Growth and structure of silicon clusters generated by low frequency square wave plasma modulation

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Introduction

Structural properties of silicon clusters grown by low pressure and room temperature modulated plasma are presented. The generated nanometric clusters with a defined value of diameter below 10 nm with a low dispersion were collected just before the agglomeration phase in order to study the structural characteristics of single clusters.
The plasma processing for the production of nanometer-scale structures appears as a way to find materials with unique properties associated to their nanometric size. Thus, the generation of particles in silane plasma enhanced chemical vapor deposition (PECVD) processes has been intensively used because of the special characteristics associated with the resulting ones, like nanometric size, high purity, compactness and the surface hydrogen coverage. One of the main goals has been finding ways to control morphological and fundamental characteristic because significantly depends on the process conditions like power, pressure, gas flow, temperature and modulation frequency of the excitation power.[1] So far, many reports deal with the influence of technological parameters on the dynamics of particle formation but mostly for sizes above 10 nm, no further details to the smallest ones, otherwise they show a wide dispersion of sizes or simply ignore the data.[2-6]

This paper is focused on the structural and morphological characterization of silicon nanoparticles obtained through low frequency square wave modulation (LF-SQWM) of plasma chemical vapor deposition. In particular, we show improvements in both the reactor and the method itself, to achieve sizes around 10 nm nanoparticles with low dispersions when at modulation frequencies between 0.1 to 0.2 Hz. The nanoparticles were characterized by transmission electron microscopy (TEM).

Concerning the experimental setup, the system used for the synthesis of nanoparticles consisting of a capacitive coupling radio frequency (RF) discharge reactor earlier described.[7] The cathode is connected to a RF power generator that operates at 13.56 MHz and the plasma excitation is modulated with a square wave, alternating periods of on (T_{ON}) and off (T_{OFF}) in the plasma for a certain number of cycles (pulses). The used power was set around 200 W. The discharge was performed with silane diluted in Ar. The flow of SiH_4 and Ar into the chamber was regulated by individual mass flow controllers.

The nanoparticles were deposited directly on holey carbon grids using remote plasma collection and sequential flow. Particle characterization was performed by TEM. Images were obtained specifically with a Philips CM30 microscope operating at 300 kV, respectively. To determine the diameter of nanoparticles (D_P) and their dispersion, histograms were generated by measuring the diameter and then through a fit of a lognormal distribution, the value was obtained for the mean and variance, respectively.

The obtained clusters are spherical in shape and are generally amorphous. The size of the clusters can be controlled with high accuracy through the plasma on time, T_{ON}. The process uses long T_{OFF} periods to facilitate the collection of clusters. As a result of dissociation of precursor SiH_4 molecules by plasma electrons and following chemical reactions, different radical-monomers and small-size (mainly neutral and negatively charged) clusters are formed. During the formation of clusters, electronic attachment can change the electrical state of a cluster. So, negatively charged clusters are electrostatically confined by the plasma sheath and continue growing up to T_{ON} period ends, due to “attachment” of monomers to clusters.

In the present study we proposes the use of the parameter T_{ON} to control the size of the clusters deposited during the plasma off period. Therefore, tuning a T_{ON} below the residence time of clusters confined plasma we can reduce considerably their size dispersion. Figure 1 shows an example of the control of size dispersion (13 %) for silicon clusters of 9 nm grown from diluted silane in Ar, at 40 Pa of pressure, 0.2 Hz of modulation frequency and T_{ON} =0.5 s.

