Fabricate Ultra Thin Alumina Membranes masks to Produce Al-Nanostructure by Using Physical Vapor Deposition Technique

Wafaa M.S. Al-Khayat¹,³, Haider Abdullah Kadhum² and Gerhard Wilde³

¹²Department of Physics, College of Science, Al-Mustansiriyah University, Baghdad, Iraq
³Institute for Material Physics, University of Münster, Wilhelm-Klemm-Str. 10

ABSTRACT

Aluminum nano particles commonly are used in energetic formulation and may be released into environment during their handling and use. In this paper aluminum nano particles are prefer by using physical vapor deposition technique (electron beam) with using ultra thin alumina membrane to get highly order array of aluminum nano particles, the results of photoluminescence (PL) measurement and scanning electron microscope image are done and described.

Keywords: aluminum nano particles, anodig alumina, UTAM templates, characterization.

1. INTRODUCTION

Multifunctional surface patterns on substrates are the foundation of semiconductor devices. To improve the performance of an integrated device, size- minimization of surface patterns (device miniaturization) is technologically required by industry to reduce the size of the individual device component. Thus, the present smallest feature size of integrated circuits has decreased to several tens of nanometers. This is the reason why surface Nano-pattern became one of the most intensively studied topics in the past decade in the fields of material science and engineering. In order to control the properties of surface nanostructures and hence devices, it is mandatory to fabricate processes of surface nanostructures are highly desirable for device application [1, 2].

There are different Nano-structuring techniques in patterning various building blocks (e.g., Nano dots, Nano particles, Nano tubes, Nano pillars, Nano wire…) on the surface of substrates, main including lithographic methods, Nano- imprinting and replica molding processes, scanning probe microscope (SPM) writing technique and template – based method. Among these technique, surface patterning methods using template-based methods are time saving approaches with low equipment cost in fabricating large-scale ordered arrays of surfaces structures compared to lithography methods especially electron-beam lithography) and SPM writing processes. So far many kinds of templates have been used to prepare surface patterns on substrates (usually semiconductor wafers). The motivation of using templates in creating surface patterns is to transfer the structural features of the templates to the surfaces structures on substrate, obtaining surface patterns with similar morphological features to those of the templates. Templates can be used for different purposes in the patterning processes, including masks for etching, evaporation, and reaction, substrates for growth and supporting, and molds for replication [3, 4].

There are three widely-used templates that are prepared using self-assembly process: ultra-thin alumina membranes (UTAM), monolayer polystyrene (PS), sphere arrays, and block copolymer (BCP) patterns. The surface patterns synthesized using these templates have promising device application potentials due to the low-cost and time-saving fabrication processes of surface structures. As three major patterning templates derived from self-assembly processes, PS, BCP and UTAM templates have their own unique aspects. First, the features size of the building blocks of the surface patterns prepared using BCP, UTAM and PS templates can be adjusted within the range of about 5-50nm, 5-500 nm and 50nm-4.5µm respectively. This means that these three template- based surface patterning techniques can cover the whole range from the quantum size range. UTAM is a hard template of metallic oxide that can only be removed by chemical dissolution. Moreover the UTAM has parallel-aligned cylindrical Nano prose [5, 6].

Nanoparticles are being used in broad range of applications; therefore, these materials probably will enter the environment during their life cycle. The objective of the present study is to identify changes in properties of Nano particles released into the environment with a case study on aluminum Nano particles. Aluminum nano particles commonly are used in energetic formulations and may be released into the environment during their handling and use.
[14]. There has been significant recent interest in the synthesis and properties of nano scale reactive metal particles, especially aluminum nanoparticles, for a number of current and potential applications. The large specific surface area and energy density and their associated high reactivity of aluminum nano particles have made them unique combustible additives in propellant formulations for significantly higher and faster energy release. Nanoscale aluminum may also offer significant opportunities in the development of high capacity hydrogen storage materials; either directly or through other reactive aluminum compounds were Nano sized for improving their hydrogen-storage-related properties. These nanoparticles supported on surface-oxidized carbon nano fibers or confined in ordered mesoporous silica exhibited lower dehydrogenation temperature and faster kinetics than those of their corresponding bulk materials [15].

