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Development of pinhole-free amorphous aluminum oxide protective layers for biomedical device applications

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ABSTRACT

This paper describes synthesis of ultrathin pinhole-free insulating aluminum oxide layers for electronic device protection in corrosive liquid environments, such as phosphate buffered saline (PBS) or clinical fluids, to enable emerging biomedical applications such as biomolecular sensors. A pinhole-free 25-nm thick amorphous aluminum oxide layer has been achieved using ultra-high vacuum DC magnetron reactive sputtering of aluminum in oxygen/argon plasma followed by oxygen plasma post-processing. Deposition parameters were optimized to achieve the best corrosion protection of lithographically defined device structures. Electrochemical deposition of copper through the aluminum oxide layers was used to detect the presence (or absence) of pinholes. FTIR, XPS, and spectroscopic ellipsometry were used to characterize the material properties of the protective layers. Electrical resistance of the copper device structures protected by the aluminum oxide layers and exposed to a PBS solution was used as a metric to evaluate the long-term stability of these device structures.

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1. Introduction

Aluminum oxide or *alumina* films are well known for their high strength, chemical stability/corrosion resistance, insulating properties, and wear resistance. The material has been extensively characterized to support an ever-growing set of applications from mechanical to optical to electronic [1–5]. In this work, application of ultra-thin pinhole-free layers of aluminum oxide for corrosion protection/electrical insulation of electrical device structures [6,7] is explored. Conformal thin-film aluminum oxide layers were deposited using DC magnetron reactive sputtering to allow protection on non-planar geometries.

2. Experimental details

2.1. Aluminum oxide deposition

All materials synthesis and optical/e-beam lithography were done in a class 100 cleanroom to avoid wafer contamination. An ultra-high vacuum DC magnetron sputtering system (a base pressure of $1.33*10^{-7}$ Pa) was used for metal and aluminum oxide depositions. Two types of wafers, highly conductive p-doped silicon wafers (etched in 10% HF buffer solution to remove native oxide) and silicon wafers coated with a 500 nm-thick silicon oxide, were used as described below.

The AJA six-source UHV sputtering chamber equipped with AJA 2″ sputtering guns in balanced magnet configuration was used. The depositions were done at room temperature. 99.99% purity aluminum target was 3″ in diameter. The center-to-center distance for metal deposition between the center of the sputtering target to the center of the wafer was 25 cm and the sputtering gun tilt was kept constant at 50 degrees off the wafer vertical direction.

The sputtering system was calibrated for every target. Based on the time of deposition of a metal and the resulting thickness measured by Focused Ion Beam (FIB), the rate of deposition of aluminum was calculated to be equal to 5 nm/min.

Aluminum oxide deposition was preceded by sputter-deposition of a 1 nm thick aluminum layer in 0.67 Pa of Argon and post-deposition oxidized in O_2 plasma to form an aluminum oxide seed layer. Aluminum oxide was then deposited by reactive sputtering from 99.99% purity aluminum target in Ar/O_2 mixture in an ultra-high vacuum system. Oxygen plasma was generated from oxygen gas using DC-powered ion source.

The deposition parameters were optimized to give an aluminum oxide layer with the best protective/insulating properties: the deposition pressure (0.33 to 2.7 Pa at 35 sccm flow rate of Ar and varying O_2 partial pressure), oxygen partial pressure (flow rate between 3 and 7 sccm), sputtering gun power (50 to 200 W), substrate RF bias power

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(5 W to 30 W), and deposition time (50 to 2000 seconds) were varied to optimize the aluminum oxide properties.

Deposition conditions were varied to adjust film properties, which were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Spectroscopic ellipsometry was used to gauge the film thickness and the corresponding deposition rates. Corrosion protection/electrical insulation properties of the aluminum oxide films were evaluated using lithographically defined metallic device structures that were overcoated with the developed material, then exposed to corrosive fluids.

It was found that the oxygen flow rate, which affects the partial pressure of oxygen in the processing gas, is the most critical parameter for a given deposition rate. Adjusting deposition rate (by increasing or decreasing the deposition power) required corresponding increase of decrease of the oxygen flow rate.

Post-deposition processing using UV/O_3 and/or O_2 plasma was used to further improve the insulating/corrosion-resistance properties (See Section 3.3).

2.2. Testing for pin-holes

The presence of pin-holes was detected by electrochemical deposition of copper onto aluminum oxide coated conducting Si wafers (from 0.1 M $CuSO_4$*$5H_2O$ in water electrolyte) using conventional 3-electrodes single compartment electroplating cell [8]. In the presence of pinholes, copper is deposited from the electrolyte into the pinholes resulting in the growth of mushroom-like structures over the pinholes easily resolvable with optical microscopy or SEM [9]. Electrochemical deposition was performed in a three-electrode plating cell with a 1 mm-diameter copper wire used as the reference electrode (at 0 V), platinum mesh was used as the counter electrode, and an over-potential of −350 mV was applied to the indium-coated back of the silicon wafer (the cathode). Pinhole density was evaluated from the electroplating current and SEM images were taken for every sample to link the pinhole density to the electrodeposition current.

