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Size-controlled formation of Cu nanoclusters in pulsed magnetron sputtering system

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ABSTRACT

Size-controlled Cu clusters are formed in a system which combines pulsed magnetron sputtering and gas condensation at room temperature. The discharge repetition frequency (0.1–25 kHz) and the duty cycles (20–90%) of the magnetron sputtering are varied systematically, the influence of discharge current (100–800 mA) and the pressure in the condensation tube (25–90 Pa) is also investigated. The cluster mass is determined by a quadrupole mass filter in the aggregation tube, and the cluster size by atomic force microscopy (AFM) imaging of deposited clusters. For all preparation conditions, the cluster mass shows a log-normal distribution. A non-monotonic frequency dependence with a maximum at 1 kHz and 20% of duty cycle is observed (about 10^5 amu, or cluster diameter 8–10 nm). By adjusting discharge frequency and duty cycle, the cluster mass can be decreased by one order of magnitude. We suggest that this effect is caused by energy dissipated into the aggregation tube; and find a critical buffer gas temperature $T_{g\text{-}cr}$ which limits cluster growth. This view is supported by the constant cluster mass flux which does not change on variation of discharge repetition frequency or duty cycle. This feature indicates mass conservation.

1. Introduction

Clusters are aggregates of atoms or molecules, generally intermediate in size between individual atoms and particles large enough to be called bulk matter [1], usually composed from 2 up to 10^6–10^7 atoms. Clusters and nanostructured surfaces are important mainly for two reasons.

First, the size regime 1–100 nm corresponds to the size of important biological molecules, e.g. DNA, proteins, etc. For example, clusters can immobilize proteins [2] or deactivate bacteria [3], and can be used in cell-based assay, biosensors, microfabricated medical devices [4]. In addition, nano-sized particles exhibit specific catalytic properties which are lost in related bulk materials [5]. Secondly, the semiconductor industry is now entering the nanometre regime [6]. Control of surface features on this length scale is therefore essential for the fabrication of microelectronic devices (memories, processors, etc.). In particular, small islands of deposited materials can be considered as quantum objects [7–9]. Other possible technological applications are listed in the review by Wegner et al. [10].

The cluster source which combines magnetron plasma sputtering with gas condensation was introduced by Haberland [11,12]; it was theoretically and experimentally studied in numerous works, e.g. in [13–15]. In this system, cluster formation processes are characterized by critical parameters like the number of collisions between aggregating species with thermalizing buffer gas particles, i.e. by the thermalization and energy transport, in a defined volume [10,14,15]. Hence, the cluster growth is strongly related with pressure, which is set to higher values (p_c~100 Pa) [11,16–18]. However, sputtering sources are usually designed to be operated at low pressure $p \lesssim 10$ Pa. At high pressures the sputtering becomes ineffective, unstable and is not compatible with UHV (Ultra High Vacuum) standards [10,18]. For these reasons, other methods of controlling of thermalization and energy transport processes in cluster-forming volume are searched for.

In this work the cluster formation in a pulse-modulated dc-magnetron sputtering system is studied in view of finding a suitable method for controlling of cluster size/mass growth in technological applications. A single-component and chemically stable system with high nucleation rate (copper in Ar discharge atmosphere) was used [13]. The effect of external reducing of temperature is negligible because the aggregation tube was cooled only by flowing water for thermal stabilization. Such conditions allowed us to study the cluster growth in detail with high accuracy (the error estimated from our measurements ≲20%). Other purpose of our careful study is to present experimental results for development of a theoretical model for cluster formation in pulsed systems. The theoretical model has not yet been published because of lack of decent experimental data and systematic studies of the respective influence of the parameters which are thought to be relevant.

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The basic property of the formed clusters–cluster size/mass distribution–was systematically investigated as a function of parameters that are responsible for growth of nanoparticles: pressure in aggregation tube p_c, repetition frequency of the discharge f and duty cycles t_a/T, where t_a denotes pulse-on time and T denotes the pulse period. The size/mass distribution function of the formed clusters was determined by two complementary methods: (i) measurement of mass distribution by quadrupole mass filter and (ii) estimation of masses from AFM (atomic force microscopy) measurements of the height of deposited clusters.

The quadrupole mass filter measurement provides direct information about the cluster mass distribution immediately after cluster formation in the aggregation tube volume. This method allows determining singly negatively charged clusters only; no information about neutral or positively charged clusters is provided. Hence, AFM imaging was used as a complementary technique to the quadrupole mass filter measurements. Combination of both methods gives us not only the relevant mass distribution but also other quantities, such as surface coverage Γ, cluster particle flux γ, and cluster mass flux Φ. All these results are discussed together with experimental conditions to explain phenomena responsible for cluster growth affection in pulsed sputtering systems.

2. Experimental setup and diagnostic methods

2.1. Cluster source

The experimental setup is based on a nanocluster source manufactured by Oxford Applied Research (OAR, Oxfordshire, UK), see Fig. 1. The experimental setup consists of three main parts: (i) sputtering and aggregation chamber followed by (ii) quadrupole mass filter and (iii) deposition chamber [19,20].

