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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.

Keywords

biosensor; corrosion; ultrathin coating; aluminum oxide; DC magnetron sputtering

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.

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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 O₂ plasma to form an aluminum oxide seed layer. Aluminum oxide was then deposited by reactive sputtering from 99.99% purity aluminum target in Ar/O₂ 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 35sccm flow rate of Ar and varying O₂ partial pressure), oxygen partial pressure (flow rate between 3 and 7sccm), sputtering gun power (50 to 200W), substrate RF bias power (5W to 30W), and deposition time (50 to 2000sec) 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 or decrease of the oxygen flow rate.

Post-deposition processing using UV/O₃ and/or O₂ 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 0.1M CuSO₄*5H₂O 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 1mm-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. 10mM 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 Figure 1. First, a 5 nm tantalum adhesion layer was deposited (35sccm flow rate of Ar, sputtering gun power 100 W, substrate RF bias power 10 W, and deposition time 45 sec), followed by spin-coating of 60 nm of polymethylglutarimide (PMGI) undercut layer and 1 μ m 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 400nm 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 cm² opening (to protect the sensor structure and leave the copper contacts bare). A schematic of the resulting copper device structure is shown in Figure 1. The device structures were built both on conducting Si wafers and on silicon oxide coated wafers.

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. 50-nm 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) O₂ 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 O₂ plasma for 5 min. These steps were repeated until the final thickness was reached. The rationale for these experiments was to test if UV/O₃ and/or O₂ plasma could help oxidize the aluminum oxide film after or during deposition process, respectively, and improve the film insulating/resistance properties. No reliably measurable changes in XPS spectra have resulted from such UV/O₃ treatments. We speculate that the observed improvements in insulating properties (see below) are mainly due to healing of a few defects in the films (the primary cause of the protective coat failure) rather than global change in aluminum oxidation state in the film. Further optimization of how the plasma treatment influences the deposition rate, density of film, FTIR and ellipsometry data for 5 and 7 sccm alumina films are a subject for future work.

3 RESULTS AND DISCUSSION

3.1 Oxygen flow rate optimization

Aluminum oxide samples were prepared using DC magnetron sputtering at 10 W bias power and 100 W target power at various flow rates of oxygen. The samples show an increase in electroplating current with time for samples made with an oxygen flow rate of 5 sccm and lower (see Figure 2). The samples made with an oxygen flow rate of 7 sccm show stable current, but are not reproducible due to spark generation from the aluminum target (due to target oxidation), resulting in film defects. The use of 6 sccm of oxygen produces reliable and reproducible results, with a low and stable electroplating current and no detectable deposition through pinholes. As a result, the pinhole-free aluminum oxide films were deposited at 10 W bias, 100 W aluminum deposition rate, 0.67 Pa process pressure, and 6-sccm flow rate of oxygen.

The aluminum oxide layer was sputtered at the optimized conditions as described above. Initial pin-hole testing (device structures on conducting Si wafers) produced a current of electroplating in the order of 10^{-3} A with the pinholes appeared along the edges of the device structures, as shown in Figure 3b. Higher aluminum oxide conformality was achieved by increasing the deposition incidence angle while moving the wafer closer to the sputtering source. The optimal center-to-center distance between the center of the sputtering target to the center of the wafer was 10 cm at the sputtering gun tilt was 50 degrees off the wafer vertical direction. This resulted in a dramatic reduction of the current of electroplating to less than 10^{-8} A.

Testing of films by spectroscopic ellipsometry (Figure 4) (J A Woollam spectroscopic ellipsometer M 2000 series; model number ESM-300 and CompleteEASE software package were used) revealed that the refractive index of the deposited aluminum oxide films increased with the increase of the oxygen flow rate, indicating composition change. X-ray Photoemission Spectroscopy was used to analyze oxygen content in sputtered films (PHI 5700 X-ray photoelectron spectrometer with monochromatic Al K $\alpha_{1,2}$ radiation as an excitation source $h\nu = 1486.6$ eV). The incident angle was set at 90° to the axis of hemispherical energy analyzer. The pass energy was set to 23.5 eV for high resolution operation. The take-off angle was 45° and the spot diameter was 1.1 mm². The chamber was

pumped down to 2.7×10^{-6} Pa and all measurements were collected at room temperature. High resolution scanning was performed individually for each element to locate the elements on the surface of each sample. Then, the survey scan was performed to locate the binding energy peak positions of the elements [11].