2. EXPERIMENTAL WORK

2.1. UTAM surface nano-pattering:

UTAM surface Nano-pattering is an emerging surface Nano-structuring technique in which UTAM’s are used as deposition [7,8], etching [9,11] or replication masks[12,14]. As a spherical type of anodic alumina membranes, UTAM is a through-hole membrane with small thickness of about several hundred nanometers. UTAM's can be placed or fabricated on substrates so as to synthesize ordered arrays of surface nanostructures. Two different types of UTAM’s can be prepared on substrate attached UTAM and connected UTAM. In this paper studies choose attached (Al) foil, an UTAM can be prepared using a very short second-anodization time, after removing the (Al) foil and a barrier layer at the back side of the sample, the UTAM is transferred to the surface of a substrate forming an attached (UTAM). A modulated anodization process was select using oxalic acid solutions; the anodization was carried out at an extremely low temperature of 8 °C. this largely decreased the growth rate of UTAM's and an UTAM with a thickness of about 80 nm can be prepared as shown in Fig.1. Moreover, we used a well-controlled pore-opening process to prepare UTAM with quantum-sized pores. There is an alumina barrier layer between the pore bottom and the Al-foil of as-prepared UTAM’s. The pore opening (etching the barrier layer) was carried out using a 5wt% H₃PO₄ solution. The diameter of pore-opening increases with the etching time, this mean that the diameter of the pore-opening can be controlled based on the adjustment of the etching time. After obtaining UTAM on substrates, regular arrays of different surface nano structure can be prepared using vacuum evaporation processes E-beam. Evaporation followed by the removal of the UTAM, nano dot array and nano particles are fabricated on substrates. In the meantime the evaporated material also deposits on the top of the UTAM forming a porous top layer. [further evaporation will close the pores of this top layer (i.e., capping the UTAM pores completely), resulting in Nano ring structures on the bottom surface of the top layer). Advantageous features of the UTAM Nano patterning technique, such as the tunable structural parameters and large pattern area (1cm²), high through put and low equipment costs of the fabrication processes, general applicability in fabricating different nanostructures, make the technique suitable to fabricate ordered surface nanostructures with tunable properties and hence Nano-devices with good performance.

![Fig.1: UTAM masks with different diameters.](image)

2.2. Al- nanostructures:

Nano dots are one of the most important building blocks of surface patterns for diverse device applications. The UTAM surface nano-pattering has been recognized as a very efficient way in fabricating arrayed Nano dots with well-defined structures that are highly favorable for different property investigations [such as surface enhanced Raman scattering(SERS)].

UTAM with quantum sized pore-opening can be used to fabricate ordered arrays of quantum dots and nanoparticles by controlling on pores diameter and thickness .The large scale ordered arrays of quantum dots and nanoparticles on substrates are promising candidate structures for new types of optoelectronic and display devices on the basis of the quantum confinement effect.

However are two challenging points preventing the UTAM patterning in synthesizing regularly arrayed quantum-sized structures (<10-20 nm). First, the arrangement regularity of pores is poor when the pore diameter is smaller than 20 nm. Second, UTAM that can be used for surface patterning should have pores with aspect ratio smaller than 10nm, e.g., the thickness of an UTAM with 20nm-diameter pores should be smaller than 200nm or difficult to be
prepared due to the large growth rate of UTAM's. Therefore to prevent this problem for this step, fabricated UTAM masks with pores diameter near to 30 nm and thickness 250 nm, also adjust the evaporation rate on 0.5 Å/sec.

Aluminum nanoparticles are receiving (being) considerable interest lately as a possible approach to enhance the energy release from energetic materials. It is well-known that fine metal particles are highly reactive and in many cases pyrophoric; however, qualification of reactivity has not been extensively explored [15]. Also aluminum nanoparticles have increasingly gained attention because of their potential incorporation in explosive and propellant mixtures [16].

Various methods were employed to produce aluminum nanodots and nanoparticles like wet-chemical and oxidation. In the present study, aluminum nanodots and nanoparticles produce by physical vapor deposition by using electron beam technique (EB), small pieces of (Al) have impurity about 99.999, put in graphite crucible after that but the samples of Si with UTAM mask in the holder and centered above the crucible, then the deposition chamber was evacuated until reach $2 \times 10^{-6}$ mbar, next the deposition procedure was carried out by apply current 15, 18, 30 m.Amp corresponding this current the deposition rate reach to 0.1, 0.2 and 0.5 respectively, after the deposition process was finished the samples were ready to measurement, this measurement consist of several analysis like SEM, PL and Regularity analysis.

