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Fabrication of ultra-flat silver surfaces with sub-micro-meter scale grains

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ABSTRACT

Most fabrication methods for obtaining metal films rely on direct deposition techniques and usually yield surfaces with small grains and a significant surface roughness. In contrast, methods based on physical vapor deposition followed by template-stripping (TS) yield surfaces with large grains separated by smaller ones. We report a fabrication method that combines TS with annealing prior to TS. By optimizing the deposition rate, deposition temperature, and the annealing temperature and time, before TS, we were able to produce high quality Ag surfaces with low root-mean-square surface roughness (0.5 ± 0.1 nm), large grains of 0.84 ± 0.23 μm^2, and a low surface fraction of pinholes of 0.01%. Thus, post-deposition annealing (prior to TS) changes the topography of Ag^{TS} surfaces significantly. The X-ray diffraction and X-ray photoelectron spectra show that the annealed Ag^{TS} surfaces are polycrystalline and consist of face-centered cubic Ag, do not contain silver oxides, and can be stored for several months. Ellipsometry shows that these Ag^{TS} surfaces have good optical properties and are promising for applications in plasmonics.

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1. Introduction

Flat surfaces with large grains and low densities of defects are important for applications in (molecular) electronics [1–4], plasmonics [5–7], nano- and micro-fabrication [8], tribology [9], and to obtain good quality self-assembly of monolayers (SAMs) [10]. The morphology of the metal surface affects the quality of an interface between an organic layer and an electrode (e.g., defects can form charge trapping sites [11,12]), and influences the supramolecular structure of the organic component which consequently affects the performance of molecular [2–4] or organic electronic devices [13,14]. The quality of dielectrics (of both organic [15,16] and inorganic dielectrics such as SiO_2, HfO_2, Y_2O_3, MgF_2, and nitride derivatives [14,17,18]) is related to the topography of the metal surface on which the dielectric is grown and is important to minimize leakage currents in transistors [19,20], capacitors [21,22], or magnetic tunnel junctions [23]. Defects in the surface induced by, for instance, grain boundaries or pinholes (deep holes in the metal layer that form due to differences in surface energies between the metal and the support; see below) [24], scatter the electrons [25], cause Joule heating [26,27], increase resistance [28], or dampen propagating surface plasmons [5,29–31]. The flatness of a metal surface affects the adhesion of the photoresist to the metal which is a common fabrication step in nano/micro fabrication [32]. We showed that for applications in molecular electronics it is important to minimize the surface fraction of exposed grain boundaries because they cause defects in the topography of the surface that exceed the dimensions of the molecules they support [2,3]. Newcomb et al. [33] showed how the surface wetting properties of SAMs depend on the roughness of the metal surface as small changes in topography of the metal surfaces induce significant changes in the surface energies [34–36].

Metal surfaces contain a large number of defects induced by grain boundaries, step-edges, and dislocations, and mostly they consist of polycrystalline surfaces exposing a variety of crystal planes [25]. The fabrication of flat surfaces with large grains, and consequently small areas of exposed grain boundaries, without pinholes has been challenging because of the large number of process parameters that one needs to control [37] (Appendix A). For metal films prepared by physical vapor deposition, control over the evaporation parameters and metal film growth kinetics (in plane growth, island formation, or layer-by-layer growth) depends on a fine balance between diffusion rates of the atoms along the surface, deposition rate, and temperature [37]. In specialized techniques, such as pulsed layer deposition [38], or atomic layer deposition [39], high quality surfaces can be obtained for particular combinations of materials, but such methods are not broadly accessible. In addition, these surfaces cannot be stored in ordinary laboratory conditions and readily adsorb contaminants from the environment and/or are not stable in ambient conditions and therefore have to be used immediately after fabrication or have to be cleaned which may cause surface defects [40–42]. Seed-layers (e.g., Ti and Ge for forming Au and Ag

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films, respectively) promote the growth of smooth metal films and yield surfaces with a low root-mean-square (rms) roughness of ~0.2 nm measured over an area of 1 μm^2 [43,44]. Williams et al. [43] showed that a Ge layer of 1–2 nm thickness form Ag films with very small grains and grain boundaries with low peak-to-valley distances of 0.6 nm. This method works well for Ag films up to 20 nm thick, but for optical applications, thick (>50 nm) Ag films are required. Carmichael et al. [45] reported a chemical mechanical polishing method that can produce adhesive-free ultra-smooth surfaces (3.8 ± 0.5 Å) of Au on a Ti adhesion layer which makes it possible to obtain both thick and smooth gold films.

Template-stripping (TS) is a useful method for fabrication of metal thin films that can resist contamination and aging [46]. Usually, clean and ultra-flat substrates (Si/SiO_2, or mica) serve as templates onto which the metal film is deposited (mostly by evaporation; here we used thermal evaporation); a composite of curable adhesive and glass help to strip the thin film away from the templates. During storage the metal surface of interest is in contact with the wafer (and not exposed to the environment) and therefore protected from oxidation and contamination. This method gives flat surfaces that are scalable (up to square centimeter range) [40,47] and is compatible with a variety of metals including Ag, Au, Pt, Pd and Ti/TiO_2 [40,46,48]. We found that these surfaces contain large grains (~0.4 μm^2), and these grains are separated by smaller grains 25–100 nm in diameter [3,40].

