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Atom Counting at Surfaces

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Multiphoton resonance ionization has been combined with energetic ion bombardment to examine dopant concentrations of indium on the surface of silicon. The results yield a linear relation between the indium concentration and the known bulk values and a detection limit of 9 parts per trillion, at a mass resolution exceeding 160. This measurement, which surpasses the limits of any previous surface analysis by a factor of 100, has been made possible with an experimental configuration that optimizes sampling and detection efficiency while reducing background noise to virtually zero. During the analysis, submonolayer quantities of the surface are removed, so that as few as 180 surface atoms may be counted.

It is now possible to spectroscopically detect extremely low concentrations of atoms and molecules in bulk phases. For example, researchers have been able to count single atoms of gaseous cesium diffusing through the path of a laser beam by taking advantage of the detection selectivity and efficiency of multiphoton resonance ionization (MPRI) spectroscopy (*1*). Similar experiments have allowed the collection of one molecule of gaseous naphthalene out of four present in the ionization volume (*2*). In solids or liquids, a variety of methodologies such as neutron activation analysis and secondary ion and glow discharge mass spectrometries offer, in special circumstances, exceptional detection limits exceeding one atom in 10^{12} background atoms (*3*).

The detection of a small number of atoms at solid surfaces has not yet been possible, primarily because of difficulties in efficient sampling of monolayers. We have proposed, however, that a few atoms could be desorbed from the top layer of a solid by means of energetic ion bombardment and that these atoms could be selectively and efficiently detected by MPRI spectroscopy (*4*). A number of groups have now demonstrated the feasibility of such an approach for the characterization of ultrapure materials, although theoretically attainable detection limits have yet to be achieved (*4–7*). We report the development of a new apparatus for MPRI studies, featuring a time-of-flight (TOF) reflectron-based detector coupled with a specially designed high-power, pulsed kiloelectron volt, ion bombardment source, which allows mass-resolved detection of just a few hundred surface atoms. The method has been applied to the study of low concentrations of dopants at semiconductor surfaces.

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The experimental system used for these measurements has been described (*5, 8*). Briefly, a pulsed beam of Ar^+ ions (5.6 μs, 10 keV) is directed upon the sample at 45° incidence, thereby desorbing some fraction of the surface material. A few hundred nanoseconds later, the frequency-doubled, unfocused output of a neodymium: yttrium-aluminimum-garnet pumped dye laser is introduced through the cloud of ejecting particles, resonantly ionizing the neutral species of interest. The photoions are extracted into a TOF mass spectrometer equipped with an ion reflector and are subsequently detected by a dual microchannel plate assembly. Mass spectra are recorded with a 100-MHz transient digitizer, while for the actual analyses single-ion counting is carried out with an amplifier-discriminator coupled to a photon counter-processor. The entire apparatus and experimental timing are shown in Fig. 1. The targets were composed of high-purity silicon (Si), uniformly doped with indium (In) at concentrations of 2 parts per million (ppm), 36.5 parts per billion (ppb), or 3.85 ppb (*9*). Each wafer was fastened to the manipulator, which was covered with either a sheet of copper (Cu) or Si to serve as a backplate (*10*).

The desorbed In may be selectively excited in a one-step resonance absorption (304 nm, 0.850 mJ per pulse), followed by ionization with a visible photon (608 nm, 7.03 mJ per pulse). This is a suitable scheme for optimizing the signal-to-noise (S/N) ratio because the power of the highly energetic ultraviolet (UV) photon is kept at a low level while the powerful visible light is reserved for the more difficult ionization step. To minimize the effects of possible contamination or surface segregation, we sputter-etched the samples before each data acquisition cycle until a steady-state, reproducible signal was obtained. The data were then accumulated for 5 min (9000 laser pulses at a repetition rate of 30 Hz), after which the background signal was measured for an equivalent period. In order to detect single pulses, we attenuated the photoion signal for the two most concentrated samples by reducing the primary ion current. Individual determinations were normalized to the measured ion current and laser power.

