

## Atom (Fast Atom Bombardment) compared to Ion-induced Static Secondary Ion Mass Spectrometry: Evidence for Charge-induced Damage in Insulators

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A comparison of the secondary ion mass spectra obtained and the surface damage caused by ion and atom bombardment of polystyrene and niobium pentoxide shows that *ion* bombardment causes significantly more disruption of the surface structure of low conductivity materials than does atom bombardment.

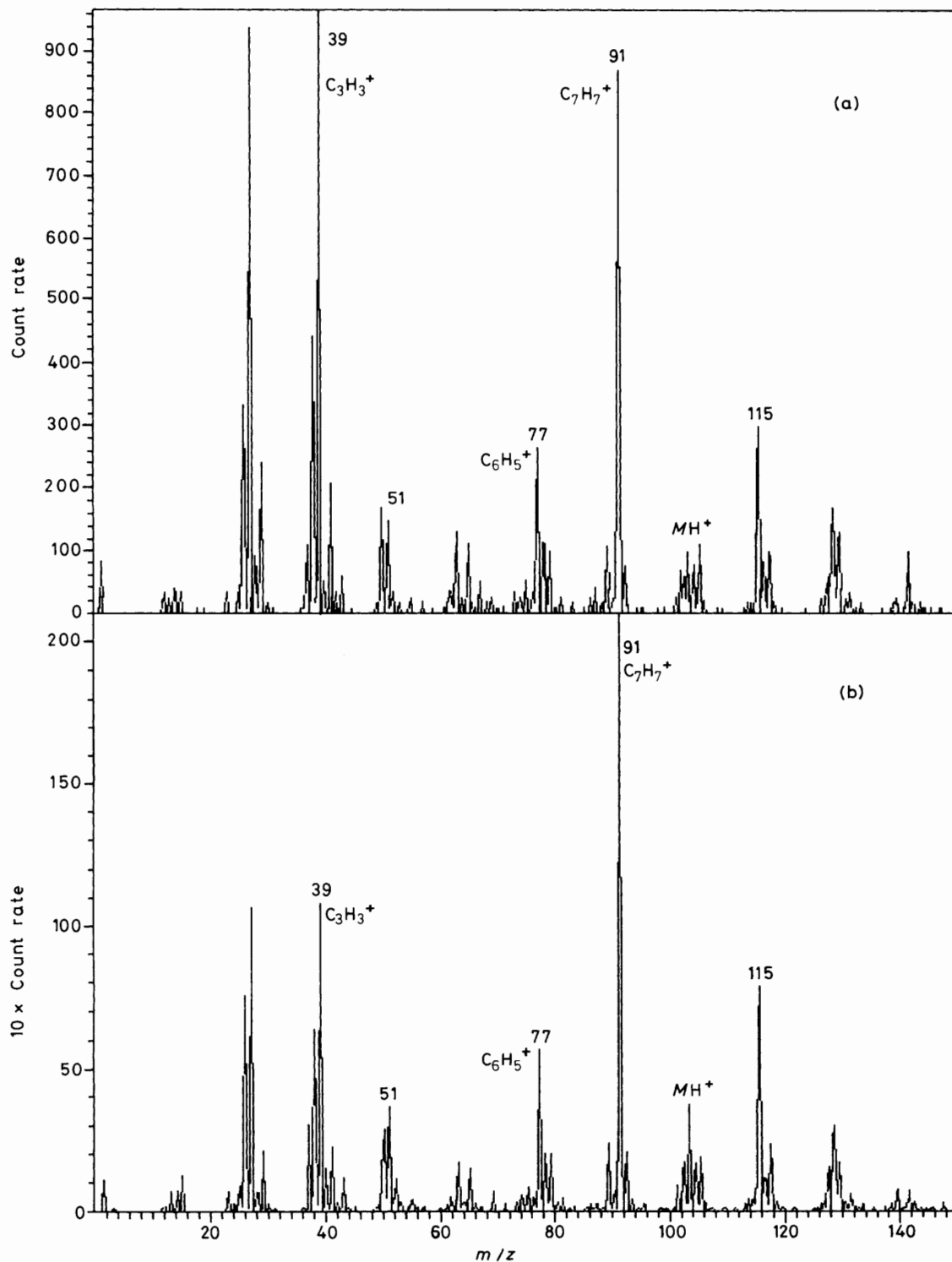
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The spectral loss or instability which results from the surface charging of electrically insulating materials under ion bombardment has been overcome in this laboratory by using a fast atom bombardment (FAB) source.<sup>1-3</sup> Although there is evidence to suggest that static secondary ion mass spectra (SSIMS) obtained from ion and atom bombardment are qualitatively similar, there is a need for systematic studies to demonstrate this.<sup>4,5</sup> Many organic and inorganic materials suffer rather rapid surface degradation under ion bombardment. Polymers have been found to 'damage' at 100-1000 times the rate of inorganic materials,<sup>4</sup> whilst it is well known that oxides are reduced. The relative effects of ion and atom bombardment in producing surface damage also require to be studied.

