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Investigation of Atomic Layer Deposited Metal Oxide Layers for Conservation of Metal Cultural Heritage Objects*

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Atomic layer deposition (ALD), a technique developed for applications in microelectronics, is finding new and interesting applications in a variety of fields. Inspired by interest in the application of new technologies to cultural heritage conservation we have recently begun investigation of the use of ALD in creating protective coatings for art objects crafted from heritage metals [1, 2]. Art conservation places multiple requirements on corrosion-barrier films, which might serve as replacements for the presently employed polymeric coatings, such as nitrocellulose. Among these requirements are higher effectiveness than polymeric coatings in impeding corrosion of the underlying object, minimal change of the appearance when coated, ease of application, and reversibility. ALD has been demonstrated to produce films of extremely high conformality [3] and continuity [4], both important considerations in such an application. In order for a preservation technique to be accepted for use on cultural heritage objects, it must meet the criteria of effectiveness, transparency, and reversibility.

We have investigated ALD film effectiveness using accelerated aging, in which the effectiveness of ALD films of various thicknesses was directly compared with that of nitrocellulose films on silver substrates under greatly elevated H_2S concentrations. The thickness of silver sulfide tarnish layer that forms as sulfur diffuses through the ALD films and reacts at the silver surface was quantified by comparing the measured reflectance in the middle of the visible range to the modeled reflectance of a known thickness of silver sulfide; this was calibrated via x-ray photoelectron spectroscopy (XPS) depth profiling. ALD films of 10 nm and 20 nm thickness were found extend the time required for a 5% change in reflectance (corresponding to 1 nm of Ag_2S) by factors of approximately 10 and 15 times, respectively, beyond that of nitrocellulose coatings. The result is an increase in the effective lifetime of the conservation treatment, in ambient, to ~100-150 years.

Conservation practice requires ALD films to be transparent, without affecting the color or appearance. We quantified color change, as determined by CIE ΔE_{2000}, to optimize simple and multilayer ALD film structures minimizing color change to acceptable values. Conservators at the American Institute of Conservation annual meeting determined ALD coated objects to have an acceptable appearance in a blind comparison with nitrocellulose coated and uncoated silver knives (see Figure 1). While the overall appearance is acceptable, ALD coatings on real 3-dimensional art objects is non-trivial, as trace contamination on the object surface can affect coating deposition and performance. A knife coated with 100 nm Al2O3 ALD was found to have hazy surface areas due to diffuse reflectance by large particles as shown by atomic force microscopy (AFM), see Figure 1. Raman spectroscopy analysis shows the particles contain higher amounts of carbon species, possibly due to surface contamination or incomplete ALD reactions.

We have recently begun to investigate the effectiveness of ALD oxide films in stabilizing bronze patinas, which have complex surface topography and varying chemical compositions. Bronze patina libraries were made using combinatorial sputter deposition of Cu and Sn, followed by patination in $CuSO_4$, and Al_2O_3 ALD coating and removal with NaOH and Na_2CO_3 etching. AFM analysis shows the surface topography was unchanged by ALD application and subsequent chemical removal. XPS depth profiling indicates Cu depletion is confined to the top 15-20 nm of the bronze substrate, when compared to the bare alloy profile, after etching with NaOH and Na_2CO_3. ALD diffusion barrier films are thus promising for preserving even patinated cultural heritage metal objects; they are more effective than conventional techniques, transparent, and nearly reversible.

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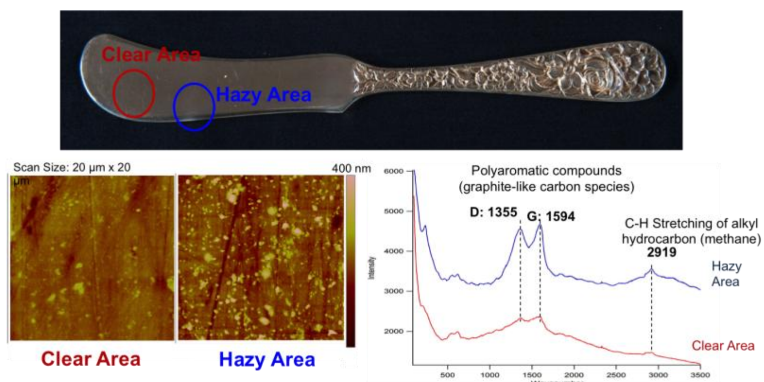

Figure 1. 100 nm Al_2O_3 ALD coated sterling silver knife; overall the appearance was judged acceptable; isolated visibly hazy areas correspond to increased roughness and carbon rich species, are due to imperfect surface pretreatment.

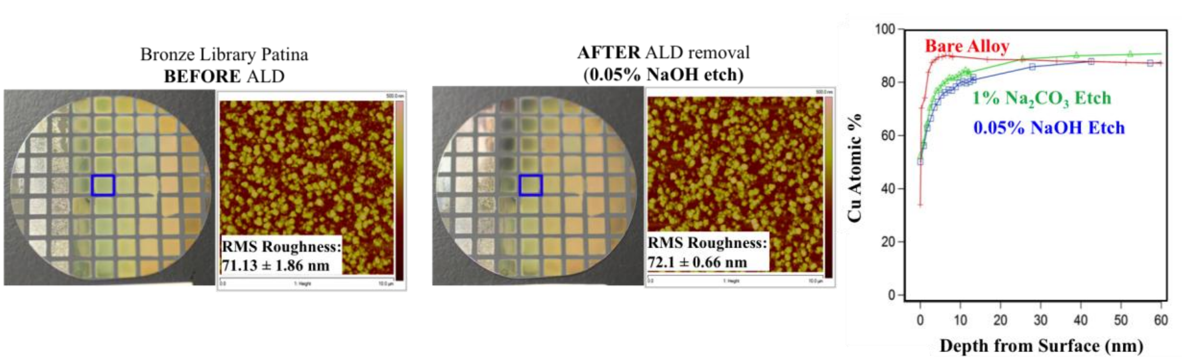

Figure 2. Effect of removal of Al_2O_3 ALD films on bronze patina libraries with NaOH and Na_2CO_2 etches; surface topography remains unchanged while XPS depth profiling indicates composition changes are limited to the top 20 nm of surface.

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