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Negative hydrogenated silicon ion clusters as particle precursors in rf silane plasma deposition experiments

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Abstract. Stable negative ions containing up to sixteen silicon atoms have been measured by mass spectrometry in rf power-modulated silane plasmas for amorphous silicon deposition. These hydrogenated silicon cluster ions reach much higher masses than the positive ions, which have no more than six silicon atoms. This supports the view that negative ions are the precursors to particulate formation in silane plasmas. The time-dependent fluxes of positive and negative ions from the plasma are shown with a 5 μs time resolution. Possible cluster reaction sequences are discussed, and the effect of visible light on the negative ion signal is commented upon.

Particulate formation in the gas phase during plasma processing for semiconductor applications is estimated to be an important cause of device rejections [1]. Modern trends towards larger wafer dimensions together with smaller feature size and higher component densities will greatly increase the risk of particle-related yield losses. Such defects during amorphous silicon deposition of a Thin Film Transistor flat screen array or a solar cell can mean the loss of large areas of the device. Low plasma power reduces particle formation, but with the penalty of low deposition rates causing bottlenecks in production throughput.

Instead of minimising contamination damage by careful design of gas flow and reactor geometry, it would be more advantageous to suppress particle formation in the plasma. This presupposes a knowledge of the powder precursor identity and of the gas phase reactions leading from the silane feed gas to particles containing millions of silicon atoms. Models for powder precursors have been proposed using either positive [2, 3] or negative [4-6] ions. Power modulation at kHz frequencies reduces plasma powder formation [7-9], and in a recent publication [10] we showed that these conditions correspond to the observation of negative molecular ions leaving the plasma volume. The interpretation was that negative hydrogenated silicon ions are the particle precursors since their loss from the plasma inhibits powder formation. However, some ambiguity remained regarding their rôle as particle precursors because the largest negative and positive ions observed were of comparable mass and not heavier than about 214 amu. Positive and negative ions of similar mass have also been observed in low pressure multipole discharges [5].

In this context, we investigated high mass positive and negative ions formed in a pure silane plasma under conditions used for amorphous silicon deposition. The reactor was a conventional parallel-plate design with two 130 mm diameter cylindrical electrodes and a 25 mm electrode gap. The silane flow rate was 30 sccm at 0.1 mbar pressure with a 150 ^{o}C substrate temperature. The rf power was on/off modulated by mixing a low frequency (kHz) square wave into the rf generator signal. The capacitively-coupled excitation frequency was 30 MHz with a peak-to-peak voltage of 110 V measured at the rf electrode for a time-averaged power of 4 W, which corresponds to 8 W during the plasma. Negative or positive ions were sampled by a differentially-pumped Hiden Analytical Limited Plasma Monitor type HAL-EQP

500 [11] for masses 1 - 500 amu. The monitor base pressure of 10^{-6} mbar was low enough for ions to reach the detector without undergoing secondary reactions with the residual gas. The grounded head of the monitor was positioned to the side of the electrode gap, 10 mm away from the electrode edge; the ion extractor electrode with an orifice of 100 μm was biased at -150 V and +40 V for positive and negative ion detection respectively. Further details of the experimental set-up are given by Howling *et al* [10].

The principal results of this work are the positive and negative ion mass spectra shown in Figure 1 for a power modulation frequency of 1 kHz. Each data point (every 0.25 amu in the figure) was acquired with a 300 ms dwell time, corresponding to a measurement averaged over 300 power modulation cycles. The mass resolution of the quadrupole mass filter was strongly degraded so as to increase its ion transmission efficiency. Each peak corresponds to a group of molecular ions containing the same number of silicon atoms without regard to the number of hydrogen atoms. The intensity of successive positive ion groups decreases rapidly with mass, becoming undetectable for positive ions with more than six silicon atoms. In contrast, the negative ions are observed right up to the mass limit of our mass spectrometer: the last negative molecular ion group contains 16 silicon atoms centred on mass 480 amu, corresponding to ions such as $Si_{16}H_{32}^-$. The transmission efficiency of quadrupole mass filters and the sensitivity of channeltron detectors both diminish for high masses, but these effects are charge-independent. Therefore, unless ion extraction through the monitor orifice differs strongly between positive and negative ions, Figure 1 shows that the negative ions attain much higher masses than the positive ions. Neutrals were also measured using the plasma monitor, but no neutral radical clusters higher than the tetrasilicon group were detected.