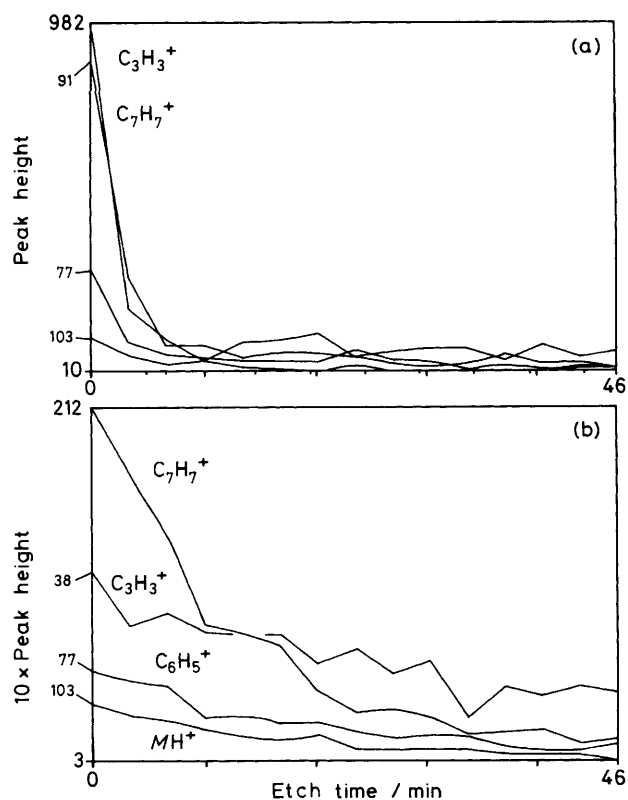
A specially designed ion atom beam source<sup>6</sup> has been used to compare the spectra and surface damage produced by ion and atom bombardment of a polymer, polystyrene, and an oxide semiconductor, niobium pentoxide. In carrying out these studies considerable care was taken to ensure that the ion and atom beam densities and beam profiles were exactly the same. The calibration procedure made the reasonable assumption that the secondary electron yield from metal targets is independent of the charge state of the impinging particle. In the case of ion bombardment, by biasing the target appropriately, it was possible to separate the contribution to measured target current due to incoming primary ions and that due to outgoing secondary electrons. Since atom bombardment gave rise to a target current dominated by

secondary electron emission, it proved possible to set up ion and atom beam fluxes yielding identical secondary electron currents and having identical beam profiles. The equivalence of the two beam fluxes was then checked by monitoring the  $Ta^+$  yields from sputter-cleaned tantalum metal. These yields can also be safely assumed to be independent of the charge state of the primary particle. They were found to be the same to within  $\pm 5\%$ .

After calibration, using the SIMS spectrometer described elsewhere,<sup>1</sup> spectra of polystyrene and niobium pentoxide were obtained as a function of time at intervals of 200 s over a period of 1 h, using atom bombardment, or ion beam bombardment with electron neutralisation. In the latter case care was taken to optimise the electron beam for maximum secondary ion yield. Separate experiments showed no evidence of electron-induced damage.



**Figure 1.** The initial SIMS spectra obtained by (a) ion and (b) atom bombardment of polystyrene: 2 keV,  $3 \times 10^9$  particles  $cm^{-2} s^{-1}$ ,  $Ar^+$  and  $Ar^0$ , respectively.



