SYNTHESIS OF SI NANOPARTICLES WITH CONTROLLED SIZE, MORPHOLOGY AND CRYSTALLINITY IN A CO2 LASER PYROLYSIS REACTOR

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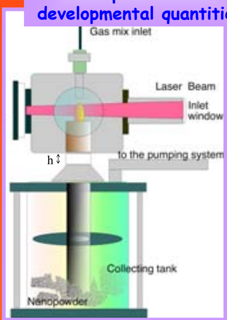
Si-nanocrystals reveal intriguing size-dependent optical properties which could be exploited in a number of fields ranging from optoelectronics to sensors and to bio-imaging.

The most challenging task in preparing Si-nanoparticles is to succeed in controlling the particle size and morphology as well as the surface properties.

CO_2 laser pyrolysis of SiH_4 gas appears as a very flexible tool for the production of Si nanoparticles in developmental quantities

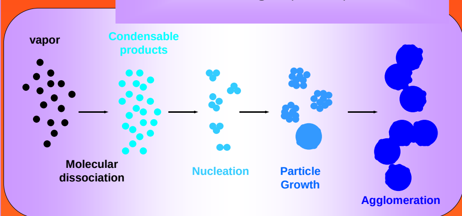


$$SiH_4 \xrightarrow{nh\nu} SiH_4^{**} \rightarrow Si + 2H_2 \qquad nh\nu \geq E_{diss}$$

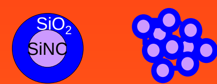
$$SiH_4 \xrightarrow{nh\nu} SiH_4^{*} \qquad nh\nu \leq E_{diss}$$

$$SiH_4^{*} + SiH_4^{*} \rightarrow SiH_4 + SiH_4^{**} \rightarrow Si + 2H_2$$

particle nucleation and growth occurs as a consequence of collisions between radicals produced by laser induced dissociation of gas phase precursors



produced nanopowders formed by aggregates of nearly monodispersed primary particles



aggregates held together either by weak bonds (soft agglomerates) or by sintered necks (hard agglomerates).

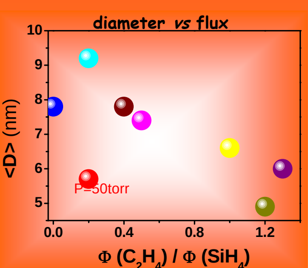
particle size — aggregation

depends on

SiH_4 concentration — Residence time

To reduce crystalline core: two strategies

Addition of C_2H_4 in the inner channel as sensitizer



The role of ethylene is twofold:

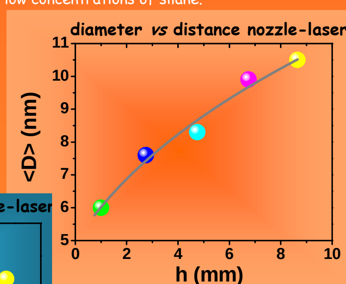
- ✓ dilution of the reactive phase and control of the particle growth by decreasing the collisions between radicals;
- ✓ increasing of the average temperature by coupling the laser energy into the system also at the low concentrations of silane.

powders with smaller particle size average diameter ≤ 6 nm

Use of a "quenching" collection system

A high dilution of SiH_4 with C_2H_4 has a detrimental effect on the nanoparticle productivity.

Further control on the final particle size without a significant effect on the process productivity was achieved by introduction of a quenching collection system, at variable distance *h* with respect to the laser beam, to freeze the particle growth process at different stages.



Assuming that the growth time *t* depends linearly on *h*, the experimental data can be fitted by the simplified formula for isothermal, coagulation-limited particle growth model

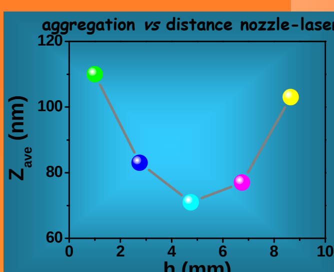
$$d \sim t^{2/5}$$

powder agglomeration

It is estimated by Z_{ave} by Dynamic Light Scattering measurements.

The aggregate size does not decrease steadily with decreasing residence time in the reactor, as expected when considering the associated reduction of the collision probability.

A possible explanation is that the aggregation rate of primary particles is proportional to the concentration of the particles, which could be higher when growth kinetics is stopped at an early stage.

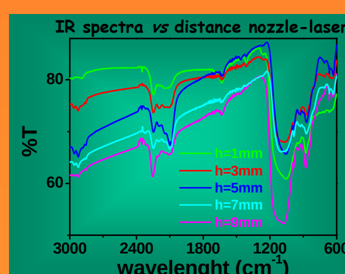


surface characterization by IR spectra

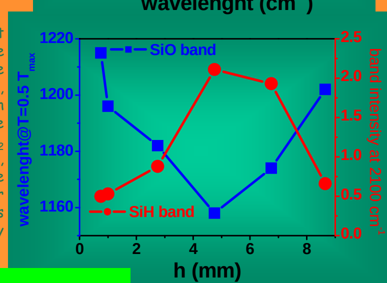
FTIR spectra are different from sample to sample, pointing out for different amount and quality of the oxide layer capping the particles

The collector position affects:

- ❖ the peaks intensity at 2100 cm^{-1} (SiH)
- ❖ the shoulder at 1200 cm^{-1} (SiO_2)

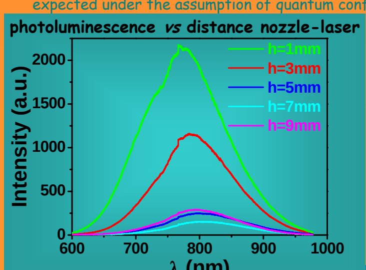


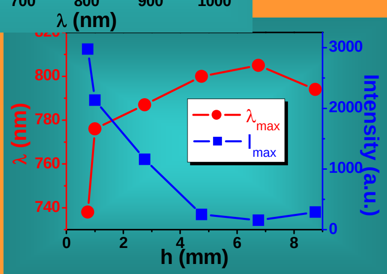
For small and large *h* both bands indicate larger amount of nearly stoichiometric oxide, while at intermediate values the amount of the oxide is at minimum. The oxidation rate mainly depends on H passivation of Si, which makes the surface resistant to oxidation, and on the presence of strained structures that weaken the Si-Si bonds and cause susceptibility to the attack of O_2 and H_2O. When powders were collected near the flame, the particles are smaller and so the surface is more strained, resulting in high oxidation rate. On the other hand, when *h* increases, the oxidation rate increases also, possibly because of poor surface passivation by hydrogen or by increased surface reactivity.



emission in the red-near-infrared region

A blue shift of the PL maximum is found when the distance collector-laser (and consequently the particle size) decreases, together with the PL intensity increase, as expected under the assumption of quantum confinement.





CONCLUSION

We show how to control and decrease the Si nanoparticle size without a drastic reduction of the productivity by two complementary techniques:

- ➢ addition of a reaction sensitiser (like ethylene) in order to dilute silane without excessive cooling of the system;
- ➢ quenching of the growth process by collecting the nano-particles at very small distances from the reaction flame.

As a consequence, sizeable quantities of Si nanoparticles with controllable optical properties can be prepared for a wide range of applications.

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