Contents lists available at ScienceDirect

Thin Solid Films

Coloration of metallic and/or ceramic surfaces obtained by atomic layer deposited nano-coatings

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ARTICLE INFO

ABSTRACT

By depositing single layer coatings by means of physical vapor techniques, tailoring of their coloration is generally complex because a given color can be obtained only by very high composition control. Physical vapor deposition (PVD) processes are expensive and cannot be easily used for obtaining conformal coating on three-dimensional objects. Moreover PVD coatings exhibit intrinsic defects (columnar structures, pores) that affect their functional properties and applications such as barrier layers.

Atomic layer deposition (ALD) technology delivers conformal coatings on different materials with very low defectiveness. A straightforward coloration can be obtained by a combination of two types of layers with different refraction index, deposited to high thickness precision.

Computer simulation studies were performed to design the thickness and architecture of multilayer structures, to a total thickness of approximately 100 nm, suitable to modify the typical coloration of some materials, without altering their other physical and chemical properties.

The most promising nano-layered structures were then deposited by ALD and tested with regard to their optical properties. Their total thicknesses were specified in such a way to be technically feasible and compatible with future industrial production.

The materials employed in this study to build the optical coatings, are two oxides (Al_2O_3, TiO_2) deposited at 120 °C and two nitrides (AlN, TiN), which need a deposition temperature of 400 °C.

The possibility of using such modern deposition technology for esthetic and decorative purposes, while maintaining the functional properties, opens perspectives of industrial applications.

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1. Introduction

Atomic Layer Deposition (ALD) is a self-limiting sequential deposition technique (i.e. amount of film material deposited in each reaction cycle is constant) that produces conformal thin films of various materials onto different substrates. ALD is similar to chemical vapor deposition (CVD), except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction. Due to the characteristics of self-limiting and surface reactions, ALD film growth makes atomic scale deposition control possible. By keeping the precursors separate throughout the coating process, the film deposition can be controlled at atomic scale through a layer-by-layer growth mechanism. Separation of the precursors is accomplished by pulsing a purge gas (typically nitrogen) after each precursor pulse to remove excess precursor from the process chamber and prevent 'parasitic' CVD deposition on the substrate [1]. Typically ALD is used to deposit inorganic compounds in which the precursor gases are haloids, alcoholic-oxides, or organo-metallic compounds [2,3]. The second precursor is a source of oxygen or nitrogen, when oxides or nitrides are desired, respectively.

A major limitation of the process is its rather low deposition rate. Typical rate values are in the range of 100–300 nm/h. Low deposition rate makes obtainment of thick films too slow and therefore ALD is best suited for applications that rely more on the conformality and uniformity than on the thickness of the film.

In addition to the anti-tarnishing protection of Ag surfaces (for which the so-called nSILVER [4] process confirmed an effective superiority over any other protection technology), ALD can find many other applications in various industrial sectors. For instance, passivation of microelectronic and photovoltaic components, due to excellent diffusion barrier effect of highly perfect, ultrathin oxide coatings, the defectiveness of ALD coatings being 3–4 orders of magnitude lower than that of conventional coatings. The ALD films deposited at low temperatures are amorphous and compact [5]. Although scanning electron microscopy (SEM) is not straightforward for such ultrathin layers, the ultra-low defectiveness was related to the excellent long term anti corrosion properties conferred to metals as Ag observed in [4,5].

The corrosion protection can be extended to several metals other than Ag (e.g. Cu, Mg, and Al) and their alloys. In particular, stainless steel can be rendered highly resistant to aggressive (marine) environments.

Using a nanoscale ALD layer as top-layer of hard micro-metric coatings, it is possible to obtain a synergistic wear-protection, even in highly corrosive environments. Finally, going beyond the constraint of transparency for protective layers, it may be possible to confer to them an esthetic coloration at will, taking advantage of optical interference effects, as exhibited by multilayer configurations. In this way, it is possible to go beyond the traditional contrast between functional and decorative films.

The materials employed in this work to build decorative coatings were two oxides (Al_2O_3, TiO_2) and two nitrides (AlN, TiN) deposited by ALD on different functional substrates: Mg, stainless steel and Au. Before the layer architecture realization, the optimal design of the deposited layers was defined by means of computer simulation of the optical properties.