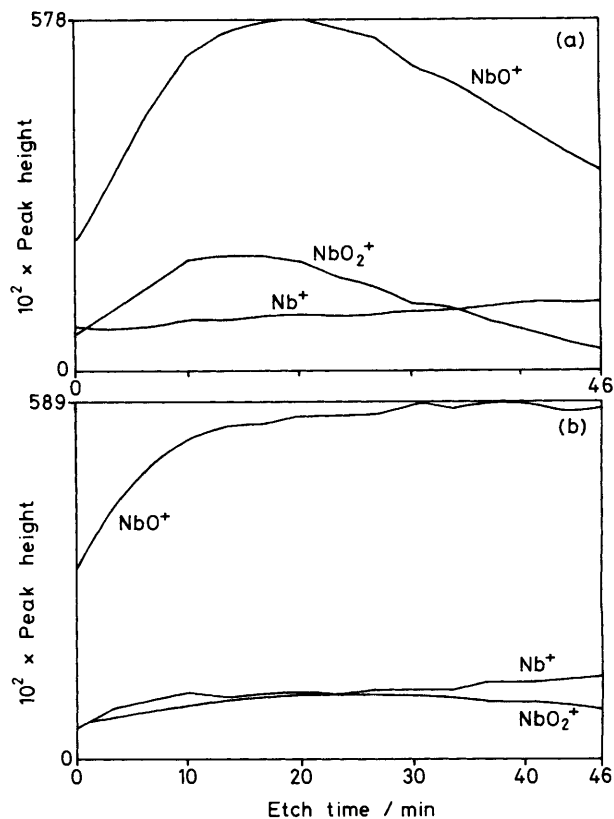
**Figure 2.** The variation of secondary ion intensities with particle bombardment time for (a) ion and (b) atom bombardment of polystyrene, conditions as in Figure 1.

Figures 1(a) and 1(b) compare the initial ion and FAB induced spectra for polystyrene under a 2 keV beam with a density of  $3 \times 10^9$  particles  $\text{cm}^{-2} \text{s}^{-1}$ . Qualitatively they are very similar though it is significant that in comparing the FAB spectrum with the ion-induced spectrum (i) the absolute intensities of the high mass fragments are more intense by a factor of 2–3 and (ii) the relative intensities of the high-mass fragments ( $m/z > 77$ ) over the low mass fragments are greater, by a factor of 2–3.

Figure 2 compares the decay curves for FAB and ion bombardment of polystyrene. There is a markedly more rapid decay of the high mass fragments under *ion* bombardment. The half life is 4 times longer under FAB.

The two sets of data taken together suggest that the molecular framework is not only susceptible to damage due to energy transfer as a consequence of the collisional impact of a particle, but also, if that particle is charged, charge dissipation within the molecular target solid will contribute significantly to the extent of damage. This is not really very surprising since charge-induced fragmentation is well known in organic mass spectrometry. Nevertheless it is the first direct evidence of charge-induced damage in SSIMS.

The initial spectra obtained from niobium pentoxide under a density of  $3 \times 10^{10}$  particles  $\text{cm}^{-2} \text{s}^{-1}$  were quantitatively almost identical. Figure 3 shows the time-dependent secondary ion curves from FAB and ion bombardment. Again a clear contrast emerges. Initially in both cases the ion intensities increase, probably owing to surface cleaning and removal of absorbed water. However under FAB a plateau region is reached followed by a *very* slow decline in  $\text{NbO}_2^+$ . Ion bombardment causes a very sharp fall in the oxygen-containing secondary ions. Again it appears that the require-



**Figure 3.** The variation of secondary ion intensities with particle bombardment time for (a) ion and (b) atom bombardment of niobium pentoxide: 2 keV,  $3 \times 10^{10}$  particles  $\text{cm}^{-2} \text{s}^{-1}$ ,  $\text{Ar}^+$  and  $\text{Ar}^0$ , respectively.

ment to dissipate the primary charge input, charge which is not easily lost owing to the low conductivity of the sample, results in a chemical or structural disruption, in this case surface reduction. It appears that oxide reduction under ion bombardment may be due more to the charge on the primary particle than to preferential sputtering due to the differences in mass between the anion and cation.

This investigation has shown for the first time that for poorly conducting materials atom bombardment causes significantly *less* surface damage and therefore probably yields a SSIMS spectrum more representative of the surface; and secondly, it highlights the contribution of charge to the phenomenon of sputter damage in insulators.

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