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NEGATIVE ION MASS SPECTRA AND PARTICULATE FORMATION IN RF SILANE PLASMA DEPOSITION EXPERIMENTS

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Negative ion mass spectra and particulate formation in rf silane plasma deposition experiments

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Negative ions have been clearly identified in silane rf plasmas used for the deposition of amorphous silicon. Mass spectra were measured for monosilicon up to pentasilicon negative ion radical groups in power-modulated plasmas by means of a mass spectrometer mounted just outside the glow region. Negative ions were only observed over a limited range of power modulation frequency which corresponds to particle-free plasma conditions. The importance of negative ions regarding particulate formation is demonstrated and commented upon.

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Plasma deposition of hydrogenated amorphous silicon by rf glow discharges in silane has found wide commercial application for the production of silicon-based devices. Extensive research has consequently been dedicated to understanding the silane discharge physics and deposition processes. Silane and its radicals are known to be electronegative,[1,2] and the probable existence of negative ion radicals in silane rf plasmas has often been invoked to explain various phenomena.[3-6] The sheath electric fields at the rf electrodes confine negative ions to the plasma and therefore, even though the electron attachment cross-sections may be small, their density could become large compared to the free electron density.[5] Plasma particulate contamination models have taken either positive[7,8] or negative[5,6] ions to be the precursors, although experimentally the importance of positive ions in this respect is inconclusive and the evidence for negative ions is indirect .[9]

Negative silane radical ions have been observed by mass spectrometry in low pressure multipole discharges.[10] In the present work, the aim was to extend measurements to rf plasmas with parameters commonly used for plasma deposition. Overzet, Verdeyen and Beberman[9,11,12] have also used a power modulation technique to extract negatively-charged species via a positively-biased orifice in the electrode. Negative ions in fluorine and chlorine etching plasmas were studied because they form relatively stable negative ions, thus facilitating their detection. Etching plasmas also avoid the practical difficulty that deposition plasmas tend to block the pinhole apertures used in mass spectrometry experiments.[12] Although the latter problem is unavoidable, we were able to measure negative ions, for the first time to our knowledge, in power-modulated rf silane plasmas with the ion extractor of the mass spectrometer just outside the glow. An important constraint is that negative ions could only be observed over a certain range of power modulation frequency corresponding to powder-free plasma conditions; they were never observed in continuous power plasmas. In this work, the negative and positive ion spectra are compared and a correlation between negative ions and plasma particulate formation is demonstrated.

The experimental apparatus[13] in Fig. 1 is a conventional rf capacitative reactor comprising two 130 mm diameter electrodes with a 22 mm electrode gap. Plasma parameters relevant to the deposition of amorphous silicon were chosen, namely : a 30 sccm flow of silane

with a pressure of 0.1 mbar and a substrate temperature on the grounded electrode of 150 °C to 220 °C; the rf electrode was maintained at ambient temperature. The rf power modulation was produced by mixing a low frequency (10 Hz to 10 kHz) square wave into the rf generator signal. The capacitatively-coupled excitation frequency was 30 MHz with a peak-to-peak voltage of 110 V measured at the electrode, giving an estimated time-averaged power of 3.5 W in the plasma.[14]

The differentially-pumped mass spectrometer was a Hiden Analytical Limited Plasma Monitor type HAL-EQP 500 for masses 1-500 amu. It consists of an ion extractor shown to scale in Fig. 1 with a 100 μm aperture followed by an electrostatic energy analyser matched to a quadrupole mass filter and a channeltron detector. The ion extractor is positioned with its axis in the electrode plane, 10mm beyond the grounded guard screen, separate from the well-confined glow region. The electrode voltage and plasma emission symmetry were unaffected by insertion of the monitor. The criticality of the ion extractor position has not yet been evaluated, but this location is perhaps well-suited to the detection of negative ions compared with implantation in the electrode because extraction takes place in a rarefied plasma instead of in the rf driven sheath region. Any modification of the ion extractor electric field by electrostatic charging of the accumulated deposition on the extraction electrode could be detected by monitoring the ion transmission of the mass spectrometer as a function of extraction voltage. A 40 V extraction potential was large enough to give good negative ion transmission into the monitor, but not so large as to create a visible secondary plasma in the extractor orifice.

