Combinatorial near-edge x-ray absorption fine structure: Simultaneous determination of molecular orientation and bond concentration on chemically heterogeneous surfaces

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We show that simultaneous molecular orientation and bond chemistry of planar chemically heterogeneous surfaces can be obtained by combining near-edge x-ray absorption fine structure (NEXAFS) spectroscopy and rastering the incident x-ray beam on the specimen. This rastering produces serially two-dimensional NEXAFS images in space and energy, revealing information about the chemistry (including bond concentration) and orientation of the surface-bound molecules with submillimeter planar spatial resolution and submonolayer molecular sensitivity. We illustrate the power of the combinatorial NEXAFS method by simultaneously probing the concentration and molecular orientation of semifluorinated (SF) molecules in double-SF molecular gradients on flat silica substrates. © 2003 American Institute of Physics. [DOI: 10.1063/1.1535271]

The demands of preparing, processing, and characterizing materials and structures and the need for full exploration of the parameter space has led to the development of a plethora of combinatorial approaches.\textsuperscript{1–3} Most experimental analytical combinatorial methods concentrate on probing only a single material property, such as chemical information, topography, etc. In this letter, we show that information about the chemistry (including bond concentration) and molecular orientation on chemically heterogeneous surfaces can be collected by simultaneously utilizing near-edge x-ray absorption fine structure (NEXAFS) spectroscopy and rastering the x-ray beam on the probed specimen. This rastering produces serially two-dimensional NEXAFS images in space and energy, with submillimeter planar spatial resolution and submonolayer molecular sensitivity. We call this technique combinatorial NEXAFS.

NEXAFS involves the resonant x-ray excitation of a K- or L-shell electron to an unoccupied low-lying molecular orbital of $\sigma$ or $\pi$ symmetry, $\sigma^*$ and $\pi^*$, respectively.\textsuperscript{4} The initial-state K- or L-shell excitation gives NEXAFS its element specificity, while the final-state unoccupied molecular orbitals provide NEXAFS with its bonding or chemical selectivity. A measurement of the intensity of NEXAFS spectral features enables the identification of chemical bonds and a determination of their relative population density within the sample. Because of the fixed geometry and the fact that the $1s \rightarrow \sigma^*$ and $1s \rightarrow \pi^*$ excitations are governed by dipole selection rules, the resonance intensities vary as a function of the direction of the electric field vector $E$ of the incident polarized x-ray relative to the axis of the $\sigma^*$ and $\pi^*$ orbitals. NEXAFS is an ideal technique for probing molecular orientation of organic molecules because sharp core level excitations for C, N, O, and F occur in the soft x-ray spectral region. Since its introduction, NEXAFS has proven advantageous in determining the orientation of both small molecules, as well as large macromolecular systems, and has evolved into a routine analytical technique. NEXAFS is a static technique: for example, it probes the bond concentration and orientation of only a given spot on the sample. In this letter, we demonstrate that a simple extension to combinatorial NEXAFS can be achieved by combining the classical ("static") NEXAFS data collection and x-ray beam rastering on the sample. The latter is accomplished by mounting the sample on a computer-controlled motorized goniometer and translating the sample along one (or more) planar direction(s), while collecting partial-electron-yield NEXAFS data at various fixed incident x-ray energies. In this serial manner, a two-dimensional NEXAFS image in space and energy is obtained. We note that scanning transmission x-ray microscopy can also be used to produce NEXAFS spectroscopic images, but with very high spatial resolution.\textsuperscript{5} Although this method offers submicrometer spatial resolution, it requires very thin specimens on substrates transparent to the x-rays, and provides primarily chemical mapping of a limited area (usually several square micrometers) of the specimen.

We demonstrate the capability of combinatorial NEXAFS by probing the chemistry and molecular orientation of semifluorinated molecules (1H,1H,2H,2H-perfluorodecyltrichlorosilane, $t$-F8H2) forming molecular gradients of F8H2 in surface coverage on the flat silica substrates. We formed double molecular gradients of F8H2 on silica substrates using a variant of the methodology proposed by Chaudhury and Whitesides.\textsuperscript{6} The silicon wafer was cut into rectangular pieces (5 cm x 1 cm) that were exposed to ultraviolet/ozone (UVO) treatment for 30 min (Jelight Company, Inc., model 42)\textsuperscript{7} in order to generate a large number of hydroxyl groups, which are required for the $t$-F8H2/silica.