As shown in Figure 4, the ratio of oxygen to aluminum did not correspond to the stoichiometric ratio of 1.5 of the crystalline aluminum oxide (Al_2O_3) and decreased with the increase of the oxygen flow rate (the increase of the oxygen partial pressure). For example, the ratio of the oxygen to aluminum in the films sputtered at 6 sccm, 0.67 Pa, 10 W substrate bias, and 60W DC power was found to be 1.62.

The resulting 25 nm alumina films have a lower refractive index than expected (1.49). However, similar results have been previously published [12], [13], [14]. Unfortunately, there is no single explanation why the index of refraction is low. Since the detailed materials characterization of the alumina films have not been performed to identify the origin of the low index of refraction in films, we would rather not speculate as to the specific reasons why the films have low index of refraction. This can be due to the fact that the films are very thin and can be structurally very different from the “bulk” alumina, thus, resulting in different properties.

3.2 Fourier Transform Infrared Spectroscopy (FTIR) analysis of Films

The chemical bonding and structure of the samples was characterized by FTIR spectroscopy using a Nicolet NEXUS-IR 670 instrument. Table II summarizes the peaks of interest [15], [16], [17].

FTIR spectra for deposited aluminum oxide films are shown in Figure 5 (the blue line corresponds to the published data on crystalline aluminum oxide [18]). As can be seen from the graph, the published data (blue line) does not correspond to the data of sputtered films. The observed vibration/stretching peaks indicate amorphous nature of the deposited materials [15], [16], [17], a desired characteristics of a protective coating to avoid defects at grain boundaries.

3.3 Cyclic voltammetry and electrochemical impedance spectroscopy

It was found that the aluminum oxide films processed with oxygen plasma had superior insulating properties. As shown in Figure 6a, the current density measured at the sample decreases in the following order: plain aluminum oxide $\approx$ UV/ O_3 aluminum oxide $>$ O_2 aluminum oxide. This indicates that oxygen plasma can induce the aluminum oxide films to be better insulators for the metal substrate, preventing high current running through the sample. In addition, the magnitude of the impedance (i.e., a vector from the highest to the lowest frequencies of length $|Z|$) of each aluminum oxide film increases in the following order: plain aluminum oxide $\approx$ UV/ O_3 aluminum oxide $<$ O_2 aluminum oxide, as shown in the Nyquist plots in Figure 6b.

The real part of the impedance (X axis) represents resistance (R) while the imaginary part (Y axis) represents reactance (X). The latter component induces a phase shift (θ) between voltage and current. Disregarding the phase shift, since it is not critical to our application, this data shows that the use of oxygen plasma in processing the aluminum oxide film provides the best insulating layer.

3.4 Corrosion resistance

Phosphate buffered saline solution (PBS) was used to test the corrosion-protective properties of the aluminum oxide films. The composition of PBS is 137mM NaCl, 3 mM KCl, 10 mM

Na_2HPO_4 , and 2 mM KH_2PO_4 at pH 7.4. PBS, which is highly corrosive to metals, is widely used in biological research to simulate the ionic concentration and osmolarity close to the one of human body [19].

3.4.1 Corrosion in PBS solutions—Two samples, one with a protective aluminum oxide layer (after UV/Ozone treatment) and another without any aluminum oxide layer, were placed in PBS solution for up to 72 hours at room temperature with gentle shaking. The samples were removed from the solution and washed with deionized water to remove any trace of PBS. The state of the device structures at each stage was checked using SEM (FEI XL-30FEG scanning electron microscope equipped with NPGS (Nabity Pattern Generation Systems) for microscopy analysis and e-beam lithography pattern generation). As can be seen in Figure 7, no visible damage was caused to the protected device structures after 72 hours exposure to PBS.

