

On Morphology and Growth in Dust-Laden Plasmas

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Carbon particles with diameters ranging from tens of nanometers to several micrometers have been formed in low power, 20 kHz, low pressure, helium plasmas with graphite electrodes. The growth kinetics and morphologies of the particles suggest that after nucleation they grow mainly by accretion of positive carbon ions rather than neutral or negatively charged precursors. Carbon atoms sputtered from the electrodes are too few to account for the rapid appearance of micrometer-sized grains. Once charged however, the ion current collected through the grain's electrostatic sheath can account for rapid dust formation. The fractal surface textures and dense, amorphous interiors of the carbon particles are also observed in grains of polythiophene, polyphenylene, silicon, and carbon nitride, suggesting a physical rather than a chemical basis for a cauliflower-like structural motif. The observed texture is interpreted using the kinetic stability methods of Mullins and Sekerka and electrostatic ion focusing at the surface of the growing particle.

Microscopic grains in plasmas dance over the patterned features of semiconductor wafers [1] and permit inference of galactic magnetic fields. [2] They are essential to formation of molecular hydrogen between stars [3] and offer new laboratories for solid-state physics. [4] Grains can arise by many mechanisms including fragmentation of supernovae, flaking from the walls of etching reactors, or homogeneous growth from chemically reactive plasmas. We have been intrigued by the recurrence of a visually striking, cauliflower-like morphology in grains grown from varied reactive plasmas (Figure 1). [5-7]

Grains formed in laboratory plasmas must be negatively charged to satisfy the floating potential required for an electrostatic probe. [8] This negative charge and the large mass of the particle compared to that of an electron suspend dust away from the walls of the vessel unless it is driven by gravitational, viscous (ionic or neutral) drag, or thermophoretic forces.

We observe dust by Mie scattering of red light 2-10 minutes after initiating a 4 watt discharge in 2 torr of helium driven at 20 kHz by graphite electrodes. The rapid evolution of a dust cloud is indicated by a

Whither surface charges?

Edge x 2

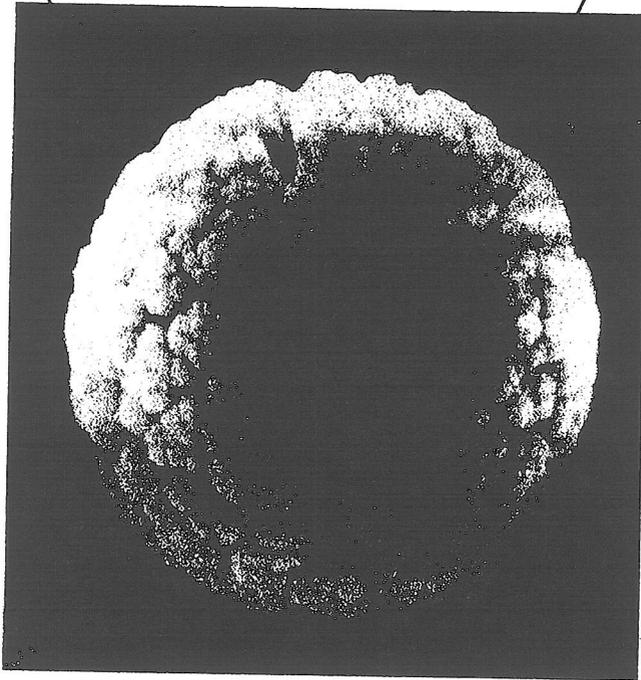


Figure 1: Typical dust grain grown in a 2 torr helium plasma driven by graphite electrodes. The projection of the grain's edge is enlarged to illustrate the influence of a nonuniform surface charge density on this $3.15 \mu\text{m}$ particle when it is immersed in a plasma.

corresponding decrease in the plasma current, so that many hundreds of thousands of particles are evident within 10-30 minutes of striking the discharge. Examination of the grains by low energy scanning electron microscopy shows monodisperse, sub-micrometer cauliflowers typified by the image shown in figure 1.

Kinetic considerations

The ion current to a growing grain immersed in a helium plasma may be estimated from probe theory [9] and is nearly independent of particle size for small particles. By contrast, the neutral flux to a growing particle increases with the square of the particle's diameter, so that the rates of growth for ionic and neutral mechanisms are qualitatively different.

Carbon atoms and radicals are sputtered from our graphite electrodes by helium ions that are accelerated through a cathode sheath of several hundred volts. At these energies the sputtering yield is between 0.05 and 0.1 carbon atoms per incident ion, so an ion current density of 1 mA/cm^2 would lead to a sputtered flux of $6 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}$ and a density of neutral atoms, dimers, or trimers of about $2 \times 10^{11} \text{ cm}^{-3}$, assuming a very compact geometry. The extent to which these carbon atoms are ionized by plasma electrons may be estimated from the ratio of the diffusion rate to the ionization rate, which for our geometry and power loading is approximately 100.

