Ionic Liquids

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Rewritable Imaging on the Surface of Frozen Ionic Liquids**

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Submicron-resolution lithographic imaging forms the basis of many industrial processes employed in the fabrication of integrated chips, memory-storage devices, lab-on-a-chip devices, microfabricated arrays, and other electronic devices.[1] Successive rounds of photolithography, or sequential milling, are used to build up complex patterns of conducting, insulating, semiconducting regions, or arrays of channels and grooves upon the substrate. In general, these techniques produce a permanent, write-once image or pattern, which is difficult or impossible to alter once they have been formed.[2] As a consequence, high levels of precision and accuracy are required at each process step. Herein, we report the serendipitous discovery of a method for producing localized charge patterns that allow the recording of a rewritable image or data set on the surface of a frozen ionic liquid and provide a fascinating probe for the conductor–insulator transition.

Room-temperature ionic liquids (RTILs) are sterically hindered organic salts with melting points below 373 K. Because they are composed entirely of ions, RTILs have almost zero vapor pressure. RTILs have found application in many areas of research including synthesis,[3] biochemistry,[4] electrochemistry,[5] analytical chemistry,[6] engineering,[7] and material sciences.[8] Indeed, several of these applications have already reached a commercial scale.[9] One of the key opportunities that RTILs offer in terms of application is the inherent flexibility and indeed tunability offered by the large number of potential ion pairings,[10] the physicochemical properties of which can be engineered to optimize melting, glass-transition temperatures, and solute solubility.

The lack of volatility associated with many RTILs allows them to be investigated by a range of analytical instruments that require ultrahigh vacuum (UHV) for their operation.[11] We have previously reported X-ray photoelectron spectroscopy (XPS)[12,13] as well as time-of-flight secondary ion mass spectrometry (TOF-SIMS) data.[13]

During our investigation of RTILs using TOF-SIMS,[13] we noted that simple and very reproducible SIMS spectra were generated with no special sample preparation by using standard instruments and stages. However, we have not yet reported, in detail, the effect of temperature and consequently the physical state of the sample on these measurements. In the case of [EMIM][$EtSO_4$] (EMIM = 1-ethyl-3-methylimidazolium), the sample was observed to solidify and turn opaque at stage temperatures less than 188 K. It became evident quite quickly that, when the sample was presented as a solid, surface charging became a problem. The quality of SIMS spectra generated was poor and peak shapes were ill-defined. This was easily overcome by flooding the charged surface with low-energy electrons during which the peak shapes and the SIMS yield were instantaneously improved.

We have observed similar effects in XPS.[13] Each of the RTILs was highly conducting in the liquid state, presumably owing to high ionic mobility leading to the rapid dissipation of charge into the sample bulk. However, upon freezing, an appreciable broadening in the XPS spectra accompanied an "offset" in measured binding energies that was proportional to X-ray exposure and associated surface charging. Compensation or neutralization of the surface was possible by flooding the surface with low-energy electrons (<20 eV), which is standard procedure in the analysis of insulating samples.[14]

Here we exploit this change in conductivity by using static TOF-SIMS to both create and image patterns with the focused Ga^+ ion beam, which is used as a primary-ion source during TOF-SIMS. The term "static" denotes that all our experiments were carried out in an extremely low primary-dose regime ensuring no significant alteration of the sample surface chemistry occurs. The upper limit for this technique is generally accepted as 10^{12} primary-ion impacts per square centimeter,[15,16] our doses were two orders of magnitude below that value throughout.