2.3. Evaluation of aluminum oxide insulating properties

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to evaluate insulating properties of the deposited aluminum oxide films. An electrochemical cell (EG&G, Inc.) with three-electrode setup and Gamry instrument were used for the measurements. Platinum was used as a counter electrode, Ag(s)/AgCl(l) was used as a reference electrode, and a specified sample was used as a working electrode. A 1-inch square sampling area was used in all experiments. Ten millimolar of a PBS solution (pH 7.4) was used as an electrolyte. The cyclic voltammograms from the CV measurement were obtained by applying a potential from 0 to 800 mV at a scan rate of 50 mV/s and the current density at the working electrode was measured and plotted against the potential. The Nyquist plots from EIS measurements were obtained by applying a DC voltage of 100 mV and AC voltage of 10 mV·rms with frequencies ranging from 100 kHz to 100 mHz.

2.4. Patterning of device structures

E-beam lithography was used for device patterning, as illustrated in Fig. 1. First, a 5 nm tantalum adhesion layer was deposited (35 sccm flow rate of Ar, sputtering gun power 100 W, substrate RF bias power 10 W, and deposition time 45 seconds), followed by spin-coating of 60 nm of polymethylglutarimide (PMGI) undercut layer and 1 μm of polymethyl methacrylate (PMMA). The PMMA layer was exposed using e-beam lithography through a stencil mask. Resist development in 3:1 IPA/MIBK (Isopropyl Alcohol/Methyl Isobutyl Ketone) for 30 seconds was followed by PMGI etching in a 2.3% TMAH solution (Tetramethylammonium Hydroxide) to form an undercut (for subsequent lift-off step). A copper layer (100 to 400 nm thick) was sputter-deposited and the PMMA was dissolved in an acetone bath to lift off the layer of copper that was evaporated on top of the PMMA, leaving behind an array of copper patterns embedded in PMGI. To remove the PMGI leftovers, the sample was placed into fresh 2.3% TMAH solution for 1 minute. Alumina films were deposited on the copper patterns through a 1 cm^2 opening (to protect the sensor structure and leave the copper contacts bare). A schematic of the resulting copper device structure is shown in Fig. 1. The device structures were built both on conducting Si wafers and on silicon oxide coated wafers.

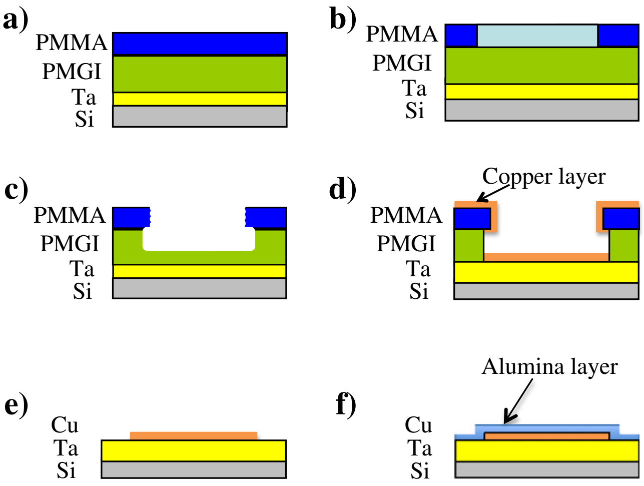

Fig. 1. Illustration of the patterning process used for making device structures.

2.5. Fourier transform infrared spectroscopy (FTIR spectroscopy)

The FTIR spectroscopy was done using a Nicolet NEXUS-IR 670 instrument. The measurements were performed on the 100- and 200-nm thick sputtered aluminum oxide samples produced at optimized conditions on silicon wafers transparent to the FTIR laser beam. Each measurement was corrected by subtracting the spectrum of a silicon wafer without aluminum oxide film. The chamber was flushed with ultrahigh-purity nitrogen gas for 10 minutes before each measurement to allow the beam to stabilize and to remove all residual gases from the chamber.

2.6. Cyclic voltammetry and electrochemical impedance spectroscopy

A commercial UV/Ozone processing tool (Model T10X10/OES by UVOCS, Inc.) was used for UV/O3 post treatment [10]. The system has no adjustable parameters except for process time. Ozone is generated as a result of UV light interaction (254 nm wavelength) with ambient oxygen. Fifty-nanometer thick aluminum oxide films deposited at three different conditions were compared: 1) plain aluminum oxide — the sputtered film at optimized conditions (10 W bias, 100 W aluminum deposition rate, 0.67 Pa process pressure, and 6-sccm flow rate of oxygen) on silicon dioxide wafer which provided the pinhole-free corrosion-protective layer, 2) UV aluminum oxide — the film described above exposed to ultraviolet (UV) for 10 min after sputtering process, and 3) O_2 aluminum oxide — a film deposited under the optimized conditions, but intermittently exposed to oxygen plasma during the sputtering process.

To prepare this film, 5 nm of aluminum oxide was sputtered on, then exposed to O_2 plasma for 5 min. These steps were repeated until the final thickness was reached. The rationale for these experiments was to test if UV/O_3 and/or O_2 plasma could help oxidize the aluminum oxide film after or during deposition process, respectively,