

Prospects for submicron molecular imaging with ion beams and lasers

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ABSTRACT: We have combined energetic particle bombardment with MPRI as a tool for analysis of atoms and molecules adsorbed on solid surfaces. The selectivity of the postionization process and the high ionization efficiency yield excellent detection limits for trace levels of surface atoms and molecules. In this work, we examine the use of a liquid metal ion source for surface studies. This source offers the unique property that it can be focused to a spot size of smaller than 400 Å. The flux of incident ions, however, is extremely low, necessitating the use of MPRI to enhance detection limits.

1. INTRODUCTION

Energetic particle bombardment of surfaces followed by MPRI detection of desorbed species has become a powerful new surface characterization methodology since its inception 10 years ago (Winograd et al 1982) (Parks et al 1983). The experiments have found several arenas where they have contributed significant new science. Initial studies focused on the high selectivity and ionization efficiency of MPRI detection for desorbed atoms. These properties extended the analytical utility of existing surface analysis techniques such as secondary ion mass spectrometry (SIMS) where large matrix ionization effects are problematic. Detection limits have ultimately reached to less than 200 impurity atoms over 1 cm² of the target surface (Pappas et al 1989). A second area has involved the use of MPRI to measure the energy and angle distributions of desorbed atoms by taking advantage of the spatial distribution of the sputtered flux. These studies have provided the first measurements of the trajectories of desorbed species which can then be directly compared with molecular dynamics computer simulations of the ion/solid interaction (Garrison et al 1988). Recently, this approach has even been successful for describing species desorbed in metastable excited states (Bernardo et al 1992). Finally, there is now considerable evidence to suggest that MPRI can be effectively used to detect molecular species desorbed from surfaces. So far, a variety of aromatic molecules, amino acids and simple polymers have been detected using a simple 1+1 ionization scheme with detection limits in the attomole range (Hrubowchak et al 1991). At this point, then, MPRI detection has offered a new window for elucidating the fundamentals of the ion/solid interaction and for expanding the applications of ion beam methods.

Let us consider here the high sensitivity of MPRI detection. To detect a small amount of an impurity element in a background matrix, for example, 1 part in 10^9 , it is of course necessary to guarantee that enough of the impurity atoms reach the laser beam to ensure a statistically accurate analysis. In the past, this has been accomplished by using a high current primary ion source which has a relatively large area of several mm in diameter. For this case, if the primary ion current, I_p , is $100 \mu\text{A}/\text{cm}^2$, is pulsed on for τ_p of $3 \mu\text{sec}$ at a 30 Hz repetition rate, and the yield, Y , of sputtered atoms per incident ion is ~ 3 , there will be 2×10^{10} atoms/s placed in the gas phase above the target. Assuming a 10% detection efficiency, then, an impurity present at 1 part in 10^9 would yield 600 counts after 5 minutes of analysis. These types of numbers have been demonstrated in real applications by a number of groups.

Where are the applications for such high sensitivity measurements? As noted, detection limits for atoms can reach $200/\text{cm}^2$ (Pappas 1989). For molecules, preliminary studies have already shown that 10^6 molecules/ cm^2 can be achieved (Hrubowchak 1991). Clearly, there are potential uses for such techniques in materials science and semiconductor processing where quality control is a critical factor. These avenues are being vigorously pursued.

Another important direction for this work involves imaging a small number of atoms or molecules from a well-defined spot. Using a liquid metal ion gun (LMIG), for example, it is possible to probe an area of less than $400 \text{ \AA} \times 400 \text{ \AA}$. The analytical difficulty arises when considering the number of atoms or molecules that are present in the surface layer of an area of this magnitude.

As seen in Table I, depending on size, there are roughly 40,000 molecules or 250,000 atoms in a spot of $1000 \text{ \AA} \times 1000 \text{ \AA}$. Hence, the need for ultrasensitive techniques is obvious for imaging experiments, particularly in the submicron regime.

