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Anionic Clusters in Dusty Hydrocarbon and Silane Plasmas

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Measurements of anions and cations are reported for hydrocarbon and silane rf capacitive glow discharges. Series of anions were observed by quadrupole mass spectrometry using power-modulated plasmas and their structures are interpreted from the form of the mass spectra. Various experiments in silane plasmas show that anion confinement results in particles and conversely, anion de-trapping can inhibit particle formation. In contrast, the polymerised neutral flux magnitudes, mass spectra and dynamics are independent of the powder formation. Powder is known to form readily in deposition plasmas containing electronegative free radicals, and the general rôle of anions in particle formation is discussed in the light of these experiments.

I. INTRODUCTION

Dust appears most readily in plasmas of gas mixtures containing electronegative radicals¹ and negative ions are also retained by the plasma sheaths, which suggests that slow plasma polymerisation might proceed via an anionic pathway.¹⁻⁶ The objective of this work was to investigate negative ion clusters in various rf discharges, using quadrupole mass spectrometry of neutrals, cations and anions in power-modulated rf plasmas⁶ to assess their rôle in particle formation.

Anion sequences are identified in silane (SiH₄), methane (CH₄), and acetylene (C₂H₂) plasmas. The anion composition and spectral pattern is different in each case and is related to the bond structure of the initial molecule. The distribution of hydrogen content in silane anion clusters is considered using random bond theory.

Partial-depth modulation of the rf power is used to determine the relative importance of negative ions and neutral radicals for particle formation in the low power, low pressure silane plasmas. Measurements performed on single plasma pulses also show the importance of anion de-trapping if powder formation is to be avoided. The results are discussed in terms of particle elimination schemes for rf plasma processing.

II. EXPERIMENTAL METHOD

The experimental apparatus⁶ is a parallel-plate rf capacitive reactor with 13-cm-diam electrodes and a 2.5 cm electrode gap. The gas inlet, in the side wall of the grounded vacuum chamber, was a 30 sccm flow of pure silane at 0.1 mbar reactor pressure. The rf power (~ 0.03 W cm⁻³) was ON/OFF modulated at kHz frequencies with an excitation frequency of 10 to 30 MHz capacitively-coupled to the rf electrode via a π matching network. The specific plasma parameters are given in each figure caption.

8.3 GHz single-pass microwave interferometry (overall response time $< 3 \mu\text{s}$) and a 1 GHz digital storage oscilloscope provided time-resolved measurements of the free electron absolute density, spatially-averaged over the electrode gap,⁷ with $10^8 \text{ electrons.cm}^{-3}$ sensitivity.

Two different quadrupole mass spectrometers were separately employed,⁸ both equipped for neutral analysis, ion extraction, mass and energy measurements: The Hiden Analytical Limited Plasma Monitor type HAL-EQP 500 measured negative ions up to the limit of 512 amu when mounted either in the ground electrode or to the side of the electrode gap; the Balzers Plasma Process Monitor type PPM 421, with mass range option up to 2048 amu, was positioned to the side of the electrode gap.⁸

For time-resolved mass spectrometric measurements, the channeltron pulses were counted cumulatively over 1000 plasma pulses by a multi-channel scalar triggered synchronously with the power modulation. The $5 \mu\text{s}$ time resolution was fixed by the scalar dwell time, and the data are corrected for the ion transit time in the spectrometer.⁶ The question of non-perturbative anionic cluster sampling is addressed in Ref. 8.

III. RESULTS

A. Ion mass spectra and anion structure in silane plasmas

Mass spectrometry can measure negative ions provided that the modulation frequency is below 10 kHz so that the sheath has time to collapse.^{6,9} Figure 1(a) shows the negative ion mass spectrum⁸ obtained in a low power, low pressure silane plasma. The mass resolution was strongly degraded to maximise transmission (see Fig. 3) and each peak represents the combined intensities of all ions having the same number of silicon atoms, irrespective of their hydrogen content. A complete sequence extends from monosilicon hydride anions through to mass 1300 amu; the latter correspond to nanometric anionic clusters containing 44 silicon atoms. This

is much heavier than the observed positive or neutral counterparts (highest mass ~ 200 amu) for these plasma parameters.^{6,10,11}

Resolution of the individual Si_nH_m^- within the broad peaks^{8,12} of Fig. 1(a) finds that anions with $n \leq 4$ present a clear maximum signal for one specific hydrogen content, namely $\text{Si}_n\text{H}_{2n+1}^-$ which is isoelectronic with the equivalent saturated neutral $\text{Si}_n\text{H}_{2n+2}$.¹² Figure 2 plots the ratio of H-atoms to Si-atoms within each anionic cluster of Fig. 1(a). Clusters with $n > 10$ have a size-independent ratio $[\text{H}]:[\text{Si}] \sim 4/3$; they are strongly hydrogen-depleted compared with the original SiH_4 molecule and consequently are highly cross-linked, three-dimensional structures. This constant $[\text{H}]:[\text{Si}]$ ratio for large cluster size shows that they are not pure Si_n cores covered with surface H-atoms; neither are they 'cluster ions' in the strict sense of the term (of type $\text{SiH}_m^-(\text{SiH}_4)_n$, for which $[\text{H}]:[\text{Si}] \rightarrow 4$).