Here we describe a procedure that yields flat Ag surfaces with average grain sizes of 0.84 ± 0.23 μm^2 that are in the same plane (the bearing volume BV (Appendix B) is $0.7 \pm 0.1 \times 10^5$ nm^3) with pinholes making up only 0.01% of the surface area. We obtained these surfaces by introducing an annealing step before TS (see below) and optimizing four parameters: i) the Ag deposition rate, ii) the temperature of the substrate during the metal deposition step, iii) the annealing temperature before TS, and iv) the annealing time before TS. We found that by optimizing the annealing temperature (200 °C) and time (30 min) before TS we minimized the formation of pinholes (defined as hole into the metal surface with a depth of >10 nm) while maximizing the average grain size. This annealing step effectively removed the small grains that are usually present in TS surfaces (the grain size increased by a factor of 20 relative to TS surfaces prepared without this annealing step; see reference [29] for instance). The annealing step did not result in the formation of silver oxides. These surfaces could be stored under ordinary ambient conditions for three months without the formation of AgO_x, or contamination from the ambient environment. These clean surfaces are available on-demand as they can simply be stripped from the template (here a Si wafer with the native layer of SiO_2; Si/SiO_2) prior to use. Despite these benefits, the stability of the TS surfaces is limited to the type of glue used which may, for instance, swell in certain solvents or decompose at high temperature. Previously we demonstrated that these surfaces are useful for applications in molecular electronics [2,3], and here we show that these surfaces have good optical properties resulting in large plasmon propagation lengths.

2. Materials and methods

2.1. Metal deposition

High grade silver (0.125″ diameter × 0.125″ length) with purity of 99.999% was obtained from Super Conductor Materials, Inc. (USA). We used silicon (<100>, p-type) wafers from University Wafers (USA) with a thickness of 525 ± 25 μm and one side polished. For metal deposition we used a thermal evaporator with a heater at the back of a sample holder (Shen Yang Ke Yi, China). The tungsten boats were obtained from Kurt J. Lesker. We started the metal deposition at a base pressure of 5×10^{-5} Pa, during the evaporation the vacuum gradually increased to ~2×10^{-4} Pa. After evacuating the evaporation system to the base pressure, we increased the temperature at a rate of 15 °C per min to the pre-determined deposition temperature which was accurate within ±2 °C. No heating was applied for deposition at room temperature (RT) which was approximately 24 °C. Before starting the metal deposition, we waited 2–4 min to stabilize the temperature. This step ensures that the deposition rate could be controlled well and removes potential contaminations from the Ag. The distance between the substrates and the silver source was kept at 40 cm and the rotation rate of the sample holder was 10 rpm. The deposition rate was controlled by a SQC-310 thin film deposition controller with a QI8010 sensor crystal. The temperature of the sample holder was controlled by substrate heating units (SHIMAX, MAC3A).

2.2. Template-stripping

We cleaned the glass slides (Sail, 7105 microscope slides, 1 mm thick) with piranha solution (H_2SO_4:H_2O_2 = 1:2) for 20 min, followed by washing with H_2O and drying in a stream of N_2 gas, followed by cleaning with a plasma of air for 1 min at a pressure of 60 Pa (Cute, Femto Science). We used an optical adhesive (OA; Norland, No. 61) to glue the glass supports to the metal layer which was cured in a UV light source of 100 W (UVP, Analytik Jena) for 1 h. Young's modulus of cured OA is ~1.0×10^9 Pa.

2.3. Characterization of the surfaces

Atomic force microscopy (AFM) images were recorded on a Bruker Dimension FastScan AFM by using tapping mode tips with intermittent contact (FASTSCAN-A, resonant frequency: 1.4 MHz, force constant: 18 N/m). We recorded the X-ray photoelectron spectra (XPS) using an ESCA/SIMSLAB system with a Mg $K\alpha$ X-ray source ($h\nu$ = 1246.6 eV) at 10 mA. The binding energy scale was referred to the Au $4f_{7/2}$ (84.00 eV) signal and the background subtraction was applied to the spectra. The X-ray diffraction (XRD) studies were carried out on a Bruker D8 ADVANCE Power X-ray diffractometer with a 2.2 kW Cu anode and step size of 0.02° at 25 °C and conventional θ-2θ "reflection" geometry. The effective dielectric functions were recorded with a Nanofilm-EP4 ellipsometer equipped with an internal solid-state laser (max. laser power: 50 mW).

2.4. Determination of pinhole area

We used the particle analysis function of NanoScope Analysis (version 1.40) to determine the pinhole area defined as the area below an arbitrary threshold value of 10 nm below the plane of the grains. The pinhole fractions (χ_{ph}; determined by Eq. (A3-1) are reported in Table 1 and determined using four AFM images of 5×5 μm^2. We noticed that some of the pinholes grew along the grain boundaries and merged in extreme conditions.

2.5. Bearing volume analysis

We use a previously reported method to determine the bearing volume (BV) that does not rely on arbitrary chosen threshold values [3]. Briefly, we estimated the grain size (A_{gr}) of the surfaces by a "split and count" method (Appendix B). We divided the 5×5 μm^2 AFM images into 400 boxes of 250×250 nm^2 (to a precision of 1/4, 1/2, or 3/4 of the area of each box) and counted the number of boxes occupied by each grain. The relative number of grains (N_{gr}) is then determined by normalization of A_{gr} to the largest grain size. We determined the width of the grain boundaries (d_{gb}) using 15 line-scans and plotted the values of d_{gb} in histograms. To these histograms we fitted Gaussians to determine the mean value of d_{gb} which was used to calculate the area of the grain boundaries (A_{gb}). Here, the errors represent the standard deviations derived from the Gaussian fits. The rms roughness was determined by using NanoScope Analysis. The BV was finally calculated with $BV = N_{gr} A_{gb}$ rms.

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