The time dependence of the ion flux to the plasma monitor at 2 kHz modulation frequency is presented in Figure 2 for the disilicon ions $Si_2H_5^+$ and $Si_2H_5^-$. Ion events are registered by a gated counter with a time window of 5 μs. When the rf power is applied, the positive ion flux through the sheath in front of the plasma monitor rises gradually and reaches steady state during the 'on' period of 250 μs. During the afterglow, the positive ion signal decays in around 110 μs and negative ions are only observed when the positive ion flux falls close to zero. The negative ion flux is cut off when the next power period begins. These observations are commensurate with the measurements of Gottscho [12] in low frequency discharges and the simulations of Overzet [13] and Boswell [14] for modulated plasmas, which can be briefly resumed as follows: During the 'plasma on' half-cycle, the presence of highly-mobile electrons means that sheaths are set up to restrain electron flux to the electrodes and maintain quasi-neutrality in the plasma. The sheath electric fields accelerate positive ions to the electrodes, but prevent negative ions from leaving the plasma volume. In the 'plasma off' half-cycle, or afterglow, the fast electron component escapes, leaving a slow ambipolar diffusion towards the electrode surfaces. When the electron density becomes much less than the negative ion density (by loss to the surfaces, recombination or attachment to electronegative species), the negative and positive species have comparable mobility and the plasma potential can become lower than the grounded electrode surfaces [12]. The negative ions then escape from the plasma volume. The measurements in Figure 1 are the time-integral of these signals over many cycles for a 1 kHz modulation frequency.

The observation of positive molecular ions in silane plasmas for amorphous silicon deposition is well-documented [15,16], but these species have been discounted as the powder precursors because the clustering reactions are effectively terminated at five or six silicon atoms [16]. Another important disqualifier for positive ions is that they are continuously removed from the plasma across the sheaths, and so there is probably insufficient time for any given positive ion to undergo a lengthy clustering reaction sequence. Neutral radicals have been suggested to be the source of particulate formation [17], although heavy neutral species have not been reported and also could not be found in the present experiments. The confinement of negative ions in a continuous plasma means that they are a candidate for the species undergoing clustering reactions even if their reaction rates are low [4-6, 13, 14], but until now the experimental evidence for negative ions with much higher mass than the positive ions has been lacking. This may be because many negative ion experiments have been performed at very low pressures, for example in crossed molecule-electron beams [18], where stabilisation and secondary reaction collision rates are negligible.

The negative ion cluster reaction sequence is a type of plasma polymerisation [19]. The simplest pathway would be the ion-molecule reaction:

$$Si_xH_y^- + SiH_4 \Rightarrow (Si_{x+1}H_{y'}^-)^* + (H, H_2 \text{ products}),$$

where the parent ion survives if a stabilising collision occurs within its auto-detachment lifetime [20]. An alternative pathway could be ion-ion recombination followed by electron attachment to the resultant neutral, thus trapping the cluster in the plasma allowing subsequent ion-ion reactions [21]:

$$\begin{array}{l} Si_xH_y^- + Si_pH_q^+ \Rightarrow Si_{x'}H_{y'} + (Si, H, H_2 \text{ products}) \\ \qquad\qquad\qquad\qquad\quad \Downarrow + e^- \\ \qquad\qquad\qquad\qquad\quad Si_{x'}H_{y'}^-. \end{array}$$

The ionisation degree of these plasmas is less than 10^{-5} and so the ion-ion reaction rate constant would have to be at least 10^5 times the ion-molecule rate constant for the ion-ion pathway to be important. The majority primary negative ion is probably SiH_3^- since the channel with the largest cross-section for dissociative attachment to silane is [22]:

$$SiH_4 + e^- \Rightarrow SiH_3^- + H,$$

and SiH_3^- is in fact the dominant monosilicon negative ion observed in these plasmas [10].