The mass spectrum curve in Figure 3 obtained with low (degraded) mass resolution of the spectrometer closely reproduces the envelope of the true intensity distribution of high-resolution spectra. The broad peak in mass distribution in Fig. 1(a) within a given n -Si cluster is therefore due to the range of numbers of H-atoms which can be incorporated in the cluster, and is not simply due to low instrumental resolution. The regular nature of the mass distribution suggests that a simple statistical approach might suffice to explain the measurements: Following random bond theory¹³ we assign a probability h that an available Si valence site is occupied by an H-atom; the corresponding probability for a Si-Si bond at this site is $s = 1 - h$ since multiple Si-Si bonds do not exist, and it is assumed that all bonds are saturated (the dangling bond density is neglected). If we allow each Si-atom to attach 0, 1, 2 or 3 H-atoms (4 is excluded), the most probable number of H-atoms in the n -Si cluster is then $3nh$. Equating with the experimentally-measured maximum abundance $[\text{H}]:[\text{Si}]$ ratio from Fig. 2 gives $h = 4/9$. The terms in the binomial expansion of $(s + h)^{3n}$ represent the sum of the

probabilities of obtaining clusters with different numbers of H-atoms from zero to $3n$. The probability of the n -Si cluster containing p H-atoms is $C(3n,p) h^p s^{(3n-p)}$ (where $C(3n,p) = 3n!/p!(3n-p)!$ is the number of combinations of p H-atoms within the n -Si-atom cluster). These isomers with p H-atoms are indistinguishable in the mass spectrum and this probability is an estimate of the abundance at mass $(28n + p)$. These binomial distributions are plotted in Fig. 1(b) where the exponential decay in amplitude is arbitrarily chosen to resemble Fig. 1(a). The similarity between Figs. 1(a) and (b) suggests a statistical nature for the hydrogen distribution within the anionic clusters.

B. Ion mass spectra in hydrocarbon plasmas: Comparison with silane

Carbon also yields electronegative free radicals whether produced from a hydrocarbon gas or sputtered from substrates containing carbon.¹ Dusty plasmas are also observed in these conditions¹ and so a comparison with silane plasmas is interesting. Figure 4 shows preliminary results of positive and negative ion spectra measured in methane (CH_4) and acetylene (C_2H_2) using the same technique as for the silane experiments. These two gases represent the extreme values for the C:H ratio within the initial molecule. C_2H_2 plasmas yield more highly-polymerised ions than CH_4 and also have a much stronger tendency to form powder in these low power rf plasmas. They also present clear sequences of ions with even numbers of carbon atoms because the acetylene $\text{H-C}\equiv\text{C-H}$ initial molecule contains a pair of strongly-bound carbon atoms. CH_4 plasma ions do not contain pairs of multiply-bonded carbon at the outset and so contain all numbers of carbon atoms. Higher resolution spectra show that CH_4 plasmas produce hydrogen-rich ions as well as pure hydrogen anions and cations, as expected from the higher proportion of hydrogen in CH_4 . On the other hand, the

majority of anions in C_2H_2 plasmas are nearly-pure carbon anions $C_{2n}H_m^-$ ($m = 0,1,2$); there is no ambiguity in the mass spectrum due to doubly-attached carbon clusters since their lifetimes are too short to be detected in these experiments.¹⁴ This is to be expected because Coulomb repulsion means that attachment of the second electron is likely to be endothermic. Furthermore, doubly-charged clusters with an odd number of carbon atoms would have half-integral charge-to-mass ratios.

In contrast to silane plasmas,⁶ the hydrocarbon positive ions polymerise to the same extent as the negative ions and so their relative importance in powder formation is not clear from the mass spectra - more specific experiments are necessary. However, if carbon cluster formation is rate-limited by the early steps¹ to form C_2 and C_3 etc, then Fig. 4 shows that the equivalent anions do exist in the plasma, and are at least sufficiently stable to cross the mass spectrometer to the detector (lifetime $> 10^2 \mu s$). Furthermore, they appear to be formed by homogeneous reactions in acetylene and methane plasmas, and not by sputtering from the electrodes, because the results were independent of discharge duration and the electrode surface material used.

Generally speaking, whereas hydrocarbon chemistry is well known, the comparative fragility of Si-Si and Si-H bonds changes this picture considerably - silicon structures are less stable than carbon cycles and show greater flexibility.¹⁵ This may be at the origin of the difference in anion mass spectra between silane and hydrocarbon plasmas. Another known property of polysilane chemistry is the ability to form radical cations and anions which leads to the properties of semiconducting elementary silicon.¹⁵

C. Negative ions and powder in low pressure silane plasmas

Three types of experiment are reported here, measuring negative ions and powder in silane plasmas as a function of power modulation frequency, partial-depth modulation, and afterglow duration:

i) Particle formation in rf silane plasmas is strongly reduced by square-wave power modulation at kHz frequencies.^{10,12,16} Previous work^{6,12,17} demonstrated that powder does not form when anions escape, and conversely, that powder does form when the anions do not have time to be evacuated in the afterglow (modulation frequency > 3 kHz). A physical explanation for the suppression of highly-polymerised anions near 1 kHz modulation frequency is that the plasma period is then too short for anions to reach high masses before the reservoir of low mass anions is evacuated in each subsequent afterglow period.^{6,17}