3.4.2 Corrosion stress test—To further explore the protective properties of the aluminum oxide coatings, the samples exposed to PBS for different periods of time were tested for presence of pin-holes. The samples were fully immersed in 100 mL of PBS solution for 24, 48, 72, and 96 hours, then taken out, rinsed with deionized water, dried with nitrogen gas, and checked for pinholes using the electroplating assay described in Section 2.2. SEM images were taken to confirm the results. The copper plating was done using Picostat for current lower than 100 nA and Potentiostat for higher currents. The stimulator was set for “Pulse” mode with pulse sent every 1 millisecond for 30 seconds. At zero hours, before the sample was placed in PBS solution, the electroplating current was approximately equal to 2.5×10^{-7} A, a current that was generally noticed on the samples with tantalum and copper layers protected by aluminum oxide.

Figure 8 shows the current of electroplating as a function of time for samples, which have been exposed to PBS for varying periods of time. The measured current of alumina-protected sample shows an increase of roughly two-fold per 24 hours in PBS in the first 30 seconds of electroplating, reaching 1.5×10^{-6} A in 30 seconds for the sample of 72 hours, as indicated in Figure 8.

3.4.3 Protected Device Resistance Measurements—The purpose of this experiment was to prove that the patterned sample protected with aluminum oxide layer would not corrode in biological solutions during an extended period of electric current application. For this experiment, 25-nm thick aluminum oxide layer was sputtered, as described in Section 3.1, on the center part of the sample (Figure 9a). The resistance measurements were done on protected and unprotected samples. The experiment was performed with a specially designed pin set-up that allows measurements to be taken without removing the pins from the surface of the sensor, as shown in 9b. This way, the position of the pins and the pressure on the sample were kept the same throughout the exposure period of 72 h to reduce the experimental error.

A rubber o-ring was placed at the center of the protected region and the PBS solution was added on top of the protected region inside the o-ring. Subsequently, in order to prevent the solution from drying out on the surface of the sample and keep PBS concentration approximately constant, deionized water was added as needed to compensate for evaporation. For the resistance measurements, a small current of 1 mA was applied to protected (Section 3.1) and unprotected samples. The results of the experiment are summarized in Table III. The resistance of the protected sample increased from 1.3 to 2.2 Ohms during the 72-hour period. This slight increase in resistance indicates that the sample was protected for this period of time. During the last 24 hours of the experiment shown (from 48 to 72 hours), one can notice an increase in the protected sample's resistance from

1.5 to 2.2 Ohms. From this, it can be concluded that the life limit of the alumina film is approximately 48 hours, which is sufficient for biofunctionalization and testing of the sensor. However, looking at the data in Table III and SEM images of unprotected samples in Figure 9a, one can see a higher corrosion level as well as broken sensors, indicating that the sample cannot withstand the applied current without proper protection layer.

The measurements of the unprotected sensor showed a slight increase in resistance for the first 4 hours in PBS solution. At 24 hours, the resistance of the sample increased to 161 Ohms, and the unprotected sensor broke after 48 hours. The large increase in resistance indicates sensor failure, as shown in Figure 10a. The SEM image in Figure 10b shows some corrosion of the protected sensor at the end of 72-hour period, but the sensor structure remains intact.

4 CONCLUSIONS

A 25-nm thick amorphous pinhole-free corrosion-protective aluminum oxide layer was made using ultra-high vacuum DC magnetron sputtering. The best film quality was achieved at a flow rate of 6 sccm of oxygen and 35 sccm of argon, process pressure of 0.67 Pa, bias power of 20 W, and target sputtering power of 20 W. We found that by exposing aluminum oxide film with the oxygen plasma during the sputtering process can successfully improve the insulation of the film on top of metal substrate.

The films were characterized using spectroscopic ellipsometry, FTIR, and XPS. All the measurements proved that the aluminum oxide layer was amorphous with Al-O₄ and Al-O₆ bonds only (from FTIR). The peaks for Al₂O₃ or Al=O double bond, which correspond to the crystalline aluminum oxide [8], were absent from the FTIR spectrum. The XPS results indicated the similarity of the protected samples before and after 72-hour exposure to PBS solution, while some additional elements (Ta, Na, Si, and Cu) were observed on the surface of the unprotected samples after 72 hours in PBS.

Unprotected sensors immersed in PBS showed a sharp increase in resistance due to corrosion, while protected sensors were relatively stable up to 72 h in saline PBS buffer. The cyclic voltammetry and electrochemical impedance spectroscopy were used to probe an insulating property of the aluminum oxide films. As a whole, the amorphous aluminum oxide film was proved to be an effective layer to protect the sensor from corrosion for at least 48 hours after exposure to the biological solution, i.e., the PBS solution in this study.