Various methods, separately or combined with power modulation, could be envisaged to inhibit the clustering reactions or to promote their inverse reactions. In the experiment shown in Figure 3, the low mass negative ion flux from the plasma increases instantly on illumination of the plasma with visible light; the signal also increases with electrode temperature. It is well known that high electrode temperature reduces particle formation, although it is not clear whether this is due to plasma-surface interaction, gas heating, or a combination of these effects [23]. It is also interesting to note that Very High Frequency (30 - 200 MHz) plasma operation produces significantly less powder than the conventional 13.56 MHz frequency [24]. Further work is in progress to investigate how particle formation could be controlled using these effects.

To conclude, we have shown that stable, high mass negative ions are formed in silane plasmas for amorphous silicon deposition. These negative, hydrogenated silicon cluster ions reach much higher masses than the positive ions, which supports the view that negative ions are the precursors to particulate formation. With this interpretation, power modulation reduces powder formation by de-trapping the negative ions, as shown in previous work [10]. The agglomeration processes which lead from negative clusters to particulates have yet to be studied. Possible methods for controlling the sequence of cluster reactions are currently being investigated.

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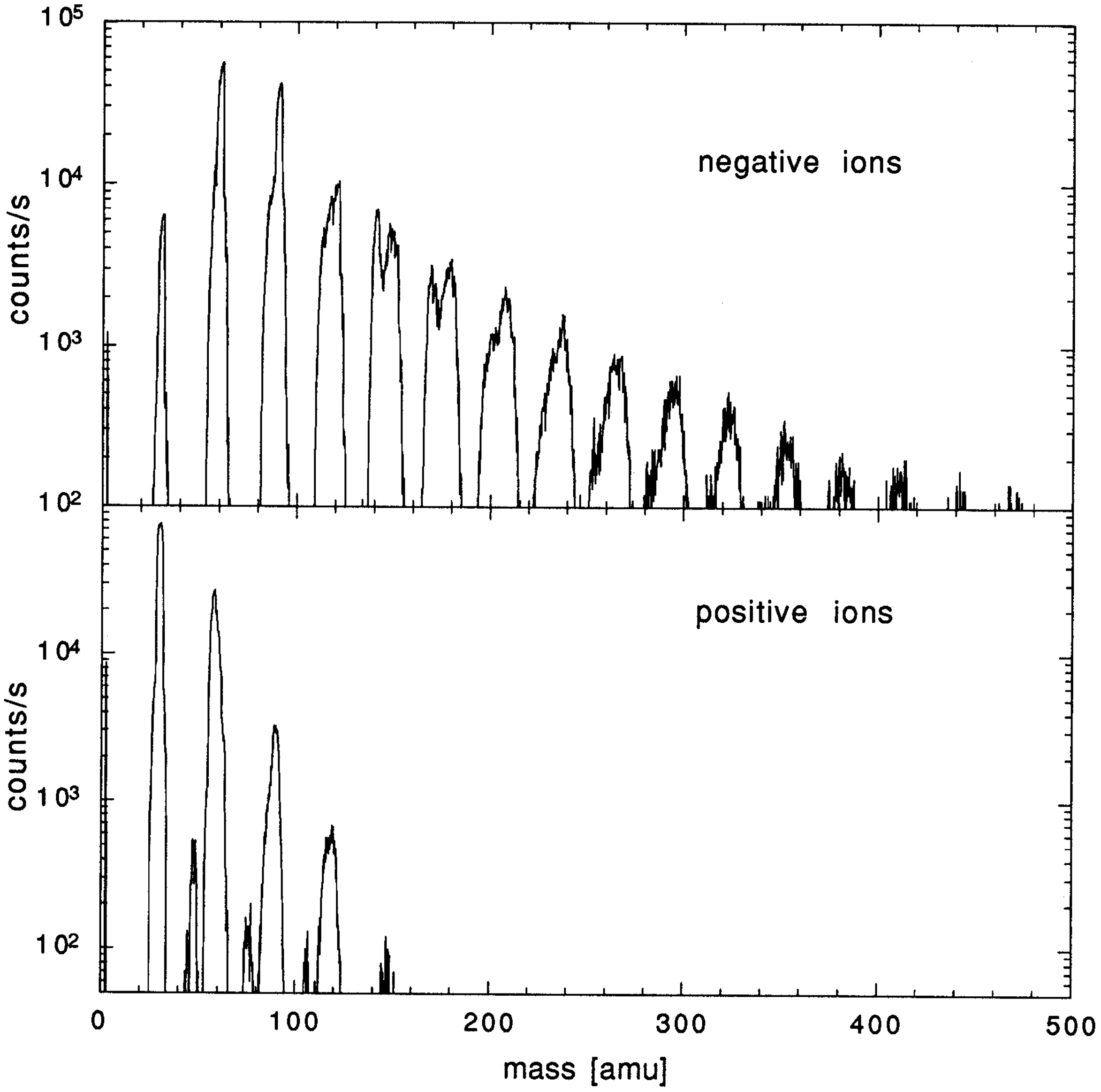
Figure Captions