There is another important issue associated with this experiment. For the earlier trace analysis studies, $I_p \sim 100 \mu\text{A}$. For the LMIG operating under conditions of maximum spatial resolution, $I_p = 60 \text{ pA}$ into a 400 \AA spot. (This value can be increased to 500 pA with a concomitant loss of spatial resolution). For $\tau_p = 500 \text{ ns}$ operated at a 30 Hz repetition rate, there will be only 15,000 atoms/s overlapping with the photon field, even though $I_p = 4 \text{ Amp}/\text{cm}^2$! The conclusions from these numbers are that the LMIG is good enough to yield measurable signals from

Estimation of Number of Molecules/Pixel

Imaged Area	Pixel Size	Pixel Area	Molecules/pixel molecular size $5 \text{ \AA} \times 5 \text{ \AA}$	Atoms/pixel
100 μm	10 $\mu\text{m} \times 10 \mu\text{m}$	10^{-6} cm^2	4×10^8	2.5×10^9
10 μm	1 $\mu\text{m} \times 1 \mu\text{m}$	10^{-8} cm^2	4×10^6	2.5×10^7
5 μm	5000 $\text{ \AA} \times 5000 \text{ \AA}$	$2.5 \times 10^{-9} \text{ cm}^2$	1×10^6	6.25×10^6
1 μm	1000 $\text{ \AA} \times 1000 \text{ \AA}$	$1 \times 10^{-10} \text{ cm}^2$	40,000	2.5×10^5
0.2 μm	200 $\text{ \AA} \times 200 \text{ \AA}$	$4 \times 10^{-12} \text{ cm}^2$	1600	10,000

small areas. It is not good enough, however, to perform analysis of trace levels of impurities that may be present within these spots. In the remainder of this paper, we present our preliminary experiments aimed toward demonstrating the applicability of ion-beam induced desorption using an LMIG to obtain submicron resolved, chemical specific images.

2. EXPERIMENTAL SETUP

A generic description of the apparatus has been described previously, although there are a number of changes and additions needed for these experiments (Pappas et al 1989). The basic instrument is a Kratos TOF-SIMS reflectron-based mass spectrometer equipped with a FEICO LMIG. The analyzer has a nominal mass resolution of 1 part in 10,000 amu with transmission of about 50%. The UHV system is ion-pumped except for the sample inlet system which is pumped by a turbomolecular pump. This pump must be turned off during imaging experiments to avoid vibrations. The laser beam is constricted to a diameter of about 1.5 mm and positioned less than 0.5 mm above the target surface. Indium is used as a model system for this work. The MPRI scheme utilizes 303.9 nm to pump the $2D_{3/2}$ state and 607.9 nm to reach the ionization level. The laser system is identical to that described previously (Pappas et al 1989).

Pulsing of the LMIG to optimize the spatial overlap between the sputtered species and the laser beam presents a number of subtle challenges and opportunities. The pulsing is typically carried out by applying a deflection voltage to a set of blanking plates, preventing the ion beam from exiting through an aperture. When the proper voltage pulse is applied to the blanking plate, the beam exits through the aperture and strikes the target. For the short pulse-length required for SIMS experiments (~ 5 ns), the movement of the beam across the aperture causes considerable broadening of the beam spot on the target. In our case, however, the optimal τ_p is 100 times longer or 500 ns. These broadening artifacts are then insignificant. Moreover, the longer τ_p partially makes up for the relatively low repetition rate of the laser experiment (30 Hz) vs the SIMS experiment (5 kHz). An example of the spatial resolution of our system obtained by collecting all the secondary electrons emitted from the sample is shown in Figure 1. The edge of the 10μ core is defined to within 2 pixels or 400 \AA .