Fig. 2 shows the raw mass spectra data for negative and positive ions for a 1 kHz power modulation frequency. The negative ion mass spectrum shows only singly electron-attached ions, whereas the positive ion peaks observed between the groups are due to doubly-ionised species. The background negative ion signal, equivalent to 30 counts per second, is due to stray electrons accelerated onto the channeltron. The signal was acquired over 500 ms for each data point (every 0.03 amu for the high resolution profiles in Fig. 2) to reduce the fluctuations in the background noise sufficiently for the weaker high mass peaks to be identified. All data are consequently time-averaged over many power modulation cycles.

Negative molecular ions were observed for each group in the range from Si_n^- up to $Si_nH_{2n+3}^-$ ($n \leq 5$). For the first four groups, the dominant negative ion was $Si_nH_{2n+1}^-$. These negative ions of mass 31, 61, 91 and 121 have the same number of electrons as the equivalent stable neutral molecule Si_nH_{2n+2}. The isotopic contributions of ^{29}Si (4.7 %) and ^{30}Si (3.1 %) modify only slightly the relative abundances shown in Fig. 2 within each group. The relative abundance between the groups themselves depends on the modulation frequency (see below), and also the spectrometer transmission may vary for widely-different masses.[10,12] It would nevertheless appear that the disilicon negative ion group is dominant, being even more abundant than the monosilicon group. The measured intensity at the ion extractor thereafter decreases for successively higher mass negative ion groups.

The measured negative ion and positive ion fluxes are comparable. Although the enhancement of negative ion flux in modulated discharges may be partly responsible for this,[12] the negative ion density is nevertheless significant. High abundances of positive ions containing several silicon atoms have been reported[15] and shown to be formed in a chain reaction by the addition of monosilane to positive molecular ions.[16] The positive ions shown in Fig. 2 are hydrogen-poor compared with the negative ions. The opposite tendency was found in very low pressure multipole plasmas in which the ion abundances were determined by their relative creation rates,[10] whereas in our higher pressure discharge it is probably the secondary, polymerisation reactions with silane gas which influence the final ion abundances.

In Fig. 3 it is shown that the negative ion intensity was significant only for modulation frequencies from about 0.5 to 3 kHz. The positive ion signal, the global SiH* emission and the volume-integrated scattered white light from powder in the plasma[13] are also shown in Fig. 3 for comparison. Significantly, the positive ion signal and the SiH* emission do not vary strongly with the modulation frequency, whereas the negative ion intensities show a clear anti-correlation with the powder signal as the modulation frequency approaches 10 kHz. In a continuous power plasma with otherwise identical conditions, copious powder production was observed several seconds after plasma ignition; the scattered white light signal was then two orders of magnitude larger than the maximum in Fig. 3. Power-modulated plasmas thus have reduced particulate contamination, as has been reported elsewhere in the literature.[9,17,18]

Boufendi *et al* .,[19] by using pulsed power plasmas, have shown that particles grow from less than 5 nm finally reaching 200 to 300 nm diameter. The particles formed in the first few seconds in our continuous plasma conditions are too small to be detected using our white light scattering diagnostic. Particle growth rates are much faster with room temperature electrodes and in this case, powder is in fact observed at low modulation frequencies.[18] We can now make an interpretation of Fig. 3 :

- At low modulation frequency (below 0.5 kHz), molecular clusters form within a plasma half-cycle and have sufficently small inertia to be ejected during the afterglow period They do not have sufficient time to grow large enough to be detected by visible light scattering.

- At high modulation frequency (above 3 kHz), the inertia of the cluster precursors reduces the probability of ejection between cycles, and cluster growth continues in successive plasma periods (thereby further increasing their inertia and retention probability) until the powder becomes visible as shown in Fig. 3.