ii) Supplementary evidence was obtained by a partial-depth modulation experiment^{2,7,8}: With ON/OFF power modulation (corresponding to 100% modulation depth) at 1 kHz, a negative ion flux is measured during the afterglow and no powder is formed, as described above. If the rf voltage during the afterglow is then increased until the sheath no longer fully collapses (at ~85% modulation depth), the anion flux abruptly disappears and powder eventually forms. The principle of the experiment is that the magnitudes and dynamics of neutral species production and loss rates are essentially unchanged by this transition since neutrals are not affected by the sheaths, whereas the anion flux is switched on or off. Corresponding time-resolved measurements of the positive and negative ions, neutrals, electron density, and electrode voltage are reported in Ref. 7. The measured mass spectrum and flux of polysilicon neutrals were unaltered by the presence or absence of powder formation, and the flux of polysilicon neutrals undergoes no significant variation during a modulation cycle. Therefore, any neutral polymerisation pathway to particle formation¹⁶ would not be affected by kHz power modulation even if the

monosilicon radical reaction times were sub-millisecond, because the intermediate polysilicon neutral species, which are the next steps in a neutral polymerisation scheme, do not react or diffuse on a sufficiently-short timescale in these low power, low pressure silane plasmas. This paradoxical situation for neutrals can be resolved by taking negative species to be the polymerisation pathway - their dwell time in continuous plasmas is indefinitely long due to sheath trapping, and their lifetime is short in modulated plasmas due to expulsion by reversed sheath fields.

iii) A third experiment employed 50- μ s-duration plasma pulses separated in time, and evaluated the powder formation and anion flux dependence on this time interval: Individual isolated plasma pulses were much too short to produce powder particles and the anions produced were principally mono-silicon hydride anions; the anions appeared and then diffused away in $\sim 200 \mu$ s after each plasma pulse as shown in Figure 5. This situation was independent of the time between pulses until the interval was reduced to 150 μ s whereupon the anions did not completely diffuse away and so were re-trapped in successive plasma periods (the waveform of the measured electron density also changed at this point) - the relative contribution from heavier anions then increased and fine powder formed in the plasma.

D. Precursors to powder formation

An interpretation of the above experiments is that negative ions are the precursors to particle growth in low pressure silane plasmas in which particles form only after many seconds. Alternatively, continual attachment/detachment cycling could be responsible for extending the cluster average lifetime.⁵ In higher power ($\sim 0.8 \text{ W cm}^{-3}$) higher pressure ($\sim 1 \text{ mbar}$) silane plasmas where particles form in a fraction of a second,¹⁶ a rapid neutral pathway via SiH_2 insertion into higher silanes is

proposed.^{16,18} If neutral clusters reach critical size⁵ or become large enough¹ to be negatively charged by the rf plasma, there is no need to invoke a slower, parallel anionic pathway. This is represented in Figure 6 where we are here essentially concerned with the plasma chemistry of the powder precursors (once a critical particle density and size is reached, agglomeration and growth would continue independently of the precursor stage). The strong fall-off with mass in the neutral mass spectrum^{6,10} could then be the low-mass portion of a bimodal mass distribution typical of strong clustering in which cluster-cluster aggregation dominates (rapid flocculation). In contrast, the exponential decay of the anion mass spectrum in Fig. 1(a) is typical of weak clustering conditions where clusters are predominantly formed by monomer addition and cluster-cluster aggregation is rare (slow flocculation); the latter condition is guaranteed since inelastic anion-anion collisions are prohibited by Coulomb repulsion.

In recent experiments,⁷ the free electron density was measured by microwave interferometry and the positive ion density was approximated by integration over the ion flux energy distribution: from the difference we infer an approximate total anion density of $\sim 7 \cdot 10^9 \text{ cm}^{-3}$ which is twice the electron density in these kHz-modulated, pure silane plasmas. This is not unreasonably high since plasmas in electronegative gases can contain at least an order of magnitude more anions than electrons.¹⁹ Shiratani *et al*²⁰ estimate $\sim 10^9 \text{ cm}^{-3}$ even for silane diluted to below 1% in helium, and a fluid code²¹ yields $n^- / n_e \sim 10^1$ for the same plasma parameters as the present work.

E. Application to particle elimination in plasma reactors

Power modulation can reduce particle contamination,^{16,17} and one interpretation of this effect is that negative precursors are periodically evacuated from the plasma volume when the sheath electric fields collapse

(and possibly reverse) during the 'power off' afterglow periods. These molecular precursors are then still small enough to be incorporated into the growing film. For this technique to be effective it would therefore be necessary to adapt the modulation frequency and duty cycle (ie the 'on' and 'off' durations) according to the plasma parameters and reactor dimensions so that the anion production rates and diffusion losses are optimally balanced.

IV. CONCLUSIONS

Series of positive and negative ions in methane, acetylene and silane rf plasmas have been studied using mass spectrometry to assess their rôles in particle formation. Nearly-pure carbon anions are observed in acetylene, whereas anions in silane incorporate a broad, statistical distribution of hydrogen atoms. Various experiments in silane plasmas show that control of the anion flux can influence the formation of powder, suggesting that anions are the initial precursors of particles for these plasma conditions.

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FIGURE CAPTIONS

Figure 1: (a) Raw data in counts/s of anions measured with the Balzers spectrometer operated at low mass resolution. Plasma parameters: 0.1 mbar silane, electrode temperature 470 K with 30 MHz, 8 W average rf power modulated ON/OFF at 1 kHz with 30% duty cycle; (b) calculated anion abundances assuming a statistical distribution of hydrogen within the clusters (the exponential decay in amplitude is arbitrarily chosen to resemble (a) for comparison).