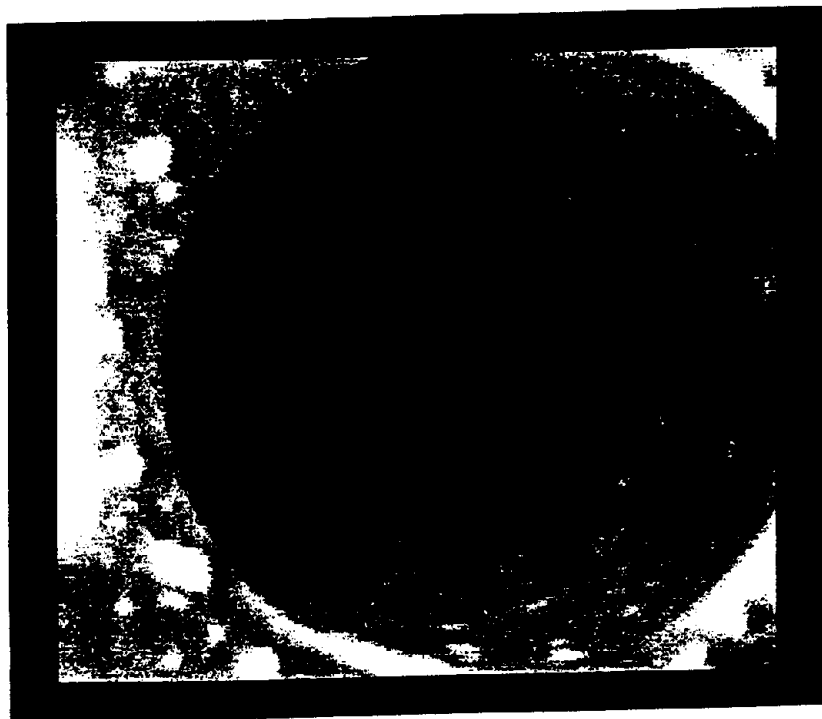


Figure 1. Secondary electron image of a 10μ fiber in a $12 \mu \times 10 \mu$ field. Each pixel measures 20 nm^2 .

3. RESULTS AND DISCUSSION

The partial TOF spectrum obtained by bombarding In foil with 25 keV Ga⁺ ions from the LMIG is shown in Figure 2. The spectrum was obtained using a single-stop time-to-digital-converter (TDC) with 1.25 ns time registration. The incident ion beam current was arbitrarily attenuated so that less than one ¹¹³In⁺ ion reached the detector for each laser shot. The expected isotope ratio of ¹¹³In/¹¹⁵In = 0.04 is not observed since there is more than one ¹¹⁵In⁺ ion per laser shot and the detector is not responding to these multiple hits. The time width of the ¹¹³In peak is 11 ns and the flight time is 60,321 ns. These results show that there is an adequate signal generated from the LMIG and that the TOF-reflector yields a mass resolution $m/\Delta m$ of ~ 2800 . Note that most of this width arises from the 7 ns laser pulse width and that the analyzer is almost completely compensating for the energy spread of the ionized In atoms, estimated to be ~ 300 eV.

The expected useful yield of In atoms detected in this experiment is easily estimated. The design parameters of the analyzer are aimed to yield about 50% collection efficiency. The laser extraction optics can draw at least 50% of the ionized atoms into the analyzer. And finally, we estimate that about 50% of the sputtered flux actually overlaps with the ionizing laser. Assuming 100% ionization efficiency, then, we expect to be able to detect $\sim 12\%$ of the sputtered In atoms. Using a 300 ns, 60 pA LMIG source, we expect to produce 338 In atoms per laser shot. It is not yet feasible to directly measure this many ions with a TDC, although the Kratos system provides a multistop, 10 ns TDC that can register more than one hit for ¹¹³In. Using this detector we find 1.3 ¹¹³In⁺ ions per laser shot or ~ 33 total In⁺ ions for a measured useful yield of $33/338 \equiv 9\%$.

We have tested the possibility of using the LMIG source to obtain spatially resolved maps of the In signal. As seen in Figure 3, 300 mesh Cu grid was placed over an In foil so as to shadow