- For an intermediate range of modulation frequency, only the cluster precursors themselves have sufficiently small mass to be ejected between cycles, and no cluster formation occurs.

If we speculate that this intermediate frequency range coincides with the observation of the negative ions in Fig. 3, we can identify the elementary negative ions with the primary cluster precursors. This interpretation is coherent with the observation, shown in Fig. 3, that the order of appearance of negative ion signal maxima, as the modulation frequency increases, corresponds to successively lower mass ions.

Further evidence supporting the hypothesis that negative ions are precursors to particulate formation is that the conditions where negative ions or particles are observed are mutually exclusive, ie hot electrodes, low plasma power, and modulated plasmas favorise the observation of negative ions to the detriment of powder formation. It remains to be shown, however, which are the subsequent reactions leading from heavy molecular negative ions to particles containing millions of atoms, because negative ions of mass greater than 213 amu were never observed in these preliminary experiments.

The role of negative ions in the formation of plasma particulates has been previously suggested,[6,9] although no negative ion measurements were made in silane plasmas. To summarise this section, it may be just because negative ions polymerise rapidly that they are difficult to observe, and our evidence would suggest that power modulation at kHz frequencies favors the escape of primary negative ions from the plasma before further polymerisation reactions can occur, thereby reducing plasma particulate formation.

In conclusion, the mass spectra of negative molecular ions have been measured, for the first time to our knowledge, in a rf silane plasma used for deposition of amorphous silicon. The mass spectrometer was outside the glow region and the plasma was power-modulated at a frequency corresponding to powder-free plasma conditions. Negative ion radical groups from monosilane to pentasilane were observed and compared with the equivalent positive ions in the same plasma. Their dependence on modulation frequency is demonstrated and an explanation is proposed in terms of negative ion ejection from the plasma afterglow. Negative ions are shown to be a candidate for the primary source of particulate contamination. Future studies of negative ions will help further the understanding and application of rf silane deposition plasmas.

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FIGURE CAPTIONS

FIG. 1 Schematic of the electrodes and the monitor ion extractor head shown to scale. The rf signal is mixed with a square-wave signal, amplified and applied to the rf electrode via a directional power meter and a π matching network.

FIG. 2 (a) Mass spectra intensities in counts per second for negative and positive ions at a power modulation frequency of 1 kHz and substrate temperaure of 220 °C; (b) High resolution mass spectra for negative ions of the first four groups in the same plasma conditions. The mass peak profiles have the expected asymmetry for quadrupole mass filters.

FIG. 3 Dependence of the negative ion intensities and the total scattered light from powder on the power modulation frequency. The positive ion signal and the global SiH* emission are shown for comparison. Closed symbols are referred to the left-hand axis, open symbols are referred to the right-hand axis. SiH_3^-, $Si_2H_5^-$, and $Si_3H_7^-$ represent the mono-, di- and trisilicon negative ion groups respectively. The positive ion intensity is taken from the integrated positive ion mass spectrum. Substrate temperaure 150 °C, time-averaged plasma power 3.5 W.

