



## Full Length Article

## Evaluation of atomic layer deposited alumina as a protective layer for domestic silver articles: Anti-corrosion test in artificial sweat

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## ARTICLE INFO

## Article history:

Received 7 August 2017

Revised 7 February 2018

Accepted 8 February 2018

Available online 9 February 2018

## Keywords:

Anti-corrosion

Atomic layer deposition

Alumina

Silver

Artificial sweat

## ABSTRACT

This study evaluated the effectiveness of alumina fabricated by atomic layer deposition (ALD) as a protective coating for silver articles against the corrosion caused by body contact. An artificial sweat solution was used to simulate body contact. ALD alumina layers of varying thicknesses ranging from 20 to 80 nm were deposited on sputtered silver samples. The stability of the protective layer was evaluated by immersing the coated samples in the artificial sweat solution at 25 and 35 °C for 24 h. We confirmed that a sufficiently thick layer of ALD alumina is effective in protecting the shape and light reflectance of the underlying silver, whereas the uncoated bare silver is severely degraded by the artificial sweat solution. Inductively coupled plasma mass spectrometry and X-ray photoelectron spectroscopy were used for in-depth analyses of the chemical stability of the ALD-coated silver samples after immersion in the sweat solution.

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## 1. Introduction

Silver is widely used for many purposes in everyday life, such as in dining and cookware, coins, souvenirs, accessories, and jewelry. However, silver easily corrodes and tarnishes when exposed to ambient air or moisturized conditions for a prolonged duration [1–3]. Accordingly, surface-coating silver with a thin oxide film is very effective in protecting silver against tarnishing [4–6]. The thickness of the protective oxide layer should be minimized to avoid an undesirable change in the color of silver. Achieving a conformal coating of thin oxide along the surface, particularly for surfaces with a high degree of corrugation, is challenging if the shape of the silver object to be coated is complicated. With respect to this, atomic layer deposition (ALD) is considered the most suitable process for surface coating [7–11]. ALD films are fabricated by alternating cycles of source precursors containing elements of the materials to be deposited. The growth rate of each cycle is solely determined by the type of precursor used in the deposition as long as the deposition temperature is appropriately set. The dose of the supplied sources, exposure time, and direction of the source flow do not influence the deposition rate. Therefore, ALD allows for a uniform growth of films along the surface of a given

substrate. The typical growth rate of ALD films is ~0.01–0.2 nm/cycle. Hence, the thickness of the ALD layer can be precisely controlled over a sub-nanometer scale [12]. Accordingly, ALD has become an inevitable process in the semiconductor and display industries [13–15].

Precious metals, such as gold, platinum, and their alloys, have been popularly used as surface protection materials for silver [16]. However, the high cost of these materials has discouraged their utilization in a wide range of applications [17]. Another issue arising from the use of gold or platinum for surface protection is the change in the color of the substrates [16]. Several metal oxides with incomparably low material cost and high transparency are excellent alternatives to these precious metals for surface protection of silver, provided that the layer is sufficiently thin [4]. Aluminum oxide or alumina is a particularly attractive material with low oxygen diffusivity and good integration with substrates [18]. ALD of alumina is one of the most well-established processes, and ALD alumina has been proven effective for protecting metals or ceramics against corrosion or chemical etching [19]. The amorphous phase of ALD alumina with no grain boundaries is advantageous for protecting the underlying substrate by preventing intergranular corrosion. However, the solubility of alumina in aqueous environments remains a problem that needs to be solved for its application as a protective layer [20,21]. Several studies on the application of multilayer structures combined with chemically stable materials, such as TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, have been proposed as a

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solution to the solubility problem [20–23]. Abdulatov et al. demonstrated that an  $\text{Al}_2\text{O}_3$  film with a  $\text{TiO}_2$  capping layer is more resistant to water corrosion of copper than a single  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  layer [20]. Härkönen et al. reported that the protective coating of a nano-laminated structure consisting of  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  is superior to a single structure of  $\text{Al}_2\text{O}_3$  or  $\text{Ta}_2\text{O}_5$  in terms of the corrosion durability of carbon steels [22]. Using another method, Correa et al. suggested that the stability of alumina in an aqueous environment could be improved by annealing at high temperatures [24]. These methods were effective in improving the stability of alumina, but were not suitable for applications, such as those involving silver products with low thermal stability in high-temperature deposition and post-annealing environments.

Recent studies confirmed the effectiveness of ALD alumina as a protective material for silver against corrosion or tarnishing [4–6]. When using silverware or wearing silver accessories, contact with silver often causes skin allergies or allergic contact dermatitis, which includes redness, itching, or bumps [25]. Excessive exposure to elemental silver or silver colloids can turn the contacted skin blue or bluish-grey in a condition, called argyria [26]. With respect to this, it is of great importance to investigate whether the surface protection ability of ALD alumina on silver is effective against corrosion as well as dermatitis. In this work, we evaluated the properties of ALD  $\text{Al}_2\text{O}_3$ -coated Ag in a human sweat environment that simulates human skin contact.