Figure 2: Ratio of the number of H-atoms to Si-atoms in the anions deduced from the mass spectrum in Figure 1(a).

Figure 3: Superposition of the Si_nH_m^- anion signals, over the same dynamic range, measured using high and low mass resolution modes of the Balzers spectrometer. The low resolution curve reproduces the intensity envelope of the individual anion peaks obtained using high resolution, with a gain factor of 25 in count rate.

Figure 4: Comparison of positive and negative ion mass spectra (raw data in counts/s) measured in methane and acetylene plasmas for low mass resolution of the Hiden spectrometer. Plasma parameters: 0.1 mbar, electrode temperature 350 K. Rf excitation at 10 MHz with 550 V amplitude at the electrode, ON/OFF modulation at 1 kHz with 30% duty cycle.

Figure 5: Time-resolved measurements of electron density (dashed curve) and low-mass anions using 50 μs plasma pulses for two different afterglow intervals: Powder formed only for intervals $\leq 150 \mu\text{s}$. Plasma parameters: 0.1 mbar silane, electrode temperature 300 K. Rf excitation at 10 MHz with 522 V amplitude at the electrode.

Figure 6: Relationship between different precursor origins in a tentative scheme for particle growth in silane plasmas.

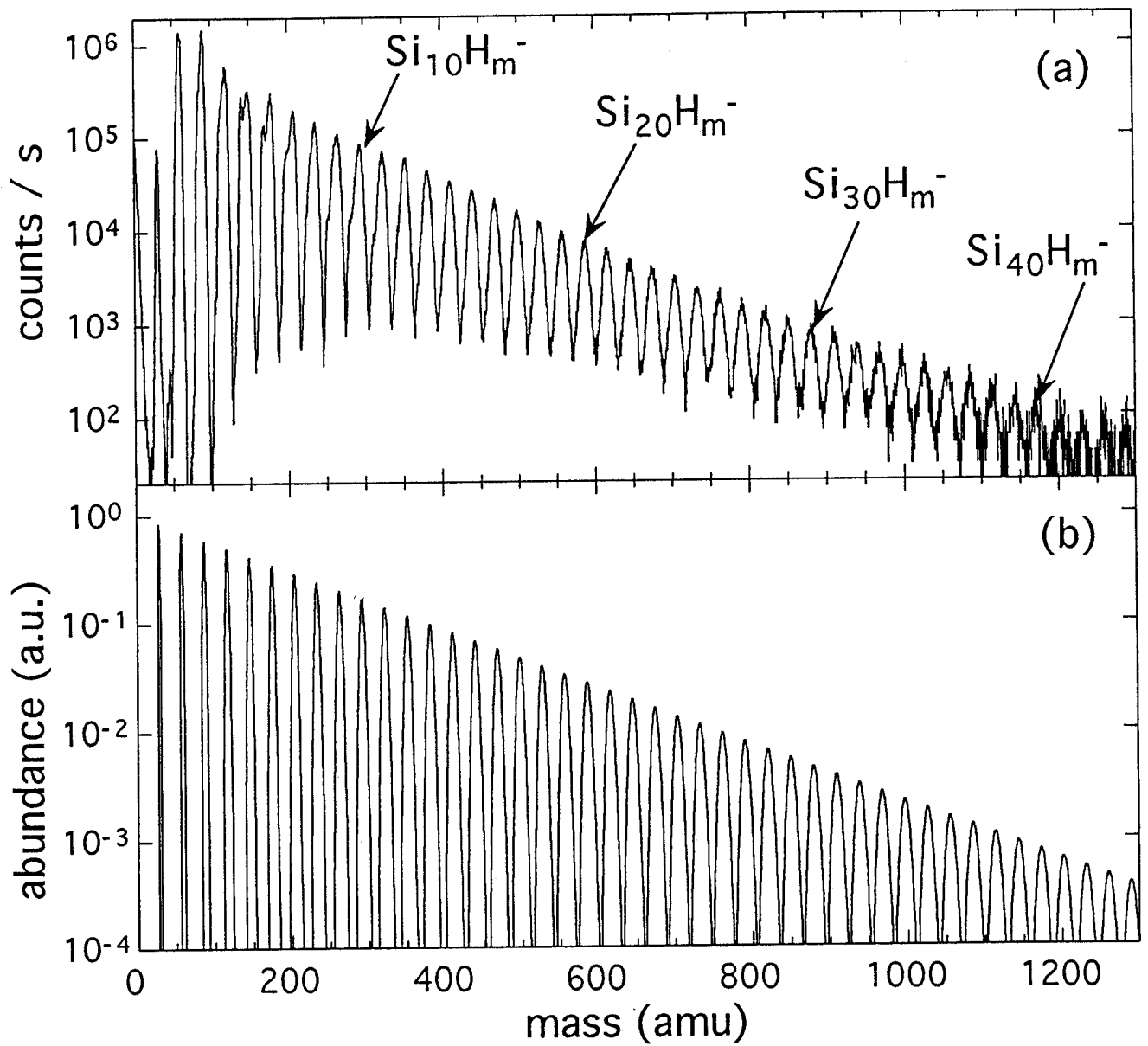


Fig. 1

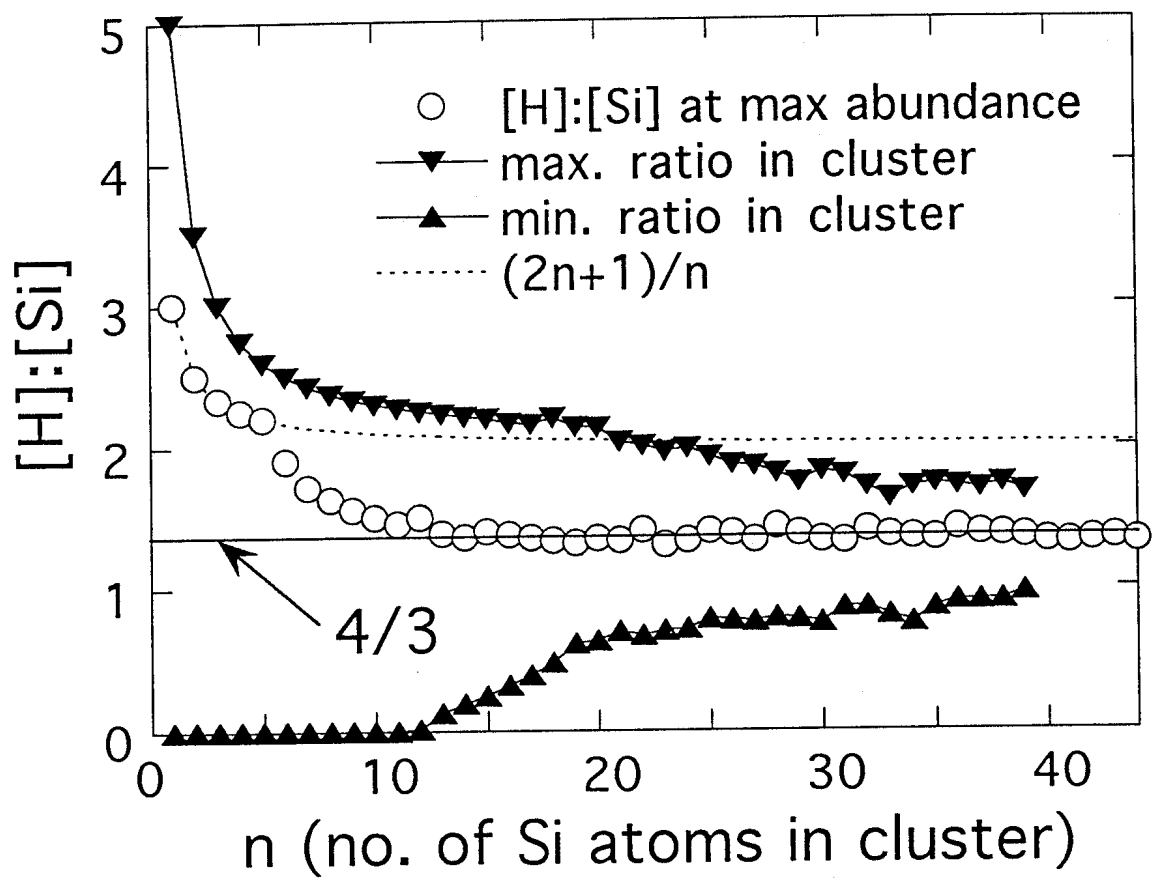


Fig. 2

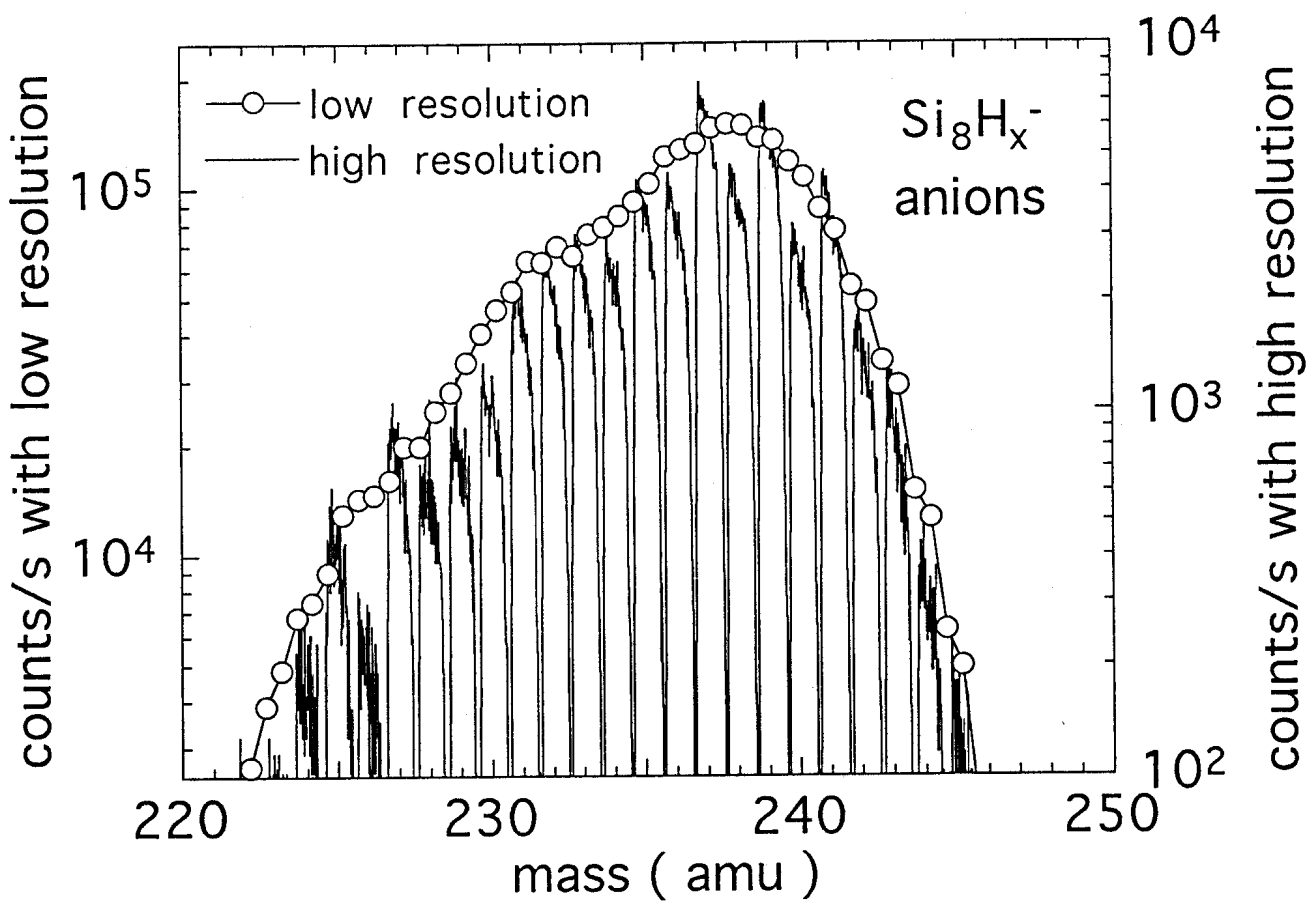


Fig. 3

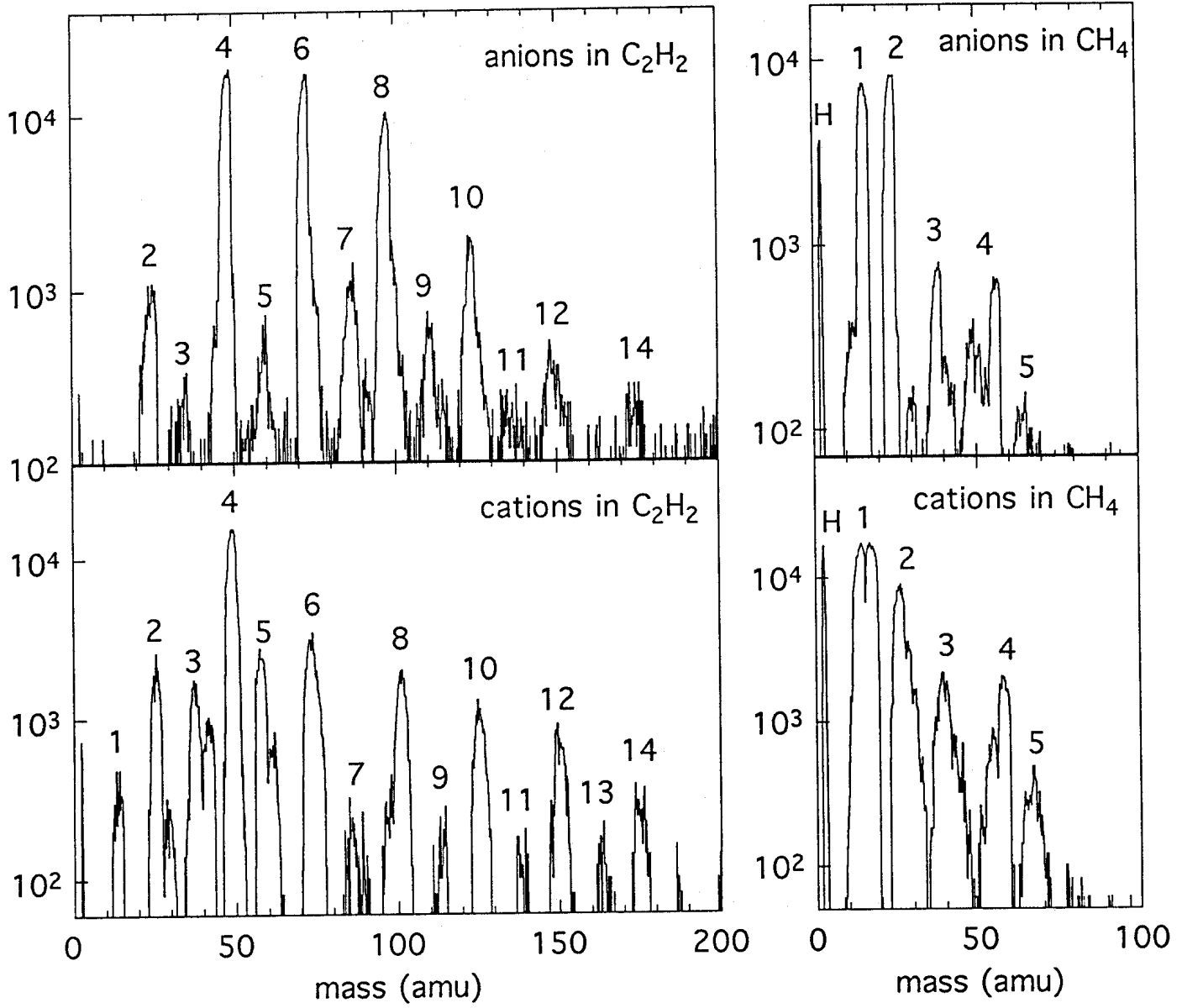


Fig. 4

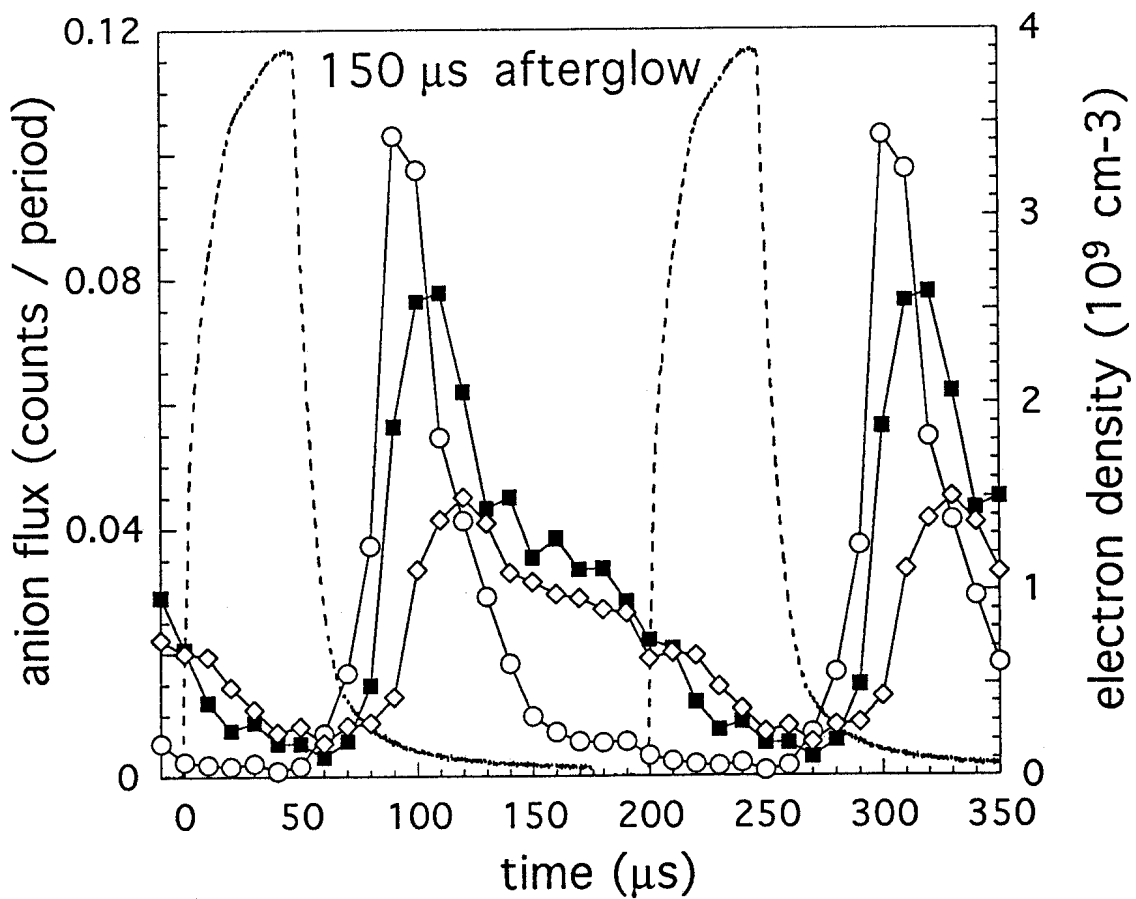
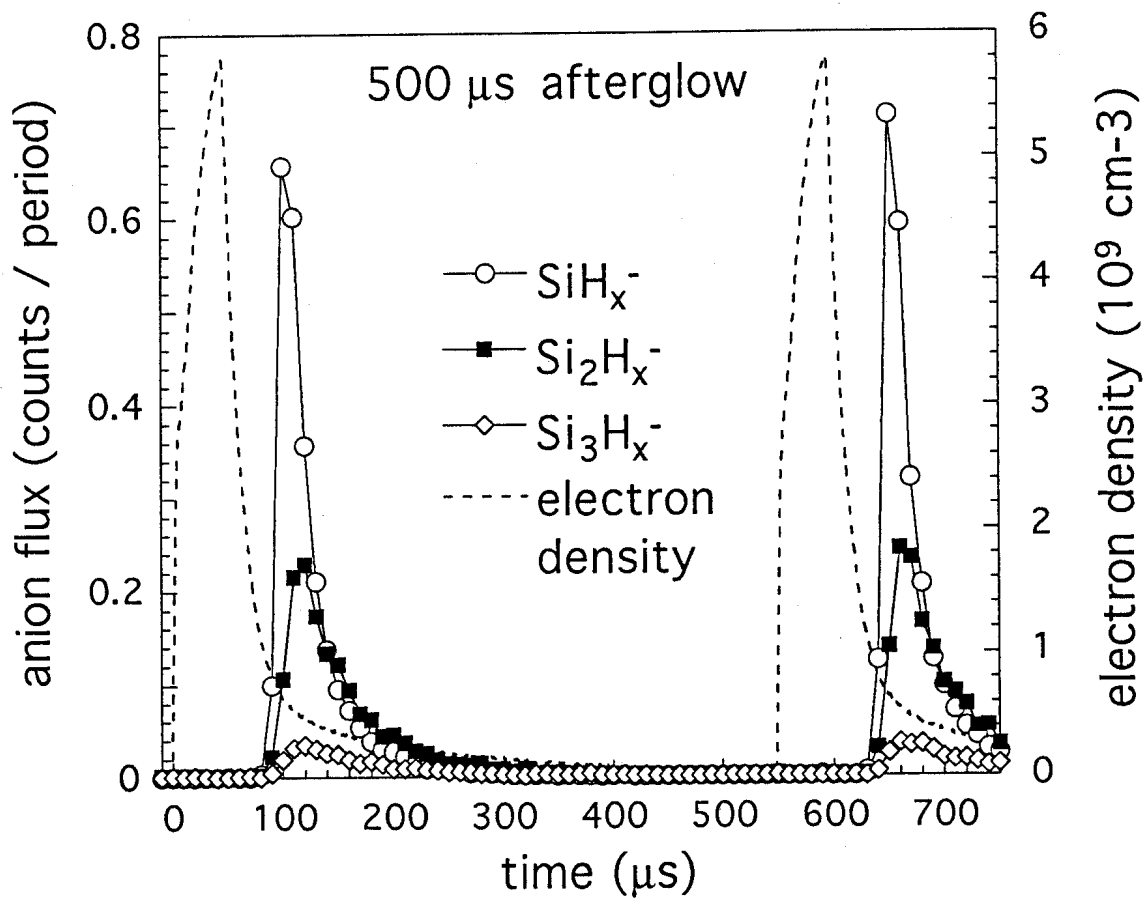


