# From Molecules to Particles in Silane Plasmas

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Particle formation during silane plasma processing is a source of contamination, all the more serious as device areas increase and feature sizes diminish. Negative ions, since they are confined by plasma electric fields, have been proposed to be the particle precursors in conditions where the particle appearance time is much longer than the residence times of neutral and positive species. The objective of this work was to investigate whether negative ion clusters do occur in rf silane plasmas.

Quadrupole mass spectrometers with energy and time (5 μs) resolution were employed to monitor positive, negative and neutral species in a low pressure (0.1 mbar) rf capacitive silane discharge. The electron density was simultaneously measured by microwave interferometry. Using rf power pulse modulation techniques and synchronous detection, low-energy (< 1 eV) negative ions were observed to diffuse from the plasma during the afterglow periods after collapse of the sheath fields.

Complete sequences of stable, singly-attached anions were identified, extending from monosilicon molecular anions up to mass 1200 amu. The latter correspond to nanometric anionic clusters containing 40 silicon atoms, much heavier than the measured positive or neutral counterparts. These hydrogenated silicon clusters tend to an average ratio [H] : [Si] ≈ 1.4. Partial-depth power modulation experiments show that the anionic flux can be switched on or off, depending on a transition zone of rf power level, controlling the eventual formation of powder. Measurements performed on single plasma pulses show the development of the mass spectra and the importance of anion de-trapping if powder formation is to be avoided.

The mass range and relative abundances could be influenced by the power modulation frequency and duty cycle. The qualitative behaviour can be reproduced by an empirical homogeneous nucleation model which allows for the trapping/detrapping aspect of anions in modulated plasmas. Particle formation is strongly inhibited at around 1 kHz modulation, where measurements and model evidence suppression of the highest-mass clusters. A physical explanation is that the plasma period is then too short for the anions to reach high masses before the supply of low mass anions is evacuated in each subsequent afterglow period.

Apart from the practical implications for particle contamination control, modulated plasmas might be of interest as anionic cluster sources. The reservoir of energetic electrons and rovibrationally-excited molecules could possibly be exploited with electronegative gases to gain access to whole series of collisionally-thermalised charged clusters.