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coupling. A mixture of t-F8H2 (supplied by Lancaster and used as received) and paraffin oil (PO) (1:5 w/w) was prepared and placed in two small rectangular containers, which were positioned near the two opposite shorter edges of the UVO-treated silicon wafer. The whole system was enclosed in a Petri dish at ambient conditions. As t-F8H2 evaporated, it diffused in the vapor phase and generated a concentration gradient along the silica substrate. Upon impinging on the substrate, the t-F8H2 molecules reacted with the substrate -OH functionalities and formed a F8H2 self-assembled monolayer (SAM). The breadth and position of the F8H2 molecular gradient can be tuned by varying the t-F8H2 diffusion time and the flux of the t-F8H2 molecules. The latter can be conveniently adjusted by varying the chlorosilane:PO ratio and the temperature of the t-F8H2:PO mixture. Further tailoring can be achieved by utilizing flexible polymeric support as substrates. After 7 min, the wafer was taken out of the container, thoroughly washed with ethanol to remove any physiosorbed silane molecules, and dried with nitrogen.

The NEXAFS experiments were carried out at the NIST/Dow soft x-ray materials characterization facility at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The principles of NEXAFS and description of the BNL beamline have been outlined elsewhere. The partial-electron-yield (PEY) signal is collected using a channeltron electron multiplier with an adjustable entrance grid bias (EGB). We have recently shown that a crude depth profiling within the top ≈5 nm is made possible by increasing the negative EGB on the channeltron detector at the highest bias, thus selecting only the Auger electrons that have suffered negligible energy loss. For these experiments, the EGB of the channeltron detector was set to −150 V. To eliminate the effect of incident beam intensity fluctuations and monochromator absorption features, the PEY signal was normalized by the incident beam intensity obtained from the photo yield of a clean gold grid.

The NIST/Dow materials characterization end-station is equipped with a computer-controlled stepping-motor-actuated sample holder, which controls the orientation of the sample with respect to the polarization vector of the x-rays, and enables rapid horizontal and vertical sample motion (cf. Fig. 1). The combinatorial NEXAFS experiments were conducted by scanning the sample in the vertical direction with 0.5-mm increments, and after each step a NEXAFS spectrum was recorded. An important issue concerning the study of organic materials is the possibility of the sample damage during the characterization with UV light, x-ray, and electron radiation. Semifluorinated materials are particularly sensitive to these effects. Because a fresh area of the sample was always exposed to the x-ray beam spot during the data PEY NEXAFS collection, possible beam damage effects were kept at minimum.

The top panels of Fig. 2 show the carbon K-edge PEY NEXAFS spectra collected from a homogeneous F8H2 SAM sample measured at θ = 20°, 50°, and 90°, where θ is the angle between the sample normal and the electric field vector of the x-ray beam. The PEY NEXAFS spectra were normalized using standard procedures by adjusting the pre-edge and post-edge signals to 0 and 1, respectively. The dashed lines in Fig. 2 denote the positions of the 1s→σ* transitions for the C–F (E = 292.0 eV), and C–C (E = 295.4 eV) bonds. The fact that the intensities originating from these transitions change with varying angle θ (as θ increases the intensity, corresponding to the 1s→σ* transitions of the C–F bond increases, while that of the C–C bond decreases) indicates that the sample is well oriented. More detailed analysis presented and discussed elsewhere revealed that the F8H2 molecules stand almost perpendicular to the sample surface. The combinatorial NEXAFS experiments on the double-gradient sample were carried out as previously described; the vertical motion (0.5-mm increments) of the sample was controlled by the computer. After each vertical increment, a carbon K-edge PEY NEXAFS spectrum was taken at photon energies around the C–F (291.4 eV ≤ E ≤ 293.0 eV) and C–C (294.4 eV ≤ E ≤ 297.0 eV) signals. In addition, PEY NEXAFS data were collected at the carbon ionization pre-edge (E = 280.0 eV) and post-edge (E = 320.0 eV). All PEY NEXAFS spectra were recorded at three different angular specimen orientations: θ = 20°, 50°, and 90°. The corresponding normalized PEY NEXAFS intensities as a function of the incident photon energy beam and the position on the substrate are shown in the bottom panel of Fig. 2. The data in Fig. 2 show that the PEY
NEXAFS intensities of the C–F and C–C bonds collected close to the edges (located at 0 and 50 mm, respectively) of the sample follow the same trends as those in the homogeneous SAM specimen. Thus, while at $\theta = 20^\circ$ the $1s \rightarrow \sigma^*$ for the C–C bond is higher than the $1s \rightarrow \sigma^*$ for the C–F bond, at $\theta = 50^\circ$ and $\theta = 90^\circ$ the situation is reversed. When moving from the two edges towards the interior of the double gradient, the $1s \rightarrow \sigma^*$ transition intensities for the C–F and C–C bonds decrease.