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REFERENCES

1. Koski K, Holsa J, Juliet P. Properties of aluminium oxide thin films deposited by reactive magnetron sputtering. *Thin Solid Films*. 1999; vol. 339:240–248.
2. Hoivik, JWE Nils D.; Linderman, Ryan J.; Bright, Victor M.; George, Steven M.; Lee, YC. Atomic layer deposited protective coatings for micro-electromechanical systems. Kidlington: ROYAUME-UNI: Elsevier; 2003.
3. Ling Feng Q, Nam Kim T, Wu J, Seo Park E, Ock Kim J, Young Lim D, Zhai Cui F. Antibacterial effects of Ag-HAp thin films on alumina substrates. *Thin Solid Films*. 1998; vol. 335:214–219.

4. Tripp MK, Stampfer C, Miller DC, Helbling T, Herrmann CF, Hierold C, Gall K, George SM, Bright VM. The mechanical properties of atomic layer deposited alumina for use in micro- and nano-electromechanical systems. *Sensors and Actuators A: Physical*. 2006; vol. 130–131:419–429.
5. Khanna A, Bhat DG, Harris A, Beake BD. Structure-property correlations in aluminum oxide thin films grown by reactive AC magnetron sputtering. *Surface and Coatings Technology*. 2006; vol. 201:1109–1116.
6. Daughton JM. Magnetoresistive Memory Technology. *Thin Solid Films*. 1992 Aug 28.vol. 216:162–168.
7. Osterfeld SJ, Yu H, Gaster RS, Caramuta S, Xu L, Han SJ, Hall DA, Wilson RJ, Sun SH, White RL, Davis RW, Pourmand N, Wang SX. Multiplex protein assays based on real-time magnetic nanotag sensing. *Proceedings of the National Academy of Sciences of the United States of America*. 2008 Dec.vol. 105:20637–20640. [PubMed: 19074273]
8. Schad R, Allen D, Zangari G, Zana I, Yang D, Tondra M, Wang D. Pinhole analysis in magnetic tunnel junctions. *Applied Physics Letters*. 2000; vol. 76:607–609.
9. Noh ES, Ulloa SE, Lee HM. A theoretical study of an amorphous aluminium oxide layer used as a tunnel barrier in a magnetic tunnel junction. *physica status solidi (b)*. 2007; vol. 244:4427–4430.
10. Christopher PG, Johnson J, McKenzie Debbie, Pedersen Joel A, Aiken Judd M. Ultraviolet-ozone treatment reduces levels of disease-associated prion protein and prion infectivity. *BMC Research Notes*. 2009; vol. 2:1–5.
11. Chang-Soo Yang J-SK, Choi Jang-Woo, Kwon Moo-Hyun, Kim Young-Joo, Choi Joeng-Gil, Kim Geug-Tae. XPS Study of Aluminum Oxides Deposited on PET Thin Films. *Journal of Industrial and Engineering Chemistry*. 2000; vol. 6:149–156.
12. Volintiru I, Creatore M, van Hemmen JL, van de Sanden MCM. Remote Plasma-Enhanced Metalorganic Chemical Vapor Deposition of Aluminum Oxide Thin Films. *Plasma Processes and Polymers*. 2008; vol. 5:645–652.
13. Kim SK, Lee SW, Hwang CS, Min YS, Won JY, Jeong J. Low temperature (<100 degrees C) deposition of aluminum oxide thin films by ALD with O₃ as oxidant. *Journal of Electrochemical Society*. 2006; vol. 153:F69–F76.
14. Chen S, Tao L, Zeng L, Hong R. RF Magnetron Sputtering Aluminum Oxide Film for Surface Passivation on Crystalline Silicon Wafers. *International Journal of Photoenergy*. 2012; vol. 2013:1–5.
15. Culcun Lin MY, Cheng Ziyong, Zhang Culmlao, Meng Qingguo, Lin Jun. Bluish-White Emission from Radical Carbonyl Impurities in Amorphous Al₂O₃ Prepared via the Pechini-Type Sol-Gel Process. *Inorganic Chemistry*. 2007; vol. 47:49–55.
16. Nilgun Ozer JPC, Yao Yong-Jin, Tomsia Antoni P. Optical Properties of Sol-Gel Deposited Al₂O₃ Films. *Solar Energy Materials and Solar Cells*. 1999; vol. 59:355–366.
17. Yunsheng Zhang HY, Wang Aili, Ren Min, Gu Zhuomin, Lui Yumin, Shen Yutang, Yu Longbao, Jiang Tingshun. Deposition and characterization of binary Al₂O₃/SiO₂coatinglayers on the surfaces of rutile TiO₂ and the pigmentaryproperties. *Applied Surface Science*. 2010; vol. 257:1351–1360.
18. Downs RT. The RRUFF Project: An Integrated Study of the Chemistry, Crystallography, Raman and Infrared Spectroscopy of Minerals [Online].
19. Ernest M. Wright DDFL, Hirayama Bruce A. Biology of human sodium glucose transporter. *Physiological Reviews*. 2011; vol. 91:733–794. [PubMed: 21527736]

