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Production of metal-oxide nanoclusters using inert-gas condensation technique

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ABSTRACT

Inert-gas condensation is a novel technique that can be used to produce nanoclusters for different applications. In the present work, dc sputtering combined with inert-gas condensation were used to produce copper oxide nanoclusters inside an ultra-high vacuum compatible system. The size and yield of nanoclusters could be controlled by adjusting the inert-gas flow rate, sputtering discharge power, and aggregation length. The results revealed that nanoclusters were formed as a result of either or both mechanisms: three-body and two-body collisions. Herein, the three-body collision mechanism is responsible for nanocluster seed production, while two-body collision mechanism is responsible for nanocluster growth through atomic condensation and coagulation of nanoclusters. The inert-gas flow rate was found to be the main factor to determine the nanocluster size. The results were compared with a discrete coagulation system model and revealed reasonable agreement. Thin film of copper oxide nanoclusters was fabricated and used to produce a device. Electrical and optical measurements of the device revealed its suitability for practical applications such as solar cells.

1. Introduction

Nanocluster is a group of atoms or small particles bonded together with nanometer dimension [1,2]. They are used in different applications such as solar cells [3], gas sensors [4], memory devices [5], and many other applications [6,7]. Nanoclusters can be synthesized using chemical [6], physical [8], and biological methods [9]. Among those, inert-gas condensation is a novel technique that allows production of nanoclusters with high purity and custom designed properties [10]. Herein, atomic vapor of a material is produced inside a chamber in the presence of cold inert-gas which causes atomic nucleation because of the high supersaturation created by fast cooling. This technique has many advantages that include: (i) it permits adequate control of nanocluster size [10,11]; (ii) nanocluster size can be selected since the majority of produced nanoclusters are ionized and they have kinetic energy upon production [12]; (iii) they can be used to produce self-assembled nanocluster devices since they are produced in unsupported beam of nanoclusters [13,14]; (iv) production of nanoclusters without any passivation layer; and (v) composite nanoclusters can be produced by controlling the composition of the sputtering target [15].

Combination of sputtering with inert-gas condensation techniques introduces a powerful method of producing different types of metal nanoclusters. Yet, nanocluster production conditions of a source chamber (that include inert-gas flow rate, sputtering discharge power, and aggregation length) need to be optimized to enable maximizing the efficiency and size control of nanoclusters for this source. In addition, nanocluster production mechanisms still need detailed investigation and they should be correlated to nanocluster production conditions to allow optimum production of nanoclusters by inert-gas condensation [16,17]. Such investigation will allow nanocluster production at large scale, and decrease the cost for commercial applications. For example, Du et al. fabricated BaO nanoclusters by inert gas condensation from a $Ba(OH)_2$ powder [18]. They claimed that nanocluster formation occurs by agglomeration of BaO monomers deposited, that exhibit a high surface mobility at raised temperatures. Mondal et al. studied the evolution of oxidation for Cu nanocluster films prepared by soft landing of size-selected nanoclusters [19]. They observed quick formation of CuO_2 crystalline by exposure to ambient.

Copper oxide (CuO) is a semiconducting material with a variable narrow band gap depending on its grain size [20–22]. Nanoclusters of CuO are of high technological an importance since are included in wide range of applications including, but not limited to, capacitors [23], memory devices [24], sensors [25,26], catalysts [27], and others [28]. However, only limited investigations were performed on in-situ production of CuO nanoclusters using inert-gas condensation combined with dc sputtering [19,29–31]. Therefore, the objective of this work is to investigate CuO nanocluster production in-situ by inert-gas condensation and dc sputtering. The dependence of nanocluster size and yield on nanocluster production conditions that include inert-gas flow rate, sputtering discharge power, and aggregation length are studied in details. Furthermore, nanocluster formation mechanisms are investigated,

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and results are compared with the discrete coagulation system model of three-body collision.

2. Experimental

Nanoclusters were produced by dc magnetron sputtering and inert-gas condensation inside an ultra-high vacuum compatible system (UHV) produced by Mantis deposition Ltd. The UHV system is shown schematically in Fig. 1 [12], and it consists of three chambers: source, mass filter, and deposition (main) chambers. Two turbo pumps were used to pump the system down to a base pressure of ~10^{-6} Pa before nanocluster production. The nanoclusters were produced from a Cu target of purity 99.99% that was fixed on a sputter head. Both sputter head and walls of the source chamber were water cooled at room temperature. Sputtering was established by applying a dc voltage to the Cu target in presence of inert gas. Herein, argon (Ar) inert gas was introduced inside the source chamber and was used to: a) produce the plasma required for sputtering, b) establish the inert-gas condensation, and c) generate pressure gradient between the source and deposition chambers that enables nanoclusters' travel between them. The source chamber has two nozzles at its exit of diameters of 5 and 6 mm in order. The inert gas flow rate (f_{Ar}) was controlled using an MKS Instruments mass flow controller in the range f_{Ar} = 0–100 sccm.

One factor that affects nanocluster size (defined as the dimeter of nanocluster assuming an approximately spherical shape) is the aggregation length (L) which is defined as the distance between target surface and source exit nozzle [12]. Variation of L could be achieved by shifting the sputter head that is fixed on a motorized linear translator. Oxidation of Cu nanoclusters was established either by allowing oxygen gas into the source chamber or to the space between the source and mass filter chambers, see Fig. 1.