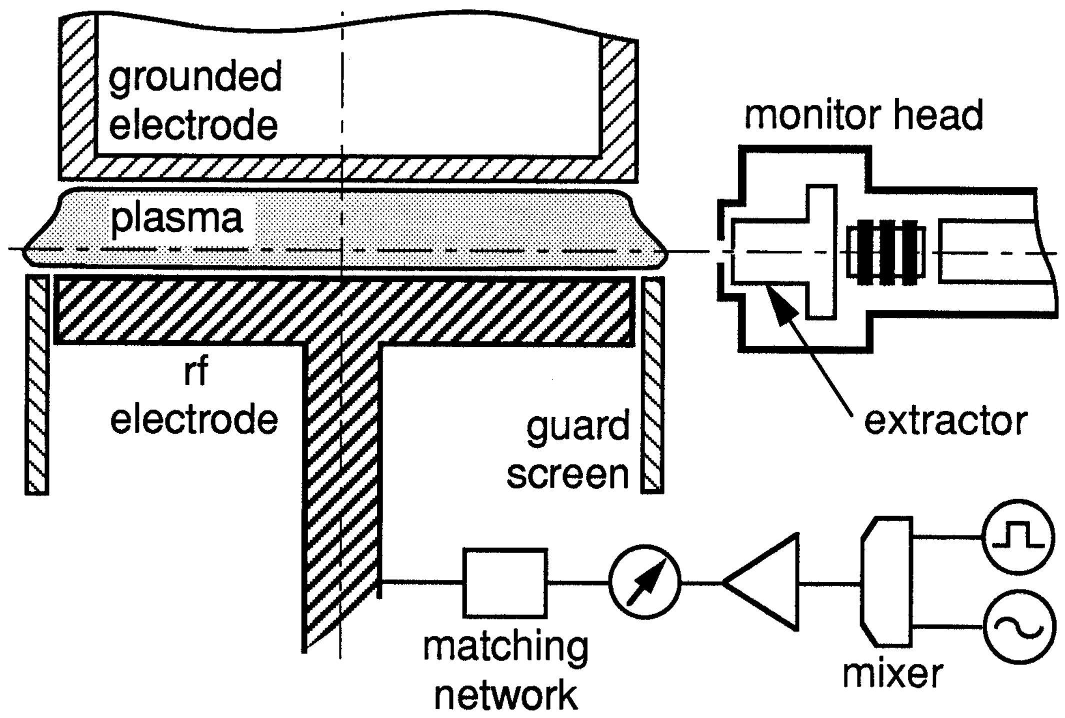
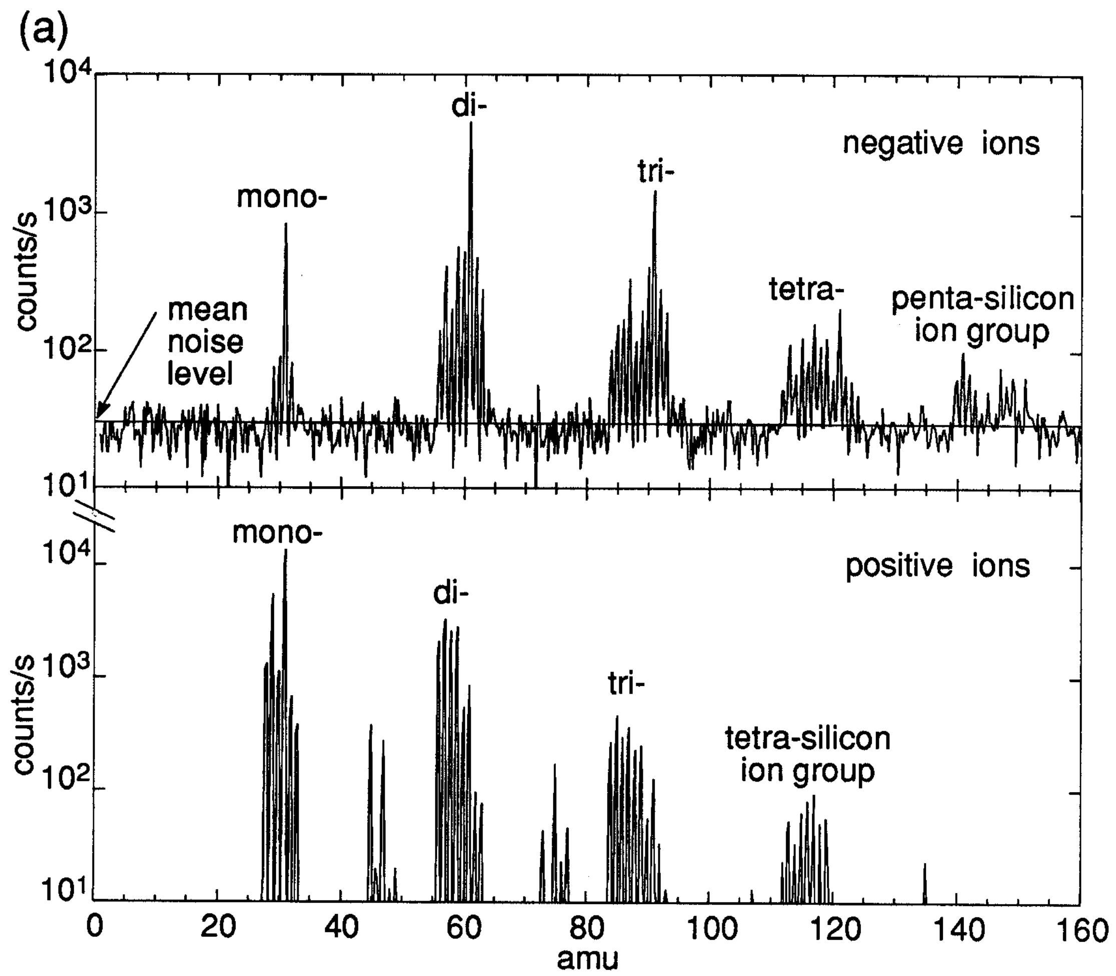