The TOF mass spectra for the Si target doped with 2 ppm In are shown in Fig. 2. Because the laser bandwidth is broader than the spectroscopic isotope shifts, the ion reflector is required to resolve the two In isotopes. For comparison, the same time interval was monitored with the laser blocked; the absence of any appreciable sec-

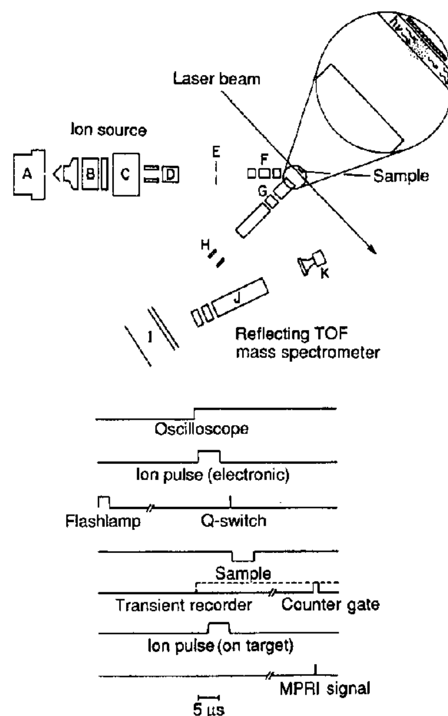

Fig. 1. Schematic diagram of the MPRI apparatus (**top**) and experimental timing sequence used for the In in *Si* experiments (**bottom**): A, duoplasmatron ion source; B, emission lens; C, E × **B** filter (where *E* is an electric field and *B* is a magnetic field); D, pulse steering plates; E, pulsing aperture; F, refocusing lens; G, extraction lens; H, deflection plates; I, ion reflector; J, lens; and K, microchannel plate detector. Expanded area (top right) shows the overlap region of the unfocused laser ($h\nu$) and the desorbed particles. The sample is held at a high potential during the time that the ion pulse is incident on the target to accelerate the secondary ions to high velocities. This is reduced to the normal extraction voltage (relative to the grounded extraction grid) during the time that the laser is active.

Table 1. MPRI experimental data for In in Si.

[In] (ppb)	Average signal*	Average back-ground*	Ar^+ cur-rent (μA)	Laser power (W)	Relative intensity†
2000	1.45×10^3	18.5	0.158	0.186	$(4.84 \pm 0.08) \times 10^4$
36.5	2.78×10^3	29.5	18.0	0.158	880 ± 62.4
3.85	9.41×10^2	9.6	47.3	0.211	93.7 ± 22.6
0.165	3.72×10^1	4.0	46.0	0.211	3.43 ± 0.58

*Signal and background are expressed as counts per 9000 laser pulses, averaged over three analyses. †Relative intensity is derived by normalizing the data for each individual analysis to the ion current and laser power and obtaining a cumulative average. The results in this column have been used to generate the calibration plot. The error limits are reported at the 95% confidence level from three independent observations.

ondary ion signal over this domain is indicative of the entire spectrum and is the result of the energy-discriminating capacity of the ion reflector (*11*).

The experimental parameters and results are presented in Table 1. An analysis of the ^{113}In isotope in the 3.85-ppb target [an effective concentration of 165 parts per trillion (ppt)] has been included. A plot of relative MPRI intensity versus bulk In concentration is shown in Fig. 3. Although a logarithmic scale has been chosen for display purposes, the results of the least-squares analysis on the normalized linear plot denote a slope of 1.00 ± 0.01. In addition, the raw data from the analysis of the ^{113}In in Si indicate a S/N ratio of ~9. If we extrapolate to S/N = 2 and scale the ionization efficiency (from 0.55 to 1) (see below) and ion current (from 46 to 100 μA) to obtainable values for this apparatus, a detection limit of 9 ppt is obtained. Similar limits are found from a direct analysis of Fig. 3.

It is known for this type of ion-induced desorption that more than 90% of the ejecting material originates from the topmost layer of the solid (*12*). Furthermore, for the 165-ppt sample, 46 μA of primary ion current was delivered to the sample in 5.6-μs pulses. For the 5-min accumulation period, this bombardment yielded a total dose of 1.5×10^{13} Ar^+ ions into the 0.071-cm^2 beam spot, corresponding to a removal of 2.0×10^{13} surface atoms (0.29 monolayer) on the assumption that the In desorbs at the same rate (1.4 atoms per incident ion) that has been observed for Si (*13*). Given the detection limit of 9 ppt, this experiment is therefore sensitive to 180 atoms. If removal of an entire monolayer is required, then as few as 640 surface atoms may be detected.

The extrapolation from a concentration of 165 ppt is justified on the basis of two criteria. First, intensity versus laser power measurements have indicated a one-photon dependence in the In MPRI signal until saturation conditions are achieved (*5*). If saturation is assumed to correspond to 100% ionization, then we have been able to estimate the ionization efficiency of our experiment to be 55%. Second, with the present ion source, ~100 μA of current can be obtained, representing approximately a twofold increase over the maximum currents used for these analyses. We have found that the measured background count does not correlate with increasing primary ion current or energy. Interestingly, the background appears to depend randomly on the sample preparation. This may be the result of significant variations in the secondary ion yields from different manipulator backing material used in these experiments.