## 2. Experimental section

The Ag samples used herein were prepared by DC sputtering on  $1 \times 1 \text{ cm}^2$  glass substrates. The deposition power for Ag was set to 245 W at 10 mTorr Ar pressure. The Ag film thickness was 160 nm. ALD  $\text{Al}_2\text{O}_3$  thin films were deposited on the Ag samples using a commercial thermal ALD system (CN1, Atomic-Class, Korea University). The chamber temperature was set to 80 °C considering the poor structural and chemical stabilities of the Ag films (Figs. S1 and S2). Trimethyl aluminum (TMA; UP Chemical) and distilled water were used as the precursor and oxidant, respectively, and vaporized at room temperature. Dry nitrogen (99.999%) was used

as both the purge and the carrier gas with a flow rate of 200 sccm. The pulse time for TMA and distilled water was set to 1 s, while the purge time was set to 30 s. The film thickness and surface morphology were analyzed by scanning electron microscopy (SEM, Hitachi S-4300, Korea University). The artificial sweat solution was prepared according to the ISO 3160-2 standard (20 g/L NaCl, 17.5 g/L  $\text{NH}_4\text{Cl}$ , 5 g/L acetic acid, and 15 g/L lactic acid; pH 4.7). The artificial sweat immersion test was performed in 5 mL of the sweat solution for 24 h at 25 and 35 °C. The samples were loaded in 50 mL conical tubes. Before the immersion test, chemically inert polytetrafluoroethylene films with a 5 mm-diameter central hole were taped to the front side of the uncoated Ag samples and Ag samples coated with  $\text{Al}_2\text{O}_3$  ALD thin films. The ions dissolved in the artificial sweat were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Sciex, Elan DRC II, Seoul Center, Korea Basic Science Institute) after the immersion test. Light reflectance was measured using an ultraviolet–visible (UV–Vis) spectrophotometer (Agilent Technologies, Cary 5000, GMRC, Korea University). The measured wavelength of the light ranged from 400 to 700 nm. The light source was a tungsten halogen lamp. The film composition after the artificial sweat immersion test was analyzed by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI X-tool, GMRC, Korea University) using  $\text{Al-K}\alpha$  radiation ( $\lambda = 0.83 \text{ nm}$ ).

## 3. Results and discussion

In this study, ALD  $\text{Al}_2\text{O}_3$  thin films were deposited on Ag surfaces over 125, 250, and 500 cycles (hereafter referred to as Ag125, Ag250, and Ag500, respectively). Fig. 1 shows the cross-sectional SEM images of the bare Ag, Ag125, Ag250, and Ag500 samples. The average thicknesses of the ALD  $\text{Al}_2\text{O}_3$  thin films for Ag125, Ag250, and Ag500 were 20, 40, and 80 nm, respectively. The ALD  $\text{Al}_2\text{O}_3$  film was uniformly grown on the rough sputtered Ag surface at a growth rate of 1.6 Å/cycle. These values were relatively greater than the reference values (1.1–1.3 Å/cycle) for ALD  $\text{Al}_2\text{O}_3$  [12,20] probably because the  $\text{Al}_2\text{O}_3$  films were deposited at a relatively low temperature (80 °C) [27,28], and the multilayer

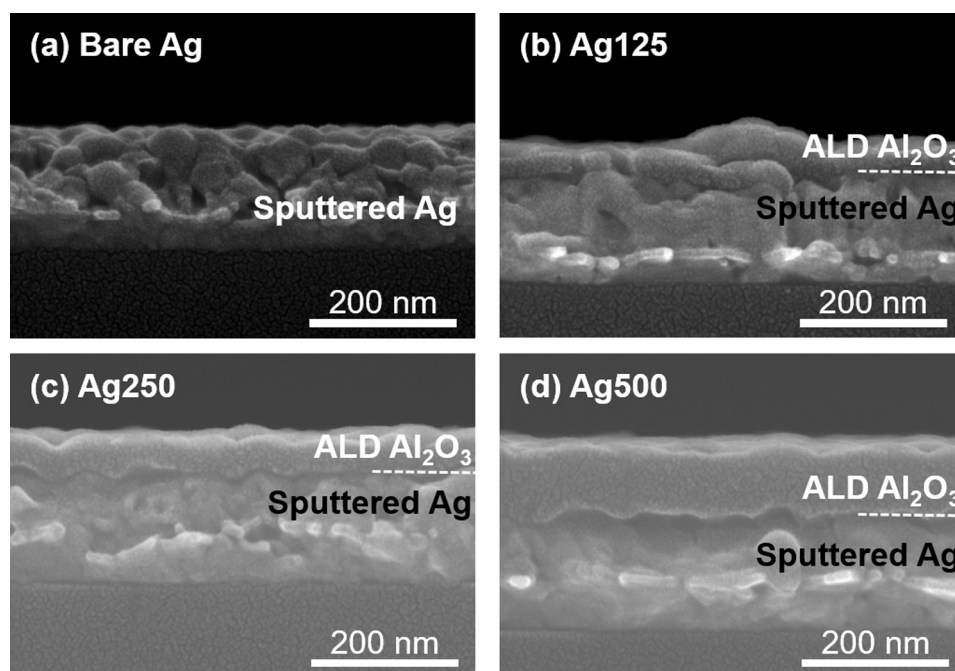


Fig. 1. Cross-sectional SEM images of the (a) bare Ag, (b) Ag125, (c) Ag250, and (d) Ag500 samples.

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