The main part in the sputtering and aggregation chamber is a magnetron sputtering source NC200, equipped with Cu target, 51 mm in diameter, operated in balanced mode [21]. The sputtering source is situated inside the water cooled tubular region termed as aggregation tube where cluster formation takes place. The distance cathode/target - outlet diaphragm was kept constant ($a = 145$ mm). The flow of the buffer gas (Ar, purity grade 0.99999) was controlled by mass-flow controllers (MKS Instruments, Andover, MA) in range 20–150 sccm. The pressure in the aggregation tube was set to values $p_c \approx 10$–100 Pa.

The QMF200 quadrupole mass filter [20] is used to analyze charged clusters from the NC200 cluster source. Clusters can be selected according to their mass-to-charge ratio using the formula [20]:

$$m_c = 7 \times 10^7 \left(\frac{kV_q}{f_q^2 d^2} \right), \quad (1)$$

where m_c is cluster mass, d denotes the diameter of the rods ($d = 0.0254$ m), k is the correction factor ($k = 1.56$) [23], V_q denotes applied high frequency voltage on the rods, and f_q represents the voltage frequency in kHz of rod voltage ($f_q \approx 9$–12 kHz).

The cluster current is measured by picoampermeter Keithley 6478 (Keithley Inst., Cleveland, OH) and the total current usually reached values $I_c \sim (1$–$15)$ nA under our experimental conditions. However, only minor part of the charged particles is detected by the plate whilst larger amount of drifted clusters is deposited on the substrate. The mass-spectra is introduced in graph V_q vs. I_{cl}, where V_q (V_q is proportional to m_c, see Eq. (1)) is varied (controlled by QMF200) and cluster current I_c is measured by Keithley 6478. The typical mass spectrum is presented in Fig. 2. No noise reducing filters were applied during data processing.

The cluster source NC200 is able to produce both positively and negatively charged clusters [22]. In our case it is expected that clusters are singly negatively charged ($q = -e$) [22]. However, measured cluster current is the total sum of current contributions of both negatively as well as positively charged clusters. Other important fact is that electrically neutral clusters are not detected by mass filter at all. For this reason, complementary AFM diagnostic of deposited cluster was employed.

The deposition chamber serves for handling the silicon substrates (Si 100). The experimental setup is equipped by a differential pumping (two independent TM pumps 500 l/s) system with pressure ratio between aggregation p_c and deposition chamber p_d is $p_c/p_d \sim (10^3$–$10^4)$. Hence the clusters formed in the aggregation tube are driven towards the deposition chamber by a pressure gradient. The drift velocity of the clusters w can be estimated from a semi-empirical formula presented in [15]:

$$w \sim n^{4/9} \left[\mathrm{cm.s}^{-1} \right], \quad (2)$$

where n represents the cluster size in atomic mass unit. In Section 4 of the paper it is shown that the produced cluster masses are on the

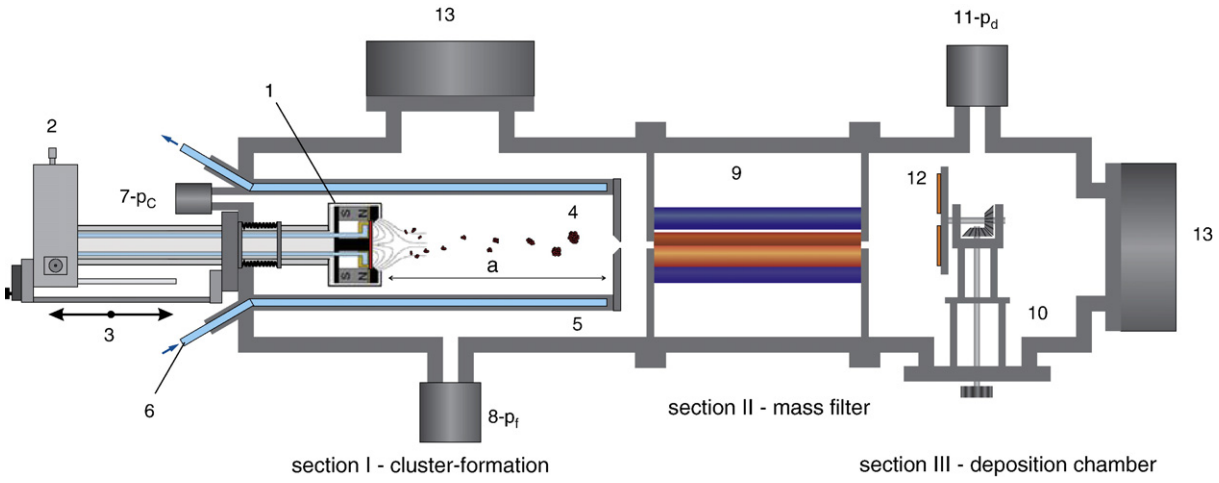

Fig. 1. The experimental setup consist of: (1) magnetron sputtering source NC200, (2) connections for buffer gas, magnetron cooling and magnetron power, (3) the magnetron is movable in axial direction, (4) aggregation tube, (a) distance between magnetron and the tube orifice, (5) cluster-forming chamber, (6) water cooling of aggregation tube, (7) pressure gauge of aggregation tube p_c, (8) pressure gauge of cluster-forming chamber p_f, (9) quadrupole mass filter QMF200, (10) deposition chamber, (11) pressure gauge of deposition chamber p_d, (12) rotational substrate holder, (13) turbomolecular pumps Pfeiffer (500 l/s).