The results presented here are made possible by several conditions. Nearly 90% of the desorbed In atoms are produced in their ground electronic state (*14*). Moreover, efficient resonance ionization may be achieved with relatively low laser power density. Laser beams with large spatial extent may then be used to efficiently overlap 25 to 75% of the desorbing material. Finally, the TOF analyzer offers an adequate degree of mass resolution at a transmission in excess of 10% and provides an efficient method for distinguishing the signal from the background (*15*). The reflector has been shown to attenuate the transmission of secondary ions by a factor of 320 because the extraction optics preferentially impart to these species a velocity greater than that of the photoions (*8*). We have been able to further improve this factor by accelerating the desorbed ions to even greater velocities by pulsing the target with a large positive voltage (Fig. 1). Finally, it is imperative to utilize low-intensity UV light for the resonance step to reduce the probability of ionization of gas phase or sputtered impurities that might overlap the analyte peaks in the time spectrum. The possible increase in noise associated with the use of excessive UV laser power has been documented (*16*).

Although these experiments demonstrate that the detection of a small number of atoms on a surface is a realizable goal, a number of possible instrumental improvements might reduce our detection limits further. For example, by shortening the duration of the incident ion pulse to a few hundred nanoseconds, it is possible to increase the fraction of desorbed atoms that intersect the photon field by more than a factor of 2. We believe that the background may be reduced by improved shielding of the target from stray ions during the time that the incident ion pulse is turned off.

The levels of detection reported here are lower by at least 100-fold than any previously reported values (*7*). Obviously, the preparation of standard samples with such low concentrations of analyte poses major difficulties in developing new applications that exploit the power of this methodology. It will also be necessary to fully characterize the types of species that are ejected. In some cases, formation of secondary ions, molecules, and excited states may bleed intensity from the ground-state channel (*5*). The analysis of the rather well-defined, high-purity Si targets in this work, however, represents

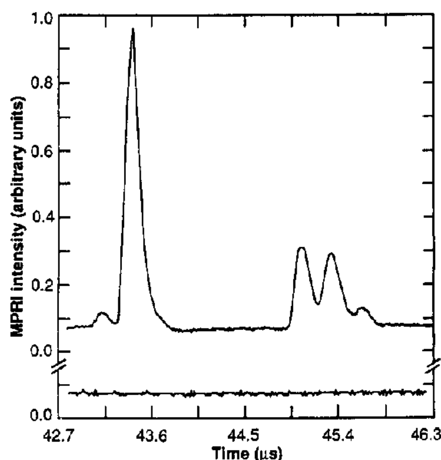

Fig. 2. Portion of the TOF mass specrum obtained from the sample consisting of 2 ppm In in Si. The In isotopes are observed at ~43 μs. The other peaks in the spectrum are associated with Cu_2 clusters originating from the sample holder. For comparison, the same time interval as observed with the laser blocked is shown at the bottom.

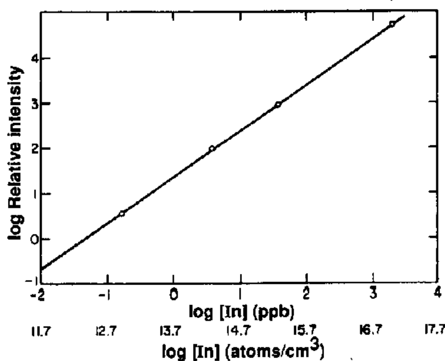

Fig. 3. The MPRI intensity of In versus the bulk In concentration. The In reference concentrations (in atoms per cubic centimeter) are 1×10^{17}, 1.83×10^{15}, 1.92×10^{14}, and 8.25×10^{12}. See Table 1 for additional information.

an important beginning for this research. A number of other novel applications also seem possible (*17*). For example, it appears feasible to collect a small number of atoms generated in rare nuclear decay events onto a surface. Present efforts are aimed toward determining the ββ-decay half-life of ^{136}Xe, a process predicted to yield annually one atom of $^{136}Ba^{2+}$ for every 8×10^{20} atoms of ^{136}Xe (*18*).

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9. The Si targets were supplied by M. Young of Hughes Research Laboratories and J. E. Parks of Atom Sciences, Inc. The wafers were prepared by liquid-encapsulated Czochralski (LEC) single-crystal growth, and the In concentrations were determined by bulk resistivity measurements. All other dopants (excluding oxygen) were present at less than 10^{13} atoms per cubic centimeter.
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