Fig. 1



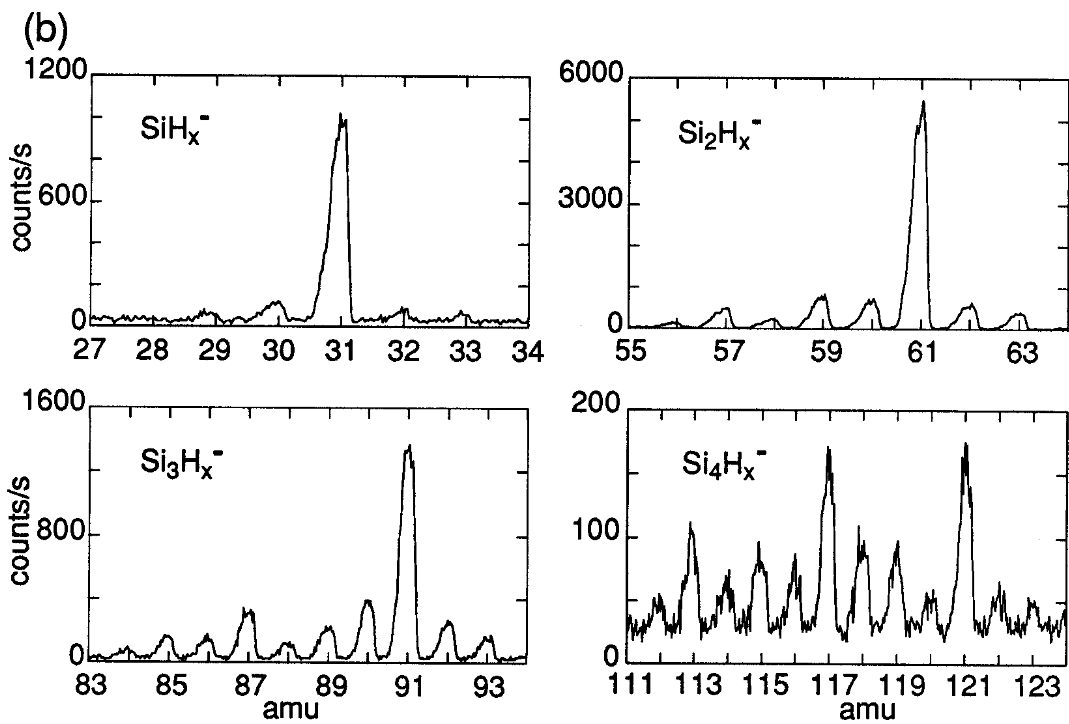


