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Formation of single-crystal silicon nanoparticles at very low gas temperature in a rf silane-based discharge

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Introduction

The synthesis of single-crystal silicon nanocrystals we present is performed in the gas phase of a radio frequency (rf) discharge. The plasma is produced in a discharge box, enclosed in a vacuum vessel, containing an Ar/SiH_4 mixture (92:8). The typical pressure is 0.12 mbar while typical rf injected power is 10 W. Gas temperature can be decreased to -40 ^{o}C. Dust particle formation and growth is monitored thanks to an electrical diagnostics based on the time evolution of the discharge current third harmonic amplitude (3H). Size, density and crystallinity of dust particles are determined thanks to microscopy (SEM, TEM, AFM).

Synthesis of silicon nanocrystals

Dust particle synthesis in silane based plasmas has been shown to be a four step process [1] occuring in the gas phase. First, nanocrystals grow from molecular species until they reach 2-3 nm in diameter, then they accumulate in the gas phase until 10^{12} cm^{-3}. Once this critical density is attained, nanocrystals agglomerate together to form polycristalline dust particles that finally grow by surface deposition of the plasma species. Dust particle synthesis is monitored using the 3H probe allowing to identify each formation step (see figure 1).

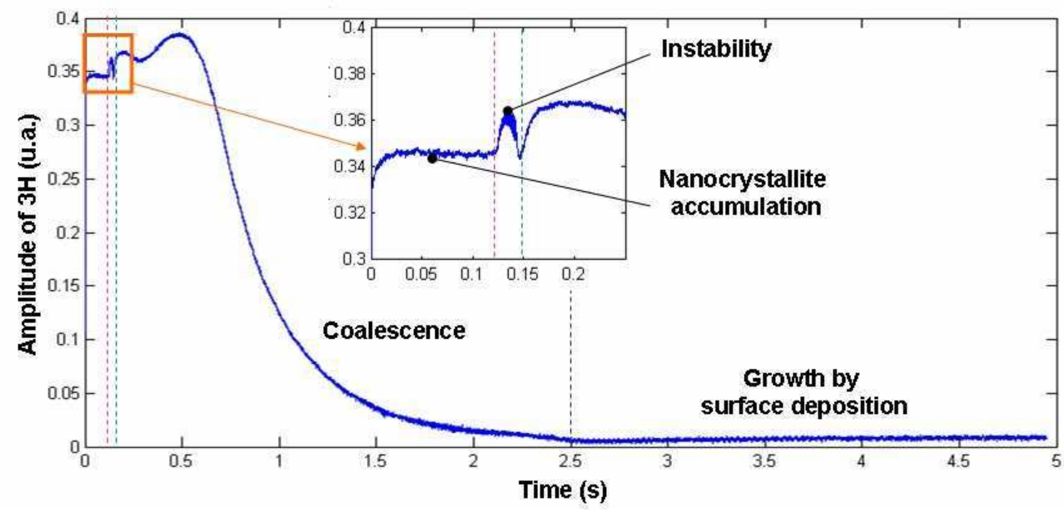

Figure 1: Identification of the different formation steps on the 3H time evolution

It has been shown that an instability appears exactly at the end of the accumulation phase and consequently is a good indicator of the coalescence beginning [2]. SEM, TEM and AFM analyses show that just before this instability, dust particles are single-crystal silicon nanoparticles [2], in the FCC phase [3]. The instability onset exactly corresponds to the first agglomeration of nanocrystals, i.e. the coalescence beginning. This instability has been widely studied in [4] and can be related to attachment induced-ionization instabilities as observed in electronegative gases [5, 6]. Indeed, it appears when dust particle size is suddenly changing (coalescence) and consequently when charging effects become stronger.

Effects of high gas temperature on dust particle formation and growth have been widely studied [1, 7]. However, until now, very low gas temperatures (lower than room temperature) were still little-known. In this work, we decreased gas temperature until -40^{o}C in order to study its effect both on formation kinetics and on nanocrystal size and crystalline phase.

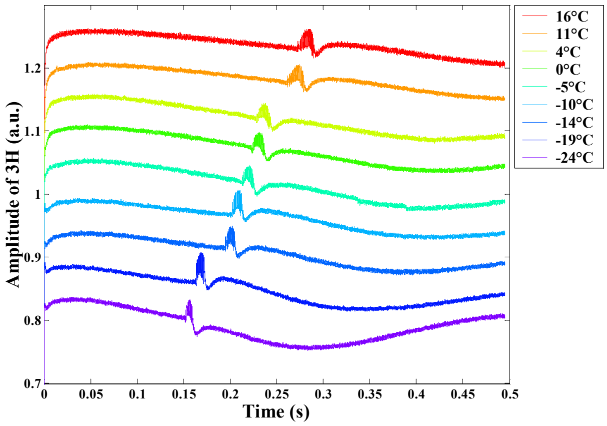

Figure 2: 3H versus low gas temperature

Effects of very low gas temperature on formation kinetics

Figure 2 shows the time evolution of 3H for different gas temperatures from 249K to 289K (-24^{o}C to +16^{o}C) from bottom to top. Curves are shifted in the 3H axis in order to get a better overview. It appears clearly that temperature decrease makes formation kinetics faster. Lower is the temperature, faster is the formation kinetics. The beginning time of the coalescence phase is a good indicator of the evolution of the kinetics versus gas temperature.

