforts to grow artificially layered cuprate structures have been restricted to sophisticated MBE-like apparatus with in situ surface analysis techniques (*8, 16–18*), we have formed these materials using only pulsed-laser deposition (PLD). By sequentially depositing from $BaCuO_2$ and $SrCuO_2$ ablation targets in a PLD system, we constructed artificially layered crystalline materials in which the layering sequence was controlled on nearly the atomic-layer scale. The $SrCuO_2$ and $BaCuO_2$ layers are epitaxially stabilized in the infinite layer structure and form the building blocks for the compounds. In the infinite layer structure, $SrCuO_2$ is an insulator, whereas $BaCuO_2$ normally does not form the infinite layer structure, even when high-pressure synthesis techniques are used.

Using this approach, we synthesized two new HTSc series, $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ and $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$, with T_c(onset) as high as 70 K and T_c(resistance $R = 0$) as high as 50 K.

The $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ series, with $n = 2$, 3, and 4, is structurally analogous to the recently discovered $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ high-pressure HTSc phase (*4–6*) and is obtained by artificially layering two unit cells of $BaCuO_2$ and $(n - 1)$ unit cells of $SrCuO_2$ in the infinite layer crystal structure. A schematic of the $n = 3$ member is shown in Fig. 1. The $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$ series, formed by layering four unit cells of $BaCuO_2$ and $(n - 1)$ unit cells of $SrCuO_2$ in the infinite layer structure, exhibits superconductivity for the $n = 3$ member with T_c(onset) = 70 K and T_c($R = 0$) = 40 K. In addition, we have epitaxially stabilized 4.0-nm-thick layers of the $n = 1$ member, infinite layer $BaCuO_2$, in $SrCuO_2$-$BaCuO_2$ multilayer structures that show metallic conductivity and superconductivity at T_c(onset) ≈ 70 K.

We prepared the films on (100) $SrTiO_3$

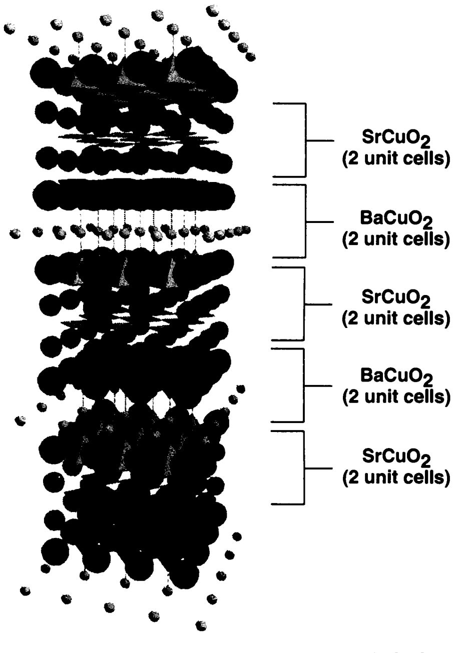

Fig. 1. Structural model of a 2 × 2 $SrCuO_2$-$BaCuO_2$ superlattice compound, also designated as $Ba_2Sr_2Cu_4O_{8+\delta}$. The Ba, Sr, and Cu atoms are represented by the large, medium, and small spheres, respectively. The CuO_4 and CuO_5 units are shown as shaded polyhedra.

Solid State Division, Oak Ridge National Laboratory, Post Office Box 2008, Oak Ridge, TN 37831-6056, USA.