Figure 1. Mass spectra intensities in counts per second for negative and positive ions. This raw data, acquired with low mass resolution, is uncorrected for any mass-dependent fall-off in sensitivity. Rf power modulation frequency 1 kHz, silane pressure 0.1 mbar, time-averaged power 4 W.

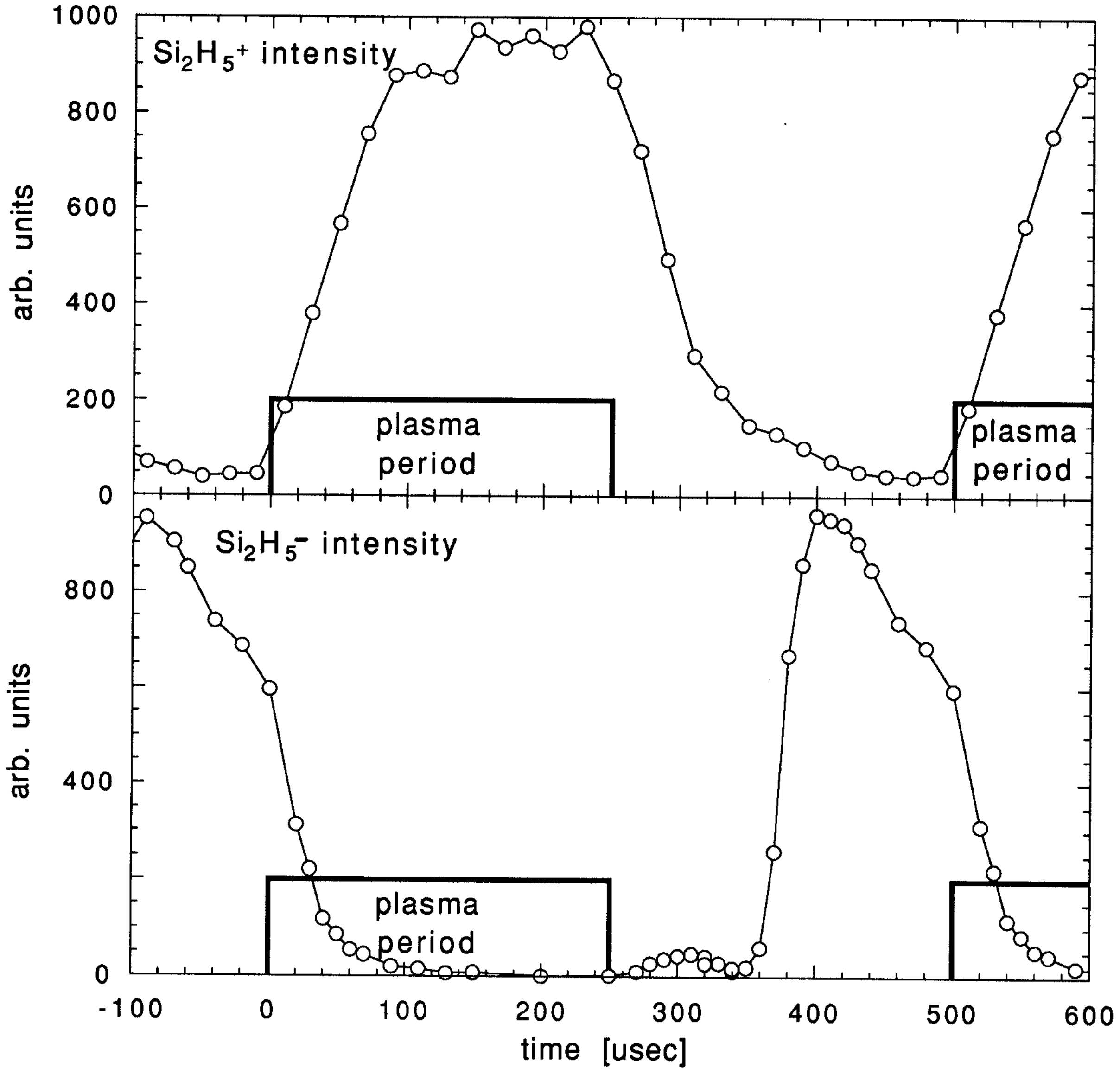
Figure 2. Time-resolved intensities for positive and negative Si_2H_5 ions at 2 kHz modulation frequency. The data is corrected for the transit time of ions in the plasma monitor.

