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Manipulation of cluster formation through gas-wall boundary conditions in large area cluster sources

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ABSTRACT

Development of industrial processes based on nanotechnology inevitably require methods to synthesise and manipulate nanoparticles. Among the different available processes, gas phase nanoparticle (cluster) formation techniques are of great interest for both large scale production and fundamental studies. Here, a plasma-gas-aggregation cluster source (GAS) apparatus with 6 in. diameter silicon sputter target has been designed and constructed. The selection of a 6 in. target represents a step towards scale up of the GAS to large-area deposition desired by industrial applications. Silicon clusters with average diameter of ca. 1–2 nm were prepared without a size-selective filtering system. From experiment and simulation, the slip flow regime of the gas in the aggregation region suggests that in addition to the sputtering conditions, the wall morphology also affects the growth process of silicon clusters. Controlling these factors influences the growth of the clusters (nanoparticles) leading to the desired size required for given properties.

1. Introduction

Studies of clusters have been motivated by their unique behaviour which are not found in the corresponding bulk materials [1–3]. The main goal of the research in this area is to understand the evolution of the properties of the clusters from atoms to bulk [4,5]. Various methods are available for the fabrication of clusters [6] and in terms of design and production of nano-particles/clusters based devices, a technique for size control and size manipulation at the nanoscale is required. Based on the molecular beam technique, which provides the possibility for investigation of free clusters in the gas phase [7,8], various gas phase techniques have been developed [9]. Clusters produced by these techniques not only provide the fundamental studies on the clusters [10] but also make their large scale production possible [11]. Among different gas phase approaches of nanofabrication, the magnetron sputtering based systems are gaining more attention due to advantages, such as production of large range of nanocluster (both metallic and non-metallic), ability to use size selection techniques without any further ionization stage (about 30–80% of the produced clusters are ionized [10], the study of Kousal et al. [12] on the gas aggregation cluster source also confirms the presence of positively, negatively and neutral species), minimization of the influence of deposition energy on the morphology of nanocluster by controlling the deposition conditions [13]. Currently the cluster sources are widely used and commercially available from companies such as Oxford Applied Research and Mantis Deposition [14]. The size of the sputter sources in these designs is typically 1–2 in. in diameter, making them well suited to laboratory based research. In order for these techniques to be appealing for industrial applications, the ability to form and deposit clusters over larger areas is desired. While a large number of studies using gas aggregation sources report the formation of metal clusters, such as Ni, Cu, Pd, Pt, Ag, Al [15–23], only a limited number of papers investigate the formation of semiconductors clusters such as silicon [24–27].

This paper reports the formation of silicon (Si) nanoclusters using a custom-built plasma gas aggregation cluster source (GAS). In contrast to the commercial and other custom-built cluster sources which are equipped with a maximum target size of 3 in., our GAS was designed and built based on a 6 in. diameter target and represents a step towards the scale up of GAS systems. The size of the Si clusters was controlled by varying the sputtering conditions such as gas flow rates and power. In addition to the sputtering conditions, based on the flow regime in the aggregation region and the gas-wall interaction, the properties of the chamber wall was also identified to influence the growth process of Si

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clusters. In particular, changes to the chamber wall in the vicinity of the orifice dividing the aggregation and deposition regions lead to changes in the deposition mechanism.

2. Experimental setup and diagnostic methods

2.1. Cluster source

Silicon clusters were produced with a custom-built GAS based on the 6 in. diameter planar magnetron unit with a 9.5 mm thick silicon target (99.99%) adhered to its front surface. As depicted in Fig. 1 GAS consists of two different sections: an aggregation or growth region where the clusters are formed, and a deposition region where the formed clusters deposit onto the substrate. The walls of the aggregation chamber are water-cooled to approximately room temperature. The clusters leave the aggregation region via an adjustable converging nozzle (with 3–10 mm orifice diameter, cone shape) by differential pumping with the exhausting speed of 250 L/s. In this study a 7 mm orifice was used. The pressure in the growth and deposition regions are measured using a Baratron capacitance manometer (MKS Instruments) and a Pirani Gauge (PFEIFFER Vacuum: D-35614 Asslar), respectively. The pressure differential between these two regions causes the formed clusters in the aggregation region to drive towards the deposition region. The length of the growth region can be varied by moving the sputter source closer to or further away from the nozzle. The aggregation length (AL) considered for this study was 126 mm. A DC magnetron type discharge is used to eject the target atoms. Typical powers of deposition are in the range between 200 and 400 W. A continuous Ar and He gas stream (purity grade 0.99) is injected directly in front of the sputtering target from small orifices (12 holes of approximately 1 mm in diameter). The flow of both Ar and He are controlled independently by mass flow controllers (Bronkhorst and AALBORG respectively) with flow rates up to 97.3 sccm and 147 sccm (standard cubic centimetres per minute) respectively. Typical pressures in the aggregation zone for clusters aggregation are ranging from 5 to 10 Pa, and are 1 order of magnitude lower than that commonly used for clusters formation. [25] Achieving higher pressures in the aggregation zones resulted in plasma instability and uncontrolled sputtering operation. The setup does not include any size selective filtering method. Freshly cleaved mica (ProSciTech Pty Ltd) was used as the substrate and was positioned 10 mm in front of the orifice in the deposition region. The centre of the substrate was marked in order to align it with the orifice. All experiments were conducted at a base pressure lower than 0.0086 Pa. The chamber was equipped with a shutter which was positioned between the substrate and the orifice during the pre-deposition sputtering.