When operating in imaging mode, the TOF-SIMS software can be used to plot the total yield of secondary ions for a specific location onto a map of the sample by using simple x,y coordinates. When the sample was liquid ($T>193$ K), consecutive images generated from the same sample area in this way displayed homogeneous images, that is, similar quantities of secondary ions were produced across the sample surface (Figure 1a). In fact, mapping the distribution of a range of secondary ions across the sample surface revealed a completely homogeneous distribution. However, when presented as a frozen solid ($T<188$ K), consecutive maps showed distinct areas as manifested by areas of differing contrast in total-ion images. It became evident that the contrasted (dark) areas coincided with the path that the primary-ion (Ga^+)

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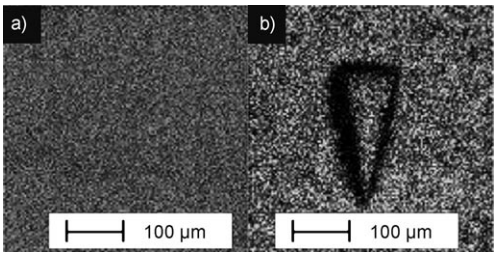

Figure 1. a) Total negative ion SIMS map of [EMIM][$EtSO_4$] presented as a liquid ($T > 188$ K). The sample appears as a homogeneous surface with no contrasting areas observed. b) Total negative ion SIMS map of [EMIM][$EtSO_4$] presented as a solid ($T < 188$ K). The sample shows an area the shape of an arrowhead as a contrast image against the background. This area coincides with the path of the primary-ion (Ga^+) beam ($\varnothing \approx 5$–6 μm) prior to the generation of this image.

beam had followed during the initial SIMS experiment (Figure 1 b).

The likely explanation for this pattern formation is that when the pulsed Ga^+ ion beam is rastered across a frozen RTIL sample, in a specific pattern, it generates areas of localized, discrete positive charge (see the Supporting Information). The creation of a positive surface charge under the exposure of a positive-ion beam is well documented in the field of TOF-SIMS analysis of insulating samples.[15,16] We found that typically 3–4 scans of the same pattern were sufficient to generate a pattern such as displayed in Figure 2. The darker, charged areas with a low secondary-ion yield can clearly be distinguished from the bright, nonirradiated (uncharged) areas.

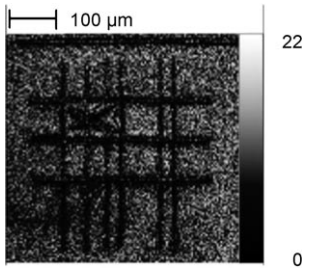

Figure 2. Total negative ion image of a pattern written on the surface of a frozen RTIL [EMIM][$EtSO_4$] at 178 K by using a focused Ga^+ ion beam ($\varnothing \approx 5$–6 μm, 0.7 pA pulsed current, primary-ion dose $< 10^{10}$ ions cm^{-2} for both pattern writing and reading). The scale at the right-hand side of the figure indicates the relative intensity of emitted secondary ions (counts per pixel).

There are two main concepts that could explain the formation of these striking patterns: 1) the primary-ion beam damages the surface layers of the sample leading to localized chemical changes at the surface; and 2) exposure to the Ga^+ ion source leaves positively charged areas that are frozen into specific sites on the sample surface. The primary-ion exposure was sufficiently low ($< 10^{10}$ ions cm^{-2}) that localized surface topography alterations need not be considered. Chemical modification, including the possible inclusion of Ga^+ ions, was eliminated as an explanation after careful analysis of SIMS spectra from both light and dark areas (see the Supporting Information). Image formation by localized or frozen charges was confirmed by carrying out two further experiments. In the first experiment, any areas of charge were mobilized by warming the sample through its apparent T_g (measured during the experiment as the point where the sample changed appearance and physical state at 188 K).[17] As the experiment was carried out, images were recorded as a function of both temperature and time. The dark regions were seen to fade, yielding a uniformly bright surface when $T > 188$ K. Furthermore, at higher temperatures (e.g. 198 K) the erasure process occurred very rapidly indeed. The disappearance of the image is consistent with dissipation of the frozen charges into the bulk of the melted, liquid sample. Rewriting of a new image was made possible by cooling the sample below the noted transition point, consequently refreezing the RTIL surface. The second diagnostic experiment carried out, which we believe confirms the charge based explanation, was simply the neutralization of the frozen positively charged areas by using a standard low-energy electron gun. Indeed, when the filament was actuated, the image was erased almost instantaneously. Charge compensation of insulating samples by using low-energy electrons is common practice in the measurement of unperturbed spectra for both XPS[14] and SIMS.[15,16]