2. Experimental details

Optical design of suitably colored layers was performed by computer simulation studies using "OpenFilters" [6] software and its library. Total thickness of the optical coating was specified in such a way to be technically feasible and compatible with future industrial production (<120 nm).

Sheets of various metals (Mg, Al, stainless steel, Fe) were cut in 10 × 10 mm samples and polished to obtain a mirror-like surface with an average roughness of less than 20 nm. Sample surface was then cleaned using ethanol in ultrasonic bath for 10 min and dried. Some samples were partially masked with heat resistant laboratory tape to prevent ALD deposition on the substrate. The samples were then coated with different ALD configurations, using a BENEQ TFS-500 apparatus. The samples were coated with the specified oxide layers Al_2O_3 and TiO_2, H_2O, trimethylaluminum (TMA) and $TiCl_4$ precursors were used at a chamber temperature of 120 °C, the purge gas being nitrogen.

The procedure for depositing one layer of Al_2O_3 from TMA and water at 120 °C was as follows: the H_2O pulse duration was of 250 ms, while the TMA pulse duration was of 250 ms; the purge duration after each precursor use was kept equal to 4 s. The growth rate obtained was 0.05 nm/cycle.

The procedure for depositing one layer of TiO_2 from $TiCl_4$ and water at 120 °C was as follows: H_2O pulse duration of 250 ms, $TiCl_4$ pulse duration of 500 ms. As above, the purge duration after each precursor use was kept equal to 4 s. The growth rate obtained in this case was 0.03 nm/cycle.

In the case of TiN, NH_3 and $TiCl_4$ precursors were employed at 400 °C, purge gas being nitrogen.

The steps for processing one layer of TiN from TiCL4 and ammonia at 400 °C were as follows: NH3 pulse of 250 ms followed by a purge of 4 s; $TiCl_4$ pulse of 500 ms followed by a purge of 4 s. The growth rate obtained in this case was 0.02 nm/cycle.

All configurations were accurately simulated using the optical design software before their experimental realization. In some cases, silicon pieces and Au (22 ct. alloy) 3D jewels were also coated.

Optical observation was then performed on the samples in order to confirm their appearance as predicted by computer simulations.

3. Results and discussion

3.1. Optical behavior of metals

Usual metals may be subdivided in two groups:

(a) "White" metals, like Mg or Al, which have a high and rather constant reflectivity as a function of wavelength; and

(b) "Gray" metals, like Fe and steels, which on the other hand, exhibit a reflectivity gradient as a function of wavelength.

As stated before, it is possible to alter the typical coloration of metal surfaces by depositing dielectric (oxide) films of controlled thickness, or even better, by applying true 'optical coatings' consisting of multilayered structures of two dielectric materials exhibiting different refraction index n, one of them being low n and the second high n. In the following paragraphs, we shall see which configurations are most suitable to confer the desired tonalities, by employing optical interference effects.

3.1.1. Simulation through optical design of colors to be conferred to magnesium

In a previous paper [7], polarization curves showed that ALD layers can be used to protect Mg against corrosion in aqueous solutions with low concentration (0.05 M) of NaCl. The results showed that, keeping the same overall coating thickness, an increase in the number of layers is a good choice to obtain a more stable coating with a wider passive region and lower corrosion current density. Nevertheless, no effort was done to confer a suitable color to the coatings.

Using the two oxide materials Al_2O_3 and TiO_2 for the single layers, the following colors were obtained on Mg coupons by depositing multilayer configurations at 120 °C. For yellow color, 15 × (5 nm Al_2O_3 + 5 nm TiO_2) layers, making 150 nm of total thickness with a total of 30 deposited sublayers. For green color, 15 × (5 nm Al_2O_3 + 10 nm TiO_2) layers, making a total thickness of 225 nm of with 30 sublayers were necessary, while violet color was obtained with 5 × (5 nm Al_2O_3 + 30 nm TiO_2) layers giving 175 nm of total thickness with 10 sublayers. These data had not been shown in reference 7.

It should be noