

Cubic and oriented Ag nano-particles by high vacuum evaporation

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ABSTRACT

Ag cubes of uniform size (70nm) and self-assembled into two dimensional arrays are formed by physical vapor deposition. The formation of the Ag cubes depends critically on the substrate composition. While heat dissipation can control the crystallization of Ag islands on surfaces, the thermal conductivity and infrared optical property of the substrate can be tuned by a suitable substrate composition. While evaporation on native SiO₂ on a Si wafer leads to the formation of flat islands, the evaporation on a thick SiO₂/ Ag/Si substrate leads to the formation of oriented Ag cubes of narrow size distribution (80-100nm).

Keywords: nano-particles, Ag cubes, physical vapor deposition, photonics, scanning probe microscopy

1 INTRODUCTION

Optical properties of metal nanoparticles depend strongly on size and shape. Controlling these parameters implies improving the control of their optical properties. Metal nanoparticles find applications in photonics, biological labeling, photography and catalysis. In case of Ag nanoparticles there has been considerable interest for their plasmon resonances in surface enhanced Raman spectroscopy.

Nanoparticles can be produced in large variety of processes such as thermal evaporation and gas condensation, laser evaporation, plasma processes, hot spray pyrolysis and other techniques [1-4]. The nanoparticles are often produced in agglomerated form and in macroscopic volumes. The coalescent particles often form a secondary fractal structure and the dispersion of the particle and the stabilization implies often wet chemical processing. When scaling down to smaller volumes and smaller linear dimensions it becomes important to control size, shape and position on a surface and at the same time keep the fabrication process sufficiently simple and cost effective. The self-assembly process is a very efficient process in biology and is particularly attractive to be used to fabricate arrays of nanoparticles on surfaces.

Metal particles with submicron size can be fabricated using spherical colloid particles as templates [2]. The metal deposition and subsequent chemical removal the template

leads to submicron sized metal particles. A number of metal nanoparticles can be fabricated within a narrow size distribution and shape through solution-phase methods. Cubic silver nanoparticles, 175nm in size have been fabricated using a solution phase method and using the crystalline silver cubes as template nano-boxes of gold have been synthesized [5,6].

We show here that metal nanoparticles with a particular shape can be obtained directly on a surface by physical vapor deposition. Deposition of a few nanometers of metal on an insulator leads in general to the formation of flat islands with circular shape which can at times be uniform in size and be arranged in a trigonal lattice. The formation of metal islands is related to the mobility of the deposited metal species on the insulating surface. The mobility and density of islands of the deposited metal depends on the temperature of the substrate and interaction with the substrate surface. At larger metal deposition the island grow in size and coalesce to form a uniform film. Island growth and shape depend on the cooling rate or heat dissipation between the deposited species and the substrate. Controlling the temperature gradient may allow to control the size and shape of the metal islands. While the cooling rate for an insulating substrate is too large to control the island shape, change of the substrate composition may help to reduce the temperature gradient to form more ordered islands or transforms the shape of the islands.

2 EXPERIMENTAL

We prepared a sample with a SiO₂ layer and a metal layer below to reduce cooling by radiation. The two layers combine a layer with low heat conductivity with a layer with high conductivity and high infrared reflectivity. We evaporated 3.5nm Ag using a resistive heating (10⁻⁶mbar) on a silicon substrate with a thin natural occurring oxide layer (1.5nm) and a silicon substrate with thick Ag layer (1200 nm) and a thick SiO₂ layer (800nm, figure 1). The Ag (3.5nm) was deposited by heating a crucible in a vacuum (10⁻⁵ torr) at a distance of 18 cm and at an evaporation rate of 0.1nm/s. The substrate was clamped on a holder and kept at room temperature. Figure 2 shows the scanning force microscopy image (CP instrument Veeco Inc) of the substrate with the thick SiO₂ layer. Cubes in the size range of 60-120nm are observed. We verified that the orientation of the Ag cubes does not depend on the scan direction. We observe that the cubes are oriented along the substrate edge.

The cube height is roughly one order of magnitude smaller than the length of the edge of the cube. They are square platelets. Figure 2 shows that some of the cubes are stacked onto one of the neighboring cubes.

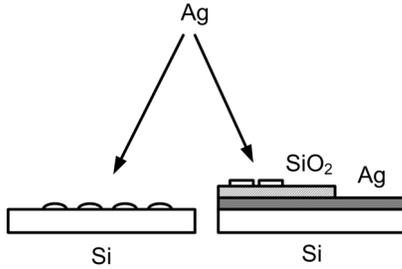


Figure 1 Substrate morphology: native Si substrate and Si substrate with Ag and SiO₂ layer.