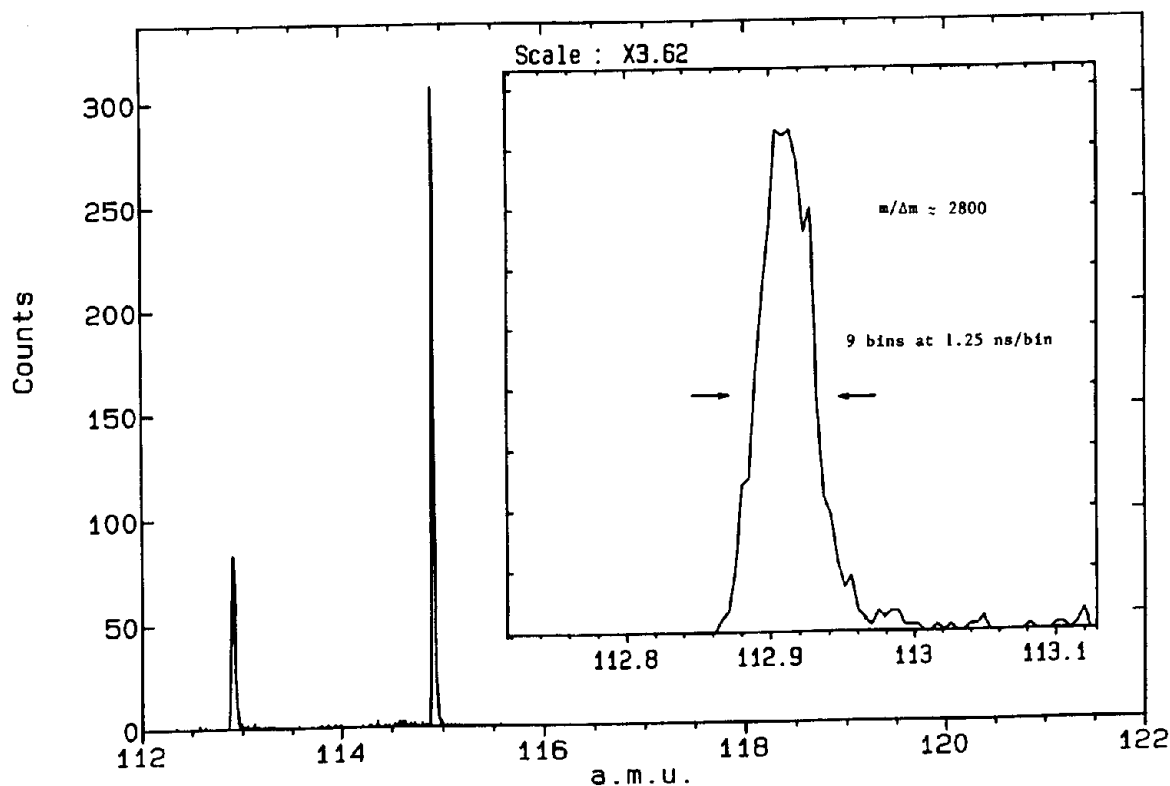


Figure 2. TOF spectrum of In atoms desorbed from In foil and resonantly ionized by a 1.5 mm laser beam.

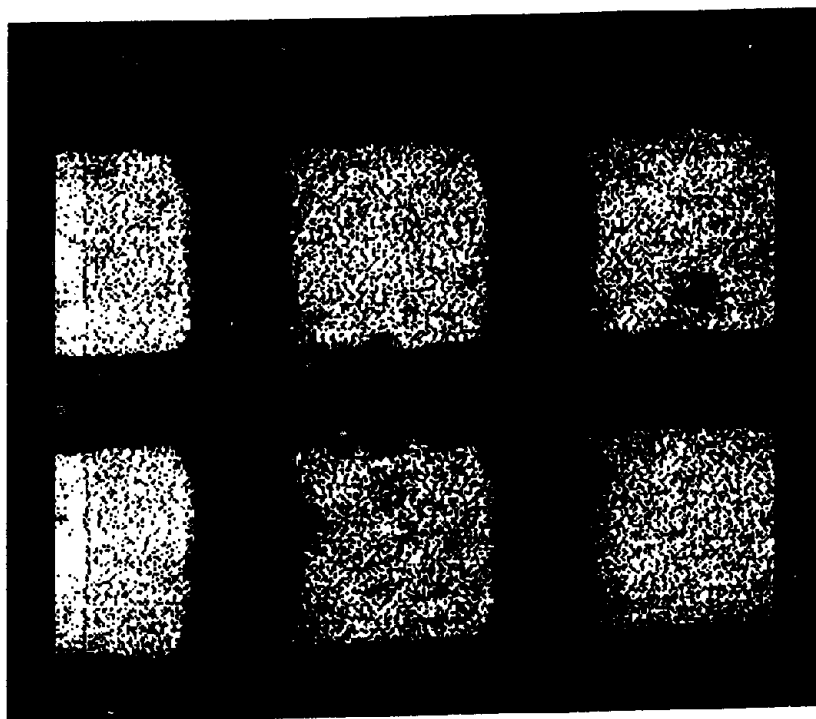


Figure 3. Indium atom image of a copper grid overlaying Indium substrate. Field of view, $150\ \mu \times 130\ \mu$. Each pixel measures $500\ \text{nm}^2$, with the brightest pixels containing 18 counts. $\sim 1 \times 10^5$ pulses, total dose $2 \times 10^7\ \text{Ga}^+$ ions or $10^{11}\ \text{Ga}^+$ ions/cm 2 .