Fig. 5

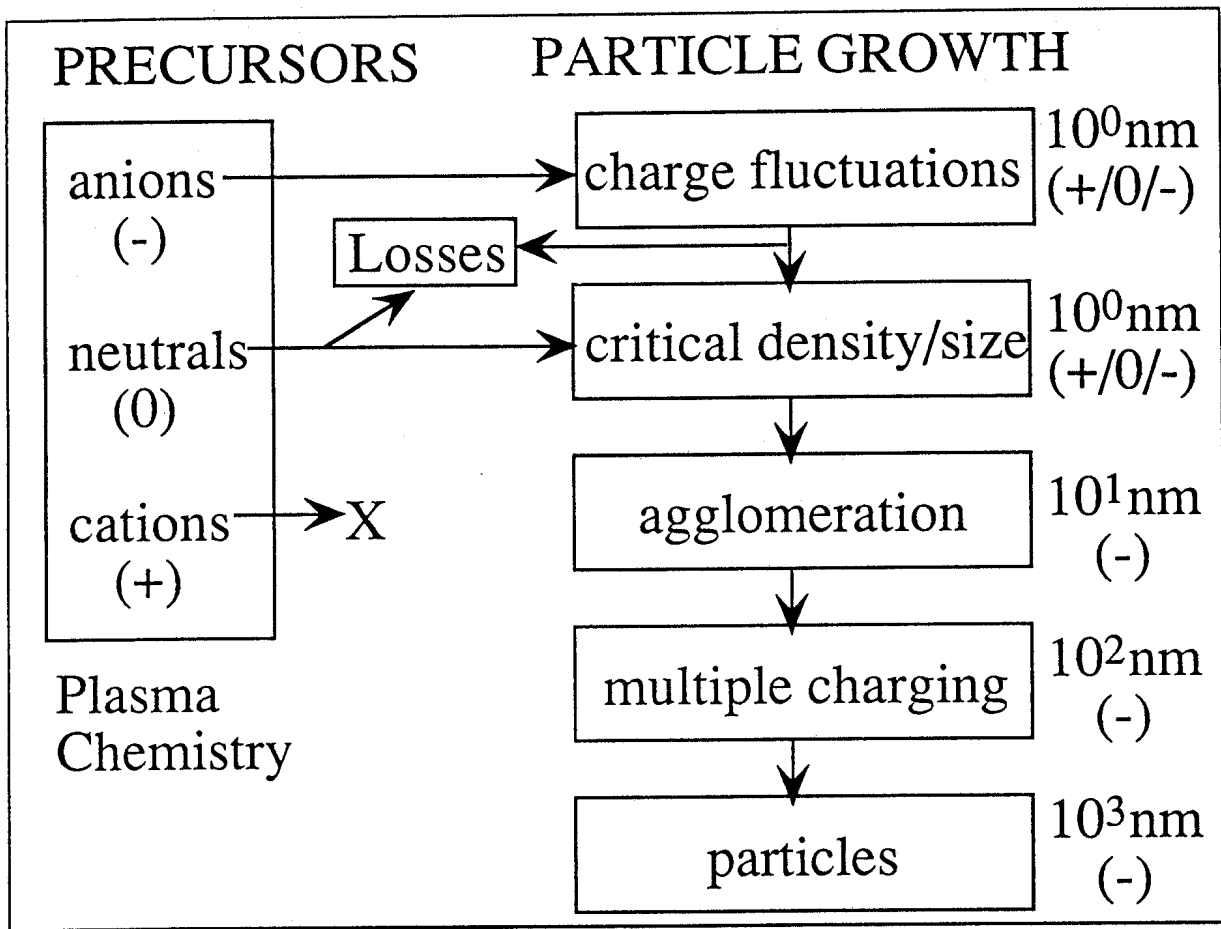


Fig. 6