Fig. 2

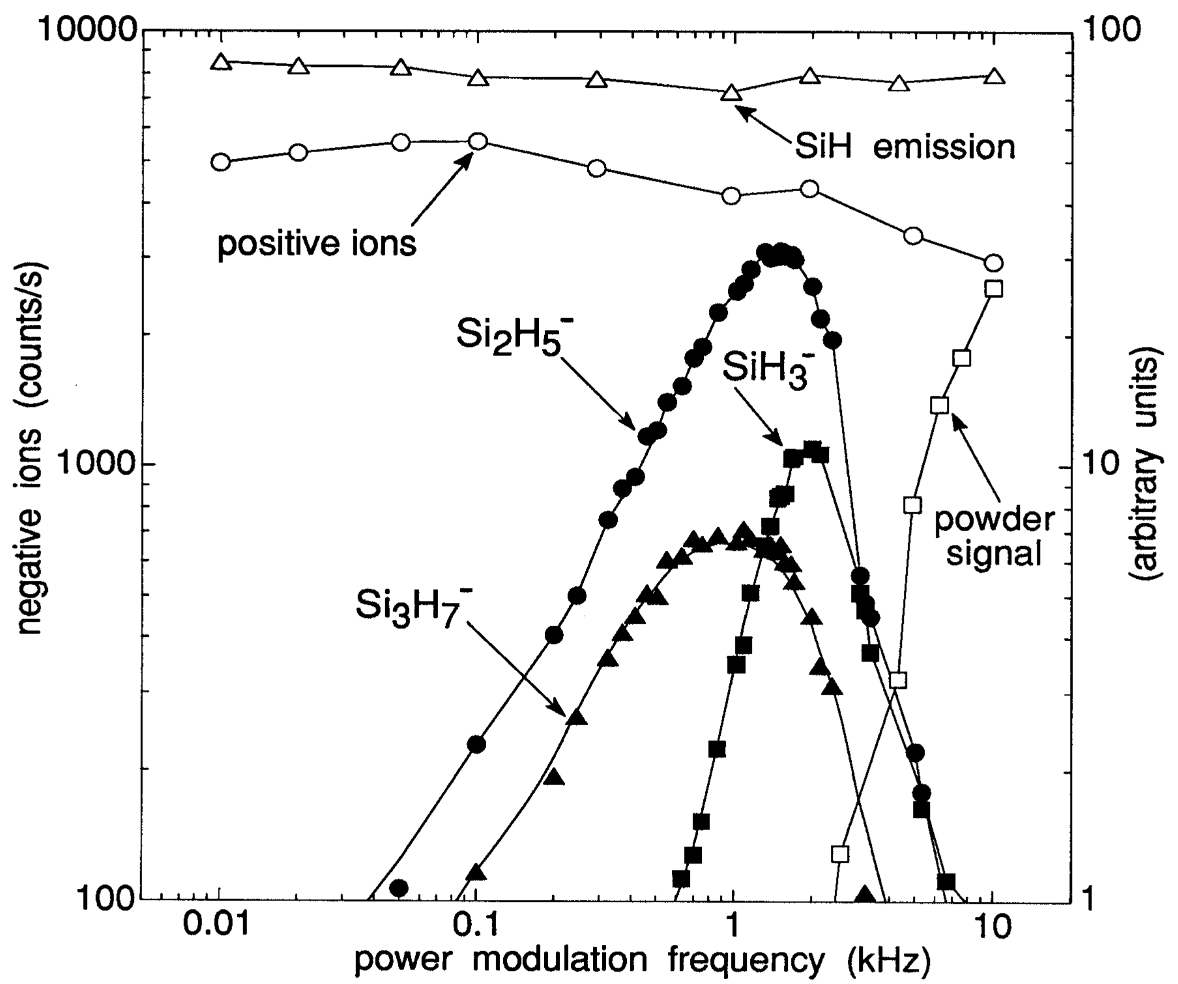


Fig. 3