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Photoluminescence from Gas-Suspended Nanoparticles Synthesized by Laser Ablation: A Pathway to Optimized Nanomaterials

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PHOTOLUMINESCENCE FROM GAS-SUSPENDED NANOPARTICLES SYNTHESIZED BY LASER ABLATION: A PATHWAY TO OPTIMIZED NANOMATERIALS

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Laser ablation of solids into background gases is a proven cluster-assembly method. It was used to synthesize the first carbon fullerenes in 1985.*(1)* In this technique, a solid material is vaporized by a high-powered laser pulse to form a partially-ionized plasma containing atoms and small molecules. The hot plasma plume quickly expands to collisionless conditions unless confined by a background gas. In this case, the plume atoms become trapped together and can form clusters as small as a few atoms, or larger clusters of 1–10 nm diameter (25–26,000 atoms for silicon).

These 1–10 nm-diameter particles are highly desirable light-emitting materials since quantum confinement (QC) of electron-hole pairs within a nanoparticle can result in bright luminescence from new or previously forbidden optical transitions.*(2)* Porous silicon (*P*-Si) luminescence is an example of this effect, in which the near-infrared emission from nanometer-sized quantum wires of crystalline Si (*c*-Si) has been traced to QC in quantum dots, i.e. particles of nanocrystalline silicon (*nc*-Si).*(3)*

Films incorporating silicon nanoparticles are among the most promising optoelectronic materials for applications requiring room-temperature photoluminescence and compatibility with existing silicon processing technology. Thin films containing photoluminescent *nc*-Si and silicon-rich silicon oxide (SRSO) nanoparticles have recently been synthesized by laser ablation *(4-8)* in variations of the pulsed laser deposition (PLD) technique*(9)*. Electroluminescent light-emitting diodes (LED's) have now been fabricated from laser ablation-produced *nc*-Si films*(10)* and surface-emitting LED's based on oxidized *P*-Si have already been successfully integrated into microelectronic circuits.*(11)*

However, until now very little was known of the temporal and spatial scales for nanoparticle formation in background gases, or how the nanoparticles are transported and deposited after their formation. It is often unclear whether nanoparticles found on substrates were grown in the gas phase or from nuclei formed on the substrate surface.*(6-8)* Here the formation and transport of silicon nanoparticles in laser ablation plumes is revealed by a comparison of Rayleigh-scattering and the first photoluminescence measurements of nanoparticles suspended in background gases. Combined with Z-contrast transmission electron microscopy (TEM) and high resolution electron energy loss spectroscopy (HREELS) analysis of individual nanoparticles, we investigate their fundamental light-

absorption and emission properties without the influence of neighboring nanoparticles or surrounding solid or liquid hosts. Such understanding is critical for the deposition of optimized films.

The experimental apparatus for ICCD (gated, intensified CCD-array) photography and spectroscopy of laser ablation plasmas has been described previously.*(12)* Polished *c*-Si wafers were ablated by KrF-laser pulses (l = 248 nm, focused to energy densities of 5–8 J/cm^2 in 28-ns pulses) inside a large, turbopumped vacuum chamber (1 x 10^{-6} Torr base pressure) maintained at 1–10 Torr of 99.9999 % He or 99.9995 % Ar.

After laser ablation, hot laser plasmas emit bright recombination luminescence from excited atoms and molecules which can be photographed at different time delays with the ICCD camera system (5 ns – 3 μs exposures). To investigate Rayleigh scattering (RS) and photoluminescence (PL) from clusters suspended in the gas phase, a sheet of light from another pulsed laser (XeCl, λ = 308 nm, hν = 4.0 eV, 30 ns FWHM pulse) illuminated a 2 mm-wide cross-section of the silicon plume from below. Probe laser light scattered by nanoparticles (with estimated diameters larger than 1 nm)*(13)* was imaged by gating the camera on *during* the XeCl laser pulse. Alternatively, the camera was gated on *after* the probe laser pulse to capture images of long-lived photoluminescence.

The dynamics of nanoparticle synthesis depend on background gas mass, pressure, and flow, and the choice of laser energy density, wavelength, and target-substrate geometry. Condensation of viable nanoparticles is governed regionally in the confined laser plasma by the temperature and the degree of saturation. PL induced by incorporation of gas-phase dopants (carried by the background gas) can be observed and optimized with these diagnostics, and compared with the efficiency of dopants incorporated into the ablation target. These effects will be demonstrated for oxidized silicon nanoparticles.

In 1-Torr argon, the first detectable PL and RS are observed at Δt = 3–5 ms after ablation, just as the last remnants of plasma luminescence disappear. A uniform and stationary cloud of nanoparticles forms and densifies over hundreds of milliseconds. The nanoparticles are then blown by a gentle flow in the chamber over a period of 10 seconds. Remarkably, no PL is observed when silicon is ablated into non-flowing argon. However RS images reveal that non-luminescing nanoparticles are present in nearly equal numbers.

A strikingly different set of dynamics are initiated by ablation of Si into He. The mass ratio between plume (Si) and background gas atoms (Ar, He) has been shown to have a major effect on the plume dynamics in the 0–1 Torr pressure range.*(15)* Experiments and multiple-scattering simulations show that Ar atoms (m=40) effectively remove Si atoms (m=28) from the forward-going flux, and can even scatter Si atoms backward, while He atoms (m=4) gradually slow Si atoms with a series of small-angle collisions.*(15)*

As a result, higher helium pressures (> 4 Torr) were required to confine the plume to form observable nanoparticle. In 10 Torr He, the first detectable PL and RS occur at Δt = 150-200 μs and the nanoparticles angularly segregate into an expanding, turbulent ring which propagates forward at

10 m/s. This appearance time and subsequent dynamics are in good agreement with recent LIF-imaging and spectroscopy of the onset of silicon dimerization measured by Muramoto, et al *(16)*.

For silicon ablation into (1–10 Torr) helium and argon gas, three broad PL bands (1.8, 2.5, and 3.2 eV) with regions of pronounced structure were measured.*(17)* The experimentally measured luminescence decay time was 1.8 ms. The broad luminescence bands at 1.8, 2.5 and 3.2 eV agree with PL observed for oxidized porous silicon and nanocrystalline silicon. However, the pronounced oscillatory structure on the bands is highly suggestive of *c*-Si phonon-assisted transitions. As-deposited films of these particles exhibited extremely weak photoluminescence. However, following standard annealing and passivation, the loosely-connected, weblike films exhibited strong red, blue-green and violet photoluminescence bands similar to those observed in the gas phase, however lacking any oscillatory structure.

Individual nanoparticles were swept from the gas suspension and imaged by Z-contrast TEM. The particles were spherical and 1–10 nm in diameter. Electron energy loss spectroscopy (EELS) of individual nanoparticles collected after bright PL in the plume indicated a silicon-rich silicon-oxide $SiO_{1.4}$ stoichiometry. EELS linescans indicate that the ~ 5-nm particles have no observable *c*-Si core, but contain homogeneously-distributed regions of pure silicon and silicon oxide.

In situ RS-imaging, PL-imaging, and PL-spectroscopy provide a powerful ensemble of techniques to understand how nanoparticles form, grow, are transported, and deposited in gas-phase synthesis methods such as laser ablation. Rapid feedback should permit desired PL-characteristics to be quickly surveyed and optimized during synthesis. The plume dimensions and dynamics suggest new modifications to laser-vaporization source geometries to optimize condensation to produce uniform nanoparticle size distributions. The versatility of laser ablation to vaporize even the most refractory materials, coupled with dopant introduction in the gas phase, provides possibilities for virtually unlimited materials-synthesis opportunities.

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