Daugherty *et al.* [10] have calculated the ion current to a small particle immersed in a helium plasma very similar to our discharges with an electron density of $6 \times 10^9 \text{ cm}^{-3}$, an electron temperature of 1.5 eV, and an ion temperature of 0.06 eV. They calculate a linearized Debye length of $32.6 \text{ }\mu\text{m}$ and an ion current of 70 pA at a self-consistent floating potential

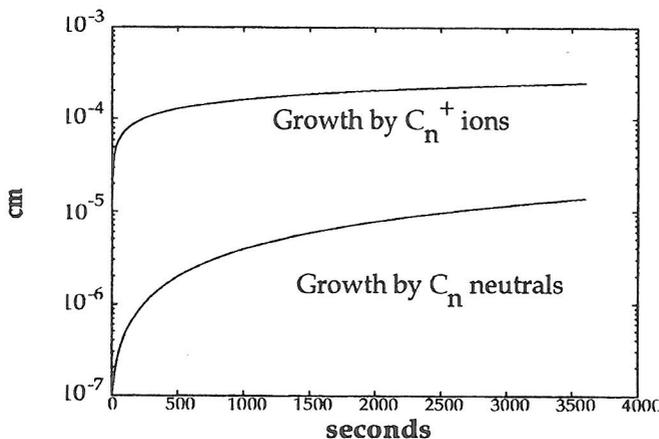


Figure 2: Calculated particle diameters for ionic deposition (upper curve) and neutral accretion (lower curve) under typical conditions for producing grains such as that shown in figure 1.

from Penning ionization of organic precursors in the afterglow. As is the case with dust in reactive plasmas the precursor ions are accelerated through a small sheath potential (1-5 eV) before they strike the surface and chemically bond with the growing film.

The influence of electrostatic fields on the growth rate of the film is illustrated in figure 3. The deposition thickness over trenches is greatest where the radius of curvature of the substrate is smallest - at the edge of the trench. The size of these features ($0.5\text{-}5\ \mu\text{m}$) is much less than the Debye length in the afterglow; we infer that the charge density of the floating surface is not uniformly distributed. The enhancement of electron density at regions of high curvature causes small electric fields perpendicular to the sheath field. The electron and ion fluxes to the surface are focused by these fields, but only the ion fluxes leave mass on the substrate. This leads to a growth instability first identified by Mullins and Sekerka [12] in models of melt solidification and Laplacian growth, since the peaks on a surface grow faster than the valleys.

We have examined the evolution of surface texture in polyphenylene films by atomic force microscopy and shown that the roughness increases exponentially with film thickness. Figure 4 shows the observed evolution of surface roughness with film thickness (as determined by spectroscopic ellipsometry) for some polyphenylene films. A growth model in which the growth rate is proportional to the local curvature is also shown in figure 4. As the film thickens the roughness saturates and a restricted range of spatial scales is observed, as predicted by the analytical approach of

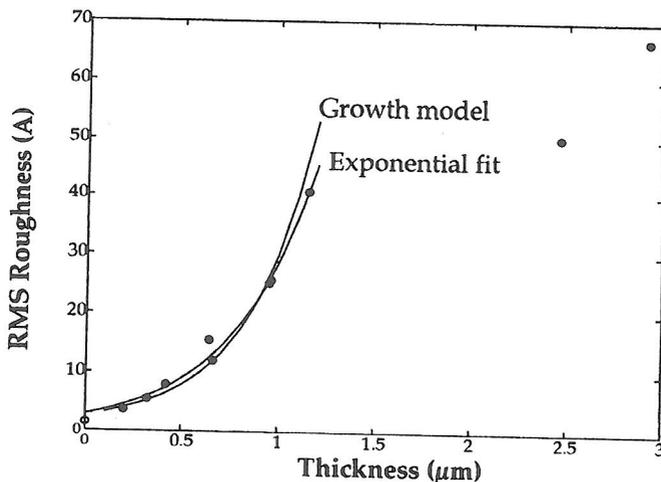


Figure 4: Evolution of surface texture in ionic deposition. The surface roughness (Angstroms) measured by atomic force microscopy varies exponentially with thickness (determined by spectroscopic ellipsometry), as expected for the growth instability of Mullins and Sekerka.

Mullins and Sekerka. We observe similar, non-random spatial scales for texture on the surfaces of dust grown in reactive plasmas. We see evidence that both the geometry of the seed particle and the growth temperature constrain the morphology of dust in reactive plasmas. The quantitative link between surface roughness, ion focusing by surface electric fields, and growth rate provides additional evidence for ionic deposition onto dust grains and is the subject of a detailed report in preparation.

In conclusion, we find that growth of dust in reactive plasmas may occur by accretion of positive ions and that, unless there is a vast supersaturation of neutral radicals, this mechanism accounts for the homogeneous growth. The surprising cauliflower-like textures have surface textures which are fingerprints of ionic deposition left by surface electric fields that focus ions onto protruding regions of higher curvature.

Acknowledgements

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