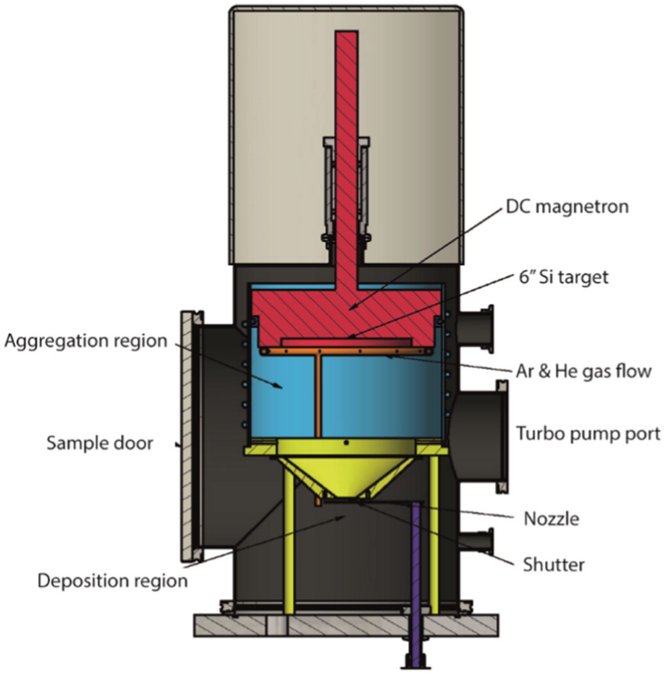

Fig. 1. Schematic diagram of the custom-built plasma-gas-aggregation cluster source (GAS), (not drawn to scale).

2.2. Cluster size characterization with atomic force microscopy

An atomic force microscope (AFM) (Multimode 8, Bruker) was used in tapping mode to measure the size distribution of the individual deposited Si clusters. Tapping mode tips (Tap 300Al-G, Budget sensors) whose tip radius is <7 nm (as per the manufacturer specifications) were used to measure the height of the clusters. Several 2 × 2 μm scans (512 lines, scan rate: 1 Hz) were performed around the central marked position in order to obtain at least 70 particles. The size distribution of the nanoclusters were determined using the “Particle Analysis” tool from the Nanoscope Analysis software (Bruker).

2.3. Computer modelling of gas flow in the aggregation region

The experimental work is complemented with a numerical model of the gas flow in the cluster source, the aim of which is to describe the slip gas flow in the aggregation region of the GAS. The numerical model is implemented with the help of OpenFOAM platform [28], specifically the *rhoSimpleFoam* solver, which solves compressible Navier-Stokes equations. The flow was considered compressible since the velocities close to the narrow inlets and the nozzle in the cluster source are expected to approach the Mach number of $M = 1$. Despite the high gas velocities, a turbulence model was not included because the relevant gas pressures of $p \approx 1$ Pa, the low gas density results in the Reynolds number of $Re \approx 10^1$. The exact form of the Navier-Stokes equations as well as the details of the numerical procedure implemented in *rhoSimpleFoam* solver is documented in [29] and the code has previously been validated by other groups, e.g. in [30].

Since the code was run on a powerful computational cloud with up to 128 cores, it was possible to solve the compressible Navier-Stokes equation in close-to-real three-dimensional computational geometry. Since the aim of the model is to describe the gas flow in the aggregation region (the equations are not valid in high-Knudsen deposition region), only the aggregation region is resolved in detail while the deposition region is substituted by a simple cylindrical cavity.

The model is constrained by several boundary conditions. At the gas inlets, the gas is expanding from nearly atmospheric pressure to pressures in the order of 1 Pa and the normal gas velocity at the inlets was, therefore, set to the approximate speed of sound, $u_{inl} = 330$ m/s. The Dirichlet boundary condition for pressure was assumed in the deposition region, and the pressure was set based on pressure measurements in the deposition region (0.5 Pa for the low pressure: conditions (a and c), 0.8 Pa for the high pressure: condition (b), see Section 3.1).

At the walls of the chamber, the partial slip boundary condition was imposed, in which the surface velocity of the gas can vary from 100% of the bulk gas velocity to 0% bulk gas velocity (equivalent to non-slip boundary condition). Slip flow regime is likely to appear since the Knudsen number is in the range $0.001 \le K_N \le 0.1$ (see Section 3.2).

OpenFOAM with the *rhoSimpleFoam* solver use the Finite Volume Method for the discretization of the Navier-Stokes equations. The computational grid consists of approximately 2 million tetrahedral elements and the model is solved on a commercial elastic computational cluster.

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