In order to quantify the degree of orientation of the surface-bound molecules, we followed the method of Outka and coworkers, and fitted the PEY NEXAFS spectra to a series of Gaussian curves representing the different $1s \rightarrow \sigma^*$ transitions, a step function corresponding to the excitation edge of carbon, and a background. The modified building-block model, described elsewhere, was used to determine the values of the average tilt angles of the fluorinated part, $\langle \tau_{\text{F}} \rangle$, of the semifluorinated chain on the sample surface by analyzing the intensities of the C–F bond at $E = 292.0$ eV and three different angles. The open circles in Fig. 3 show the variation of $\langle \tau_{\text{F}} \rangle$ as a function of the position on the double-gradient sample.

Because of the nature of NEXAFS, spectral intensities collected at so-called “magic angle” are independent of the molecular orientation. For a 100% polarized beam, the magic angle is $\theta = 54.5^\circ$. The x-ray beam at the NSLS is about 80% linearly polarized, which gives a magic-angle value of $\approx 51^\circ$. Hence, the PEY NEXAFS spectra collected at $\theta = 50^\circ$ would allow for determining the concentration of the t-F8H2 molecules in the molecular gradient. The concentration of the t-F8H2 molecules was inferred from the difference between the pre- and post-edge normalized intensity of the C–F peak, as described elsewhere. The solid circles in Fig. 3 show the dependence of fraction of the F8H2 molecules on the surface (normalized by the maximum SAM coverage) as a function of the position on the double gradient.

By comparing the combinatorial NEXAFS information about the concentration and orientation of F8H2 in the molecular gradient the following picture emerges. Close to the diffusing source, the F8H2 organosilanes form complete SAMs, with the molecules oriented roughly perpendicular to the sample surface. This situation is similar to the organization of the F8H2 moieties in a homogeneous SAM made of t-F8H2. At larger distances from the diffusing sources, the concentration of the F8H2 molecules decreases; the functional dependence resembles that of typical diffusion profiles, in accord with previously reported results. From Fig. 3, $\langle \tau_{\text{F}} \rangle$ increases as one moves into the center of the double gradient, suggesting that the F8H2 molecules start tilting away from the sample normal. The situation is likely more complicated, however. Considering that the spot size of the x-ray beam on the sample during the NEXAFS experiments, $\approx 1$ mm$^2$, is much larger than the area occupied by a single F8H2 molecule, the tilt angle $\langle \tau_{\text{F}} \rangle$ determined from NEXAFS represents only an average value. Hence, there is no straightforward way to discriminate between the case of all F8H2 molecules homogeneously tilting by the same angle and the case of a disordered system with a broad distribution of tilt angles. Therefore, the increase in $\langle \tau_{\text{F}} \rangle$ observed in the region of the gradient in which the concentration decreases cannot be interpreted unambiguously by using the NEXAFS data alone. Complementary measurements of another physical property along the gradient, such as the density and/or the thickness, are required.

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Fig. 3 show the dependence of fraction of the F8H2 molecules on the surface (normalized by the maximum SAM coverage) as a function of the position on the double gradient.