The structure of the deposited clusters is sensible to the depositing parameters like pressure and RF power. Figure 2 shows a HRTEM image of a single crystallized silicon cluster deposited from diluted silane in Ar at 8 Pa of pressure and, 250 W of RF power. The crystallization of the cluster is a consequence of the high temperature reached owing to the ion bombardment.[8]

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References

[1] E. Bertran, J. Costa, G. Sardin, J. Campmany, J. L. Andujar, and A. Canillas, Plasma Sources Sci. Technol. **3**, 348 (1994).
[2] A. Bouchoule and L. Boufendi, Plasma Sources Sci. Technol. **2**, 262 (1993).
[3] M. Shiratani, H. Kawasaki, T. Fukuzawa, H. Tsuruoka, T. Yoshioka, and Y. Watanabe, Appl. Phys. Lett. **65**, 1900 (1994).
[4] Z. Shen, T. Kim, U. Kortshagen, P. H. McMurry, and S. A. Campbell, J. Appl. Phys. **94**, 2277 (2003).
[5] S. Nunomura, M. Kita, K. Koga, M. Shiratani, and Y. Watanabe, J. Appl. Phys. **99**, 083302 (2006).
[6] Kwangsu Kim, Jin-hwan Park, Seok-gwang Doo, Jae-do Nam, and Taesung Kim, Thin Solid Films **517**, 4184 (2009).
[7] J. Costa, G. Sardin, J. Campmany and E. Bertran. Vacuum **45** 1115 (1994).
[8] G. Viera [Ph.D.Thesis], UB(2000) 44.

Figures

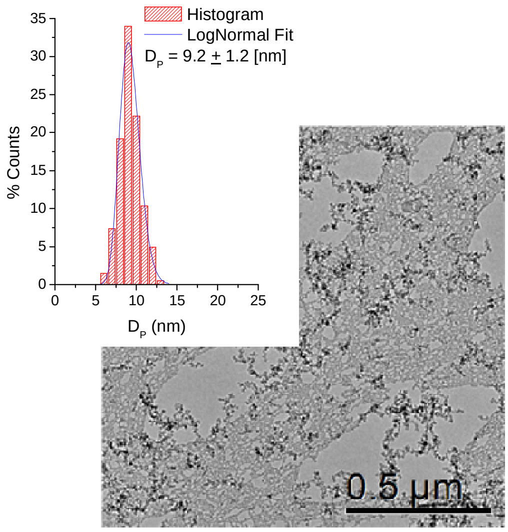

Fig. 1. TEM image and this histogram of a deposit using remote plasma collection and sequential flow. Silicon clusters were grown from diluted silane in Ar, at 40 Pa of pressure, 0.2 Hz of modulation frequency and T_{ON} =0.5 s.

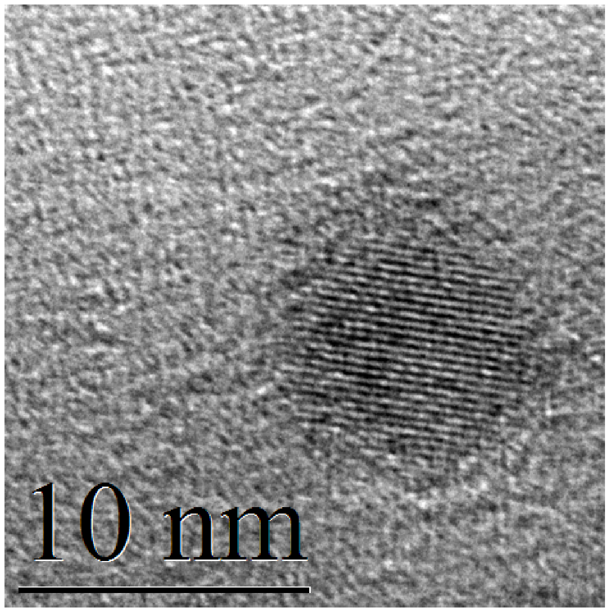

Fig. 2. HRTEM image of a single crystallized silicon cluster deposited using remote plasma collection and sequential flow. Silicon cluster was grown from diluted silane in Ar, at 8 Pa of pressure, 250 of RF power, 0.2 Hz of modulation frequency and T_{ON} =0.5 s, 250 sccm of total gas flow with 2% silane.