specific regions of the In surface. For this image, each pixel measures $5000\ \text{\AA} \times 5000\ \text{\AA}$ and the total field of view is $150\ \mu \times 130\ \mu$. Each pixel was produced by summing the results of two laser shots. The image, which contains about 50,000 pixels was recorded in about 45 min. We estimate that the data acquisition efficiency can be improved by a factor of 4 when using a transient digitizer rather than a multihit TDC. Moreover, if the LMIG is employed using the larger aperture, the count rates improve by an additional factor of 8 with only a small loss in spatial resolution.

Will it be possible to record comparable images for molecules on surface? It is, of course, well-known that ion beams can effectively desorb a wide array of fragile molecules intact, forming the basis for much of SIMS research. Our group has also reported that a number of polycyclic aromatic hydrocarbons (PAH) can be desorbed and resonantly ionized using UV lasers with detection limits near 10^6 molecules (Hrubowchak 1991) per cm 2 . In many cases, the signals obtained using laser postionization are several orders of magnitude larger than those obtained using SIMS, indicating that the resonance ionization probability can be as high as 1%. A recent example of a laser postionized PAH is shown in Figure 4. Given the magnitude of the signals observed for In, these data suggest that it will certainly be feasible to detect the molecular ion of these types of molecules using the LMIG and that submicron molecular imaging is indeed a feasible objective.

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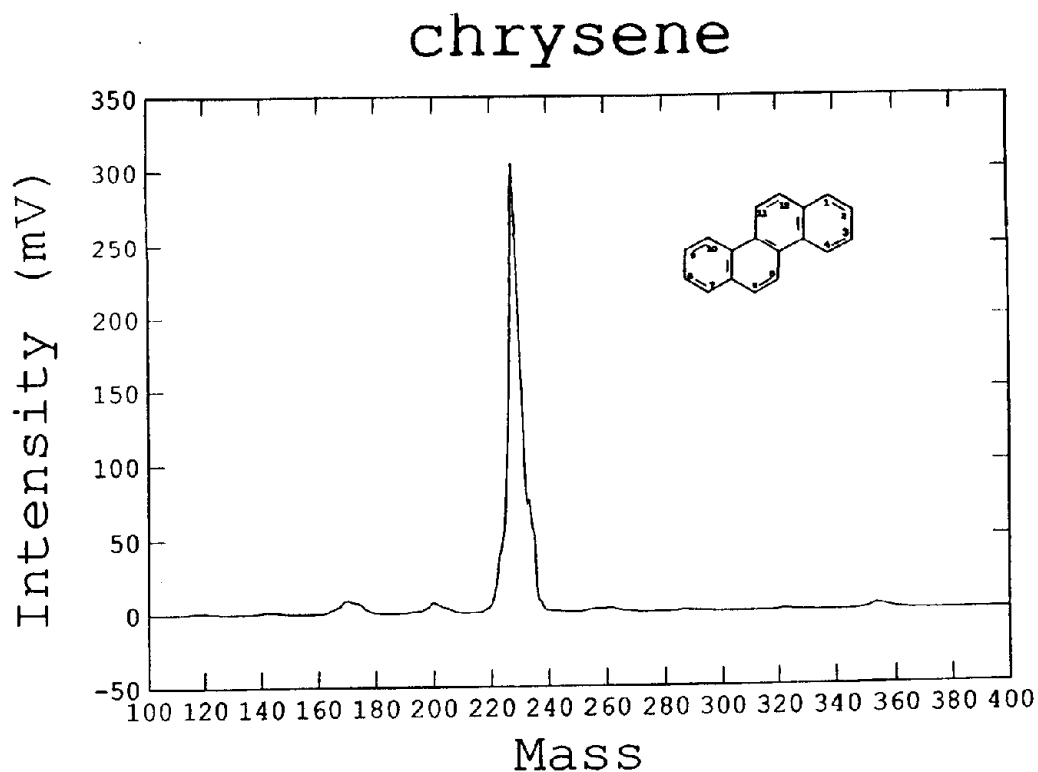


Figure 4. TOF spectrum of a thin film of chrysene ionized by 280 nm laser light after bombardment by 5 keV Ar⁺ ions.

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