Figure 3. Dependence of the $Si_2H_5^-$ intensity on visible light illumination (indicated by 'I'); and during an electrode temperature ramp from 150 to 220 °C (indicated by 'TR'). Modulation frequency 1 kHz.



10^5
10^4
10^3
10^2
counts/s
negative ions
10^4
10^3
10^2
counts/s
positive ions
0
100
200
300
400
500
mass [amu]

FIGURE 1



1000
800
600
400
200
0
arb. units
$Si_2H_5^+$ intensity
plasma period
plasma period
800
400
0
arb. units
$Si_2H_5^-$ intensity
plasma period
-100
0
100
200
300
400
500
600
time [usec]

FIGURE 2

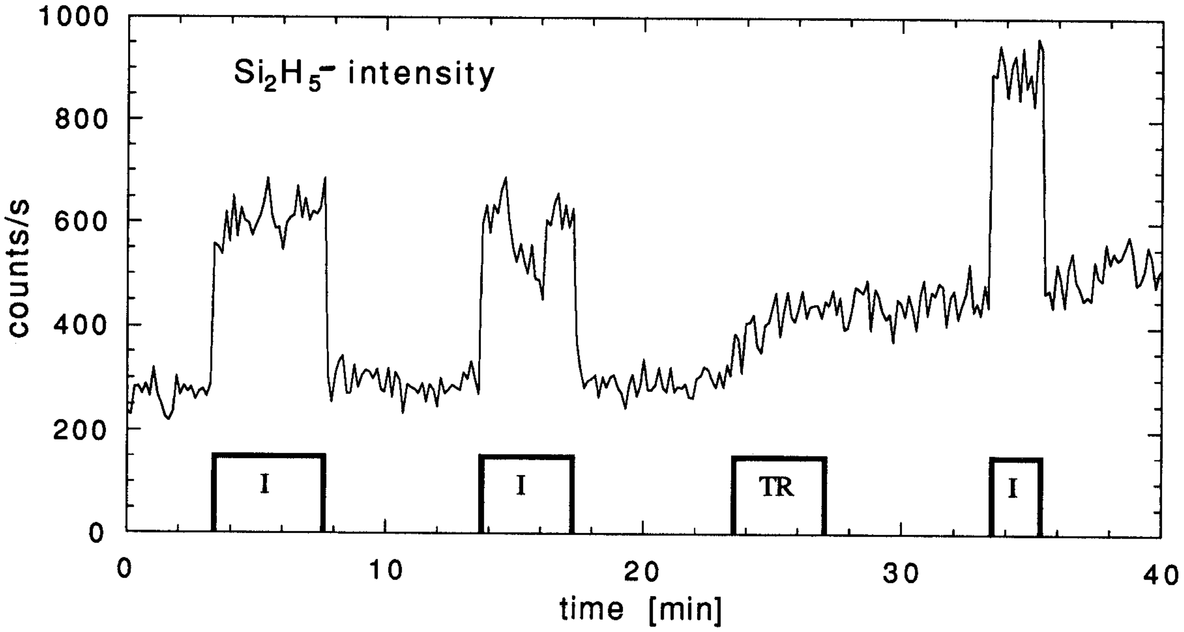

Si$_2$H$_5^-$ intensity
counts/s
1000
800
600
400
200
0
time [min]
0
10
20
30
40
I
I
TR
I

FIGURE 3