Nanocluster size was determined using a quadrupole mass filter (QMF) that consists of four parallel metal rods. Each two opposite rods were electrically connected to a potential of $(U + V\cos(\omega t))$ or $-(U + V\cos(\omega t))$, where $V\cos(\omega t)$ is an ac voltage and U is a dc voltage. The resolution of the mass filter was determined by the ratio U/V which could be varied up to 0.168. In this work, U/V was set to 0.14. The nanocluster size was scanned by changing the frequency, ω. A faraday cup was located at the exit of the QMF and connected electrically by a picoammeter was used to measure nanocluster flux, where electrical current signal represents nanocluster intensity [32].

Nanoclusters left the mass filter chamber forming a beam of nanoclusters, and they were deposited on a substrate fixed at a sample holder. The nanocluster deposition rate was measured using a quartz crystal monitor (QCM). Both sample holder and QCM were fixed on motorized linear translators so that deposition can be performed either on the sample or QCM without venting the system.

Electrical measurements were performed for devices based on thin films of nanoclusters with pairs of electrical electrodes. For device fabrication, nanoclusters were deposited on a SiO_2/Si substrate (SiO_2 thickness is 200 nm) with pre-formed electrical Au/NiCr electrodes of 50 nm for Au and 5 nm for NiCr. During nanocluster deposition, the device was connected electrically to a source measurement unit (Keithley 236). Herein, a constant voltage of 100 mV was applied across the

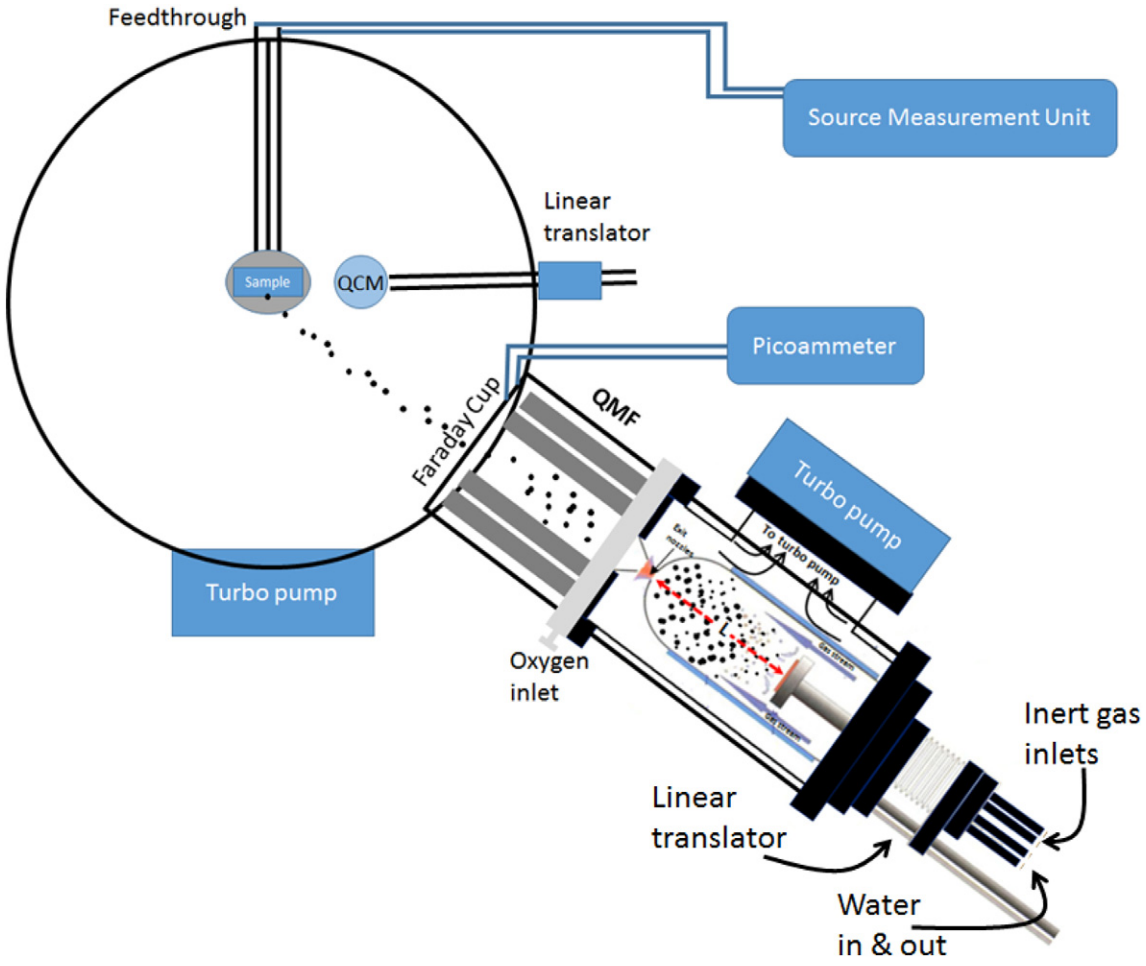

Fig. 1. Schematic diagram of the UHV system [12,32].