By using this method, we quickly established the fact that by programming the path of the primary-ion beam and controlling the surface temperature, we could easily construct patterns of moderate resolution and complexity. Both the writing and erasure procedures are highly repeatable and no deterioration in the quality or intensity of the pattern was observed, even after a significant number of write/erase cycles. Experiments are ongoing in our laboratories to investigate the potential application of these processes; furthermore we are expanding our work to include other RTILs, specifically those with transition temperatures at or above ambient room temperature. Early indications suggest that this is a general phenomenon as similar experiments have been carried out for other RTILs, including the archetypal [BMIM][Cl], which has a melting point of 340 K (BMIM = 1-butyl-3-methylimidazonium).[18]

A further series of experiments was carried out to investigate the stability of our patterns under non-vacuum conditions in which collision with charged species in the atmosphere could lead to image fading. After an image was written on a surface of frozen [EMIM][$EtSO_4$], the sample stage was transferred to a preparative chamber adjacent to the analytical chamber of the TOF-SIMS instrument. The preparative chamber was subsequently vented to 1 atm of dry N_2 gas, and during this process a minor temperature increase at the sample stage was noted ($T \approx 188$ K). The preparative chamber was then re-evacuated and the sample returned to the main chamber for visualization. The image was still present, however, minor deterioration in the contrast was noted. The particularly low transition temperature of [EMIM][$EtSO_4$] made this experiment extremely difficult to conduct. It is very likely that the fading observed is linked to the temperature increase noted during the venting process as the N_2 gas used in this step was not precooled.

This methodology has allowed the investigation of changes in the thermal and physical properties of RTILs at and in the region of their melting points. In-depth studies on the subtlety of the conductor–insulator properties of these interesting materials at these temperatures is ongoing. We believe that the experiments outlined herein are the first reports of the use of RTILs as a substrate for image formation and, in principle, as a rewritable data-storage medium. There is significant scope for image-writing processes at even higher resolution: focused-ion-beam technology is a rapidly moving field. The minimum beam width generated by state-of-the-art instruments is currently less than 10 nm. If image formation can be achieved with such instruments, then the density of data storage will be extremely high. Furthermore, the application of RTILs as temperature-sensitive substrates for data storage offers tremendous flexibility as the physicochemical properties of RTILs can be fine-tuned through manipulation of the chemical/structural composition of the individual ions employed.

Experimental Section

RTIL samples were prepared in our laboratories by using literature methods.[18,19] All UHV experiments (base pressure less than 5×10^{-9} mbar) were carried out in a TOF-SIMS IV instrument (ION-TOF GmbH, Münster, Germany) equipped with a liquid-nitrogen-cooled variable-temperature sample stage, a liquid-metal (Ga) ion gun, and a single-stage reflectron analyzer. Typical operation conditions comprised a pulsed-target current of approximately 0.7 pA and a primary-ion energy of 25 keV. All experiments were carried out with an ion-beam diameter of approximately 5 μm. Samples were presented on clean aluminum foil.

In initial experiments, it was found that [EMIM][$EtSO_4$], which was simply deposited on the foil, would present as a sessile bead owing to the moderate surface tension of the ionic liquid sample. This had the effect of varying the distance between the sample surface and the focal plane of the analyzer, thus reducing the quality of imaging. The use of a Mo grid ensured that the RTIL was presented as a thin film with a uniform distance between the sample surface and the focal plane of the analyzer system. A pulsed low-energy electron gun supplied low-energy electrons (< 20 eV) for charge neutralization as and when required.

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