3. RESULTS AND DISCUSSION

3.1 Photoluminescence (PL):

Figure (2) displays the PL spectra of Al nanoparticles and nanodots measured at room temperature for different deposition rate (0.1, 0.2, 0.5 Å/sec) respectively. All plots extend to cover blue and red emissions. The fact that distinct peaks are not observed might be related to the substrate or to size confinement effects [17-19]. The appearance of broad peaks centered in the red region of the visible spectrum is attributed to the presence of silicon vacancies in the lattice. The emission results from the recombination of photo-generated charge carriers that are bound to shallow traps. The other peak centered in the blue region of the spectrum is due to the band-to-band transition in nanocrystalline regions.

![Figure 2: Photoluminescence spectrum of Al nanoparticles and nanodots on a Si wafer.](image)

- a) Deposition rate of 0.1(Å/sec).
- b) Deposition rate of 0.2(Å/sec).
- c) Deposition rate of 0.5(Å/sec).

3.2 Scanning Electron Microscope (SEM):

Figure (3) shows scanning electron micrographs of the deposited Al nanoparticles prepared by electron beam deposition. The Si wafer substrates were placed directly above the target. The sample generated at $2 \times 10^5$ mbar showed a rough surface structure composed of Al dot and spherical nanoparticles. These spherical particles are observed to be formed from the affect of using UTAM masks, UTAM masks prepared a suitable surface to build many particle on it. The average diameter are (0.51nm, 0.45nmv, 0.441nm) respectively and the average height are (90nm, 84.686nm, 83.886nm) respectively [20, 21].

![Figure 3: Scanning electron micrographs of Al nanoparticles.](image)
In order to analyze the obtained regularity, \( R \) of the nanoparticle arrays quantitatively, a method based on the Voronoi tessellation has been applied, as illustrated in Figure 4, and Figure 5 shows the results of the regularity analysis of Si nanoparticles as obtained by applying the following equation:

\[
R = \frac{1}{N} \sum_{i} \frac{\text{length of the shortest side}}{\text{length of the longest side}} \leq 1 \quad \ldots \ldots \ldots (2)
\]

The calculated hexagonal regularity, which equals \( R = 1 \) for perfect hexagonal order is equal to:

\( R_{\text{Al}} = (0.464, 0.4742, 0.5996) \) respectively

This value corresponds to a medium regularity with the size of the hexagonally ordered regions that span about the first and second nearest neighbor shells.

The atomic force microscope produces topological images of surfaces at very high magnification and it is even possible to observe the atomic structure of crystals. The aim of this study with the atomic force microscope is to obtain information about the formation of the surface.

The morphology of the Al-nanoparticles film is very sensitive to the deposition parameters, such as the deposition rate, the position of the substrate and the regularity of the UTAM mask.

**Figure 4:** Principle of the regularity analysis, depending on the Voronoi tessellation.

**Figure 5:** Regularity analysis of Al nanoparticles. a) Deposition rate of 0.1(A°/sec). b) Deposition rate of 0.2(A°/sec). c) Deposition rate of 0.5(A°/sec)

**4. CONCLUSIONS**

1. This article focusing on the important of used templates prepared by self-assembly processes (UTAM), to obtain large scale array of nano dots and nanoparticles, The cost-effective and time-saving fabrication processes of template-based surface nano-patterning methods are highly desirable for industrial applications in fabricating different nano-devices, giving rise to broad application of template-prepared surface nanostructures. Also the effect of pores diameter and thickness of UTAM on the type of shapes and configurations nanostructure.

2. When the electron beam procedure carried out at deposition rate (0.1, 0.2) A°/sec, the result obtain Al- nanoparticles but when deposition occurs at deposition rate (0.5) obtain Al- nanodots.
3-The photolumince (PL) spectra at room temperature revealed a broadband spectrum in a range 400nm to 700nm and another small beak from 700nm -900nm for Al-nanoparticles but for Al-nanodots notice peak at 420nm, 550nm and 875.

4- The SEM images show array of Al-nanodots and nanoparticles ,the analysis depends on Quantitative Hexagonal Regularity Calculation principles show the calculated hexagonal regularity which equals R=1 for perfect hexagonal order is equal to :

\[ R = (0.464, 0.4742, 0.5996) \]

REFERENCES