Highlights

- 25-nm thick alumina film was made using ultra-high vacuum DC magnetron sputtering
- Exposure to oxygen plasma after sputtering improves insulation properties of film
- SEM of protected samples indicates no change after 72-hours exposure to PBS
- XPS of unprotected samples indicates additional elements on surface
- Resistance of protected sensors remained low after 72 hour exposure to PBS

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

Figure 2. Results of copper electroplating on 10W bias power samples with various flow rates of oxygen.

Figure 3.

(a) SEM image of the pattern structure used for corrosion testing. An aluminum oxide layer was sputtered on the structure of a sensor. The height of the sensor structures was varied from 100 to 400 nm and the thickness of aluminum oxide was held constant at 25 nm; (b) SEM image of copper deposition along the edges of the device structures.

Figure 4.

(a) Refractive index versus sputtering time for different flow rates of oxygen based on spectroscopic ellipsometry measurements; (b) XPS result for oxygen and aluminum content in sputtered aluminum oxide films.

Figure 5.

FTIR of amorphous aluminum oxide 450–1200 cm⁻¹. 100- and 200-nm thick aluminum oxide samples were made using DC magnetron sputtering. The FTIR results show that all of the existing peaks correspond to the signal from amorphous aluminum oxide, comparing with the published records on crystalline aluminum oxide.

Figure 6.
Cyclic voltammograms (a) and Nyquist plots (b) of each processed aluminum oxide film.

Figure 7. Corrosion in PBS solution of device structures without (left) and with (right) protective aluminum oxide layer; from top to bottom: 4 hrs, 24hrs, 48hrs, 72hrs.

Figure 8.

Current of electroplating for protected sample. Aluminum oxide layer of thickness 25-nm was sputtered on the sensor surface and samples were immersed in PBS solution for varying periods of time. The samples were checked for corrosion every 24 hours and show increase in current approximately two-fold for the first 30 seconds, but holding constant, indicating that no copper was depositing on the surface of the sample during electroplating. After 72 hours in PBS solution, the current was increasing significantly during the first 30 seconds, indicating copper plating on the area damaged by PBS.

Figure 9.

SEM image of the sensor structure (a) and schematics of the pin set-up used for resistance measurements (b). The image on the left shows 12 pairs of copper contacts connecting 12 sensors, and that on the right provides the schematics of the pin set-up. The pins are placed in touch with copper contacts to connect to the sensor structures; therefore, the copper contacts were not protected with a layer of aluminum oxide for the purpose of electrical conduction. Accordingly, the region designated with transparent blue color (in (a)) was protected with aluminum oxide layer, while the rest of the sample was left unprotected.

Figure 10.
SEM images of (a) unprotected and (b) protected sensors after 72 hours in PBS solution.

Table II

FTIR peak positions of aluminum oxide sample

Peak position	Corresponding vibration
460 and 640 cm^{-1}	Al-O ₆ stretching
590 cm^{-1}	Al-O ₆ vibrations
705 cm^{-1}	Al-O ₄ stretching
768 cm^{-1}	Al-O ₄ vibrations (shoulder)

Table III

Resistance data of protected and unprotected samples

Time (hrs)	Protected Sample Resistance (Ohms)	Unprotected Sample Resistance (Ohms)
0	1.3	1.3
4	1.3	4.8
24	1.4	161
48	1.5	162
72	2.2	infinite