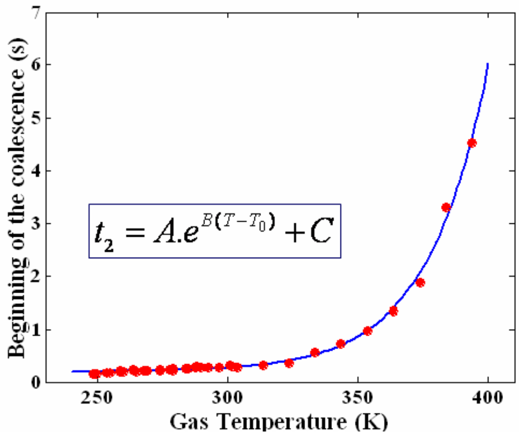

Figure 3: Kinetics versus gas temperature

The temperature dependence of this time is shown in figure 3. This curve was realized thanks to previous results obtained at high temperatures (298K to 389K) and very new results obtained at low temperatures (249K to 289K). The new results perfectly meet the older ones and an exponential behavior of nanocrystal formation is evidenced on this curve whatever the temperature range.

Effects of very low gas temperature on nanocrystal radius

It has been shown that the number of negative ions SiH_3^-, which are the first nuclei involved in nanocrystal synthesis, is the same whatever the gas temperature in the plasma. This medium can thus be considered as a supersaturated medium. In the theory of crystal nucleation in supersaturated media, nanocrystal critical radius corresponds to the maximum free enthalpy and increases when temperature decreases. Figure 4 shows the measured nanocrystal radius as a function of gas temperature. This radius evolves as $1/T$ as predicted by the theory and is rapidly increasing when gas temperature is decreased below 0^oC.

A single particle radius of 40 nm has been reached for T = -40^oC as can be seen on SEM image in figure 5. Dust particles from 0.9 nm to 3 nm in radius have been shown to be single-crystal silicon nanoparticles in the FCC phase [3]. Some TEM analyses are underway concerning bigger nanoparticles obtained at gas temperature below 0^oC. They are expected to be still crystalline but maybe presenting a diamond phase due to the higher stress caused by their bigger size.

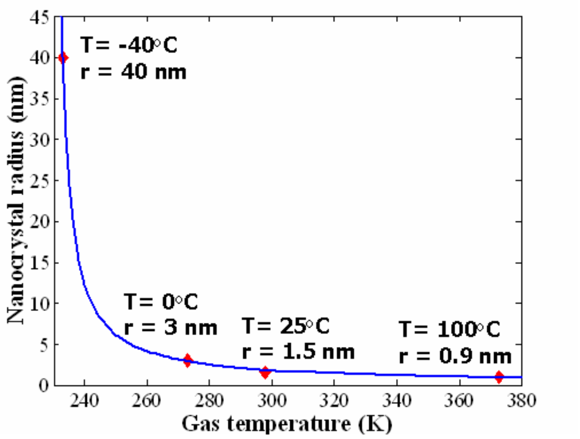

Figure 4: Nanocrystal radius versus gas temperature

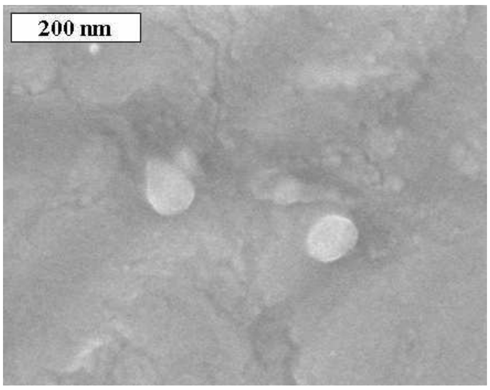

Figure 5: Nanocrystals of 40 nm in radius obtained at T = -40^oC

Conclusion

In this paper we present first results concerning dust particle formation and growth in Ar-SiH_4 plasmas at very low gas temperatures (below 0^oC). This work underlines effects of very low gas temperature on the synthesis of single-crystal silicon nanoparticles in a silane based plasma. Formation kinetics is shown to accelerate when gas temperature is decreased, while nanocrystal radius is shown to increase as $1/T$. These results, based on decrease of gas temperature and non-perturbative monitoring, allow to control depositions of single-crystal silicon nanoparticles of a well-defined size distribution with the highest density available during the synthesis process. These results are very promising in terms of dust nanoparticle tailoring and are of special interest for industrial applications in nanotechnologies (such as single electron devices or nanostructured materials) in which well-known crystal size and density are required (see for example [8]).

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