The stacking occurs mostly on the upper right corner (Fig1.a). The flatness of the cubes and compression through entropy reduction might induce the stacking. Most cubes are not in direct contact with their neighbors. This might be due to repulsion caused by charging of the metal cubes on the insulating substrate.

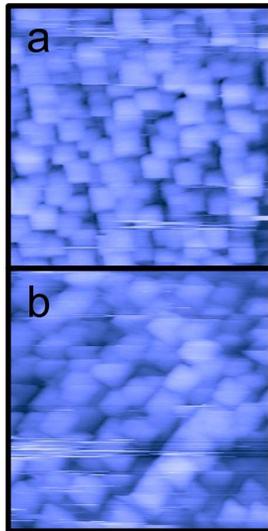


Figure 2 Contact mode scanning probe image of oriented and cubic Ag nano particles. Image size: 1 μm, vertical contrast 20nm. Average cube size: 90nm; a) scan direction parallel to cube orientation and b) scan direction rotated by 45 deg.

Inspection of the Ag cubes over larger distances shows that the densely packed oriented Ag cubes form wide cracks. To explain the formation of Ag cubes from circular shaped islands on the substrate with thick SiO₂ one has to consider self-assembly caused by Brownian motion, selective surface adsorption and weak substrate interaction. The lower cooling rate brings the system into higher ordered state to reduce the entropy of the nanoparticle system. The thermally evaporated species transfer their heat energy to the substrate. By increasing the SiO₂ layer thickness the thermal conductivity is significantly reduced (thermal conductivity of Si: 148 W/m K, SiO₂: 1W/m K).

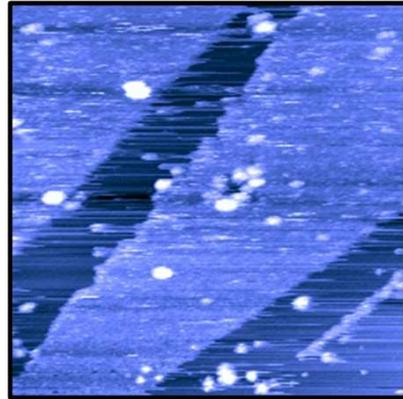


Figure 3 Contact mode scanning probe image of oriented and cubic Ag nano particles. Image size: 60 μm. Formation of wide cracks.

Furthermore the thick Ag layer serves as a perfect mirror for heat radiation below the plasmon resonance (3.92eV). The lower thermal conductivity slows the cooling rate of the deposited species which makes a transition to a next achievable ordered form possible: the formation of flat cubic shaped islands. Cubic shaped islands increase the contact between neighboring islands and this leads to a more compact island film. Interestingly we do not find a periodic arrangement of the cubes despite the narrow size distribution of the cubes. This might be explained by the fact that the system of cubes is in a state where they start to stack and form layers by compression. Figure 2 shows a larger scan (60μm) and the formation of the wide cracks. The island film is expected to contract when the cubes are formed. The formation of wide cracks can then be explained by the stacking of the cubes.

When repeating the experiment and scanning several different locations of the surface we noticed that apart of the formation of isolated cubes, round shaped islands are also often found which are on some places aligned. The cubes as shown in figure 1 are preferentially found in the center of the sample (sample size 5x8mm).

Visible inspection showed that the substrate with the Ag cubes has a reddish-brown color as compared to the grey color of the island film on the silicon wafer with a natural occurring oxide layer. Diffusive reflectance measurements confirm the shift of the reflected spectrum by 50nm to the red spectral region. For comparison no color change is observed for an equivalent Ag island film on a Si wafer [7]. We note that the reflectance spectrum is influenced by the substrate structure. Depending on the thickness of the Ag cube layer light, more or less light will reach the reflective layer in the substrate. The Ag layer on top and in the substrate, form a cavity. The color change is also related to the particular substrate structure in the form of a semi-cavity. As a result the change in the diffuse reflectance spectrum cannot directly be related to the properties of the Ag nanoparticles.

3 CONCLUSION

Our experimental findings suggest that the cooling rate of the substrate for ultra-thin films can be sufficiently reduced by changing the architecture of the substrate. By combining a thick insulating SiO₂ layer with a highly reflective metal layer, the cooling is reduced and this causes the formation of cubic and oriented Ag nanoparticles (80x80x4nm³) in the center region of the substrate. Stacking of the nanoparticles along the cube diagonal and the formation of wide cracks are observed. The orientation of the cubes and the uniform size distribution shows the importance of collective effects and self-organization. Tuning the substrate architecture to reduce the cooling rate of the evaporated metal species is a possible low cost root to fabrication of self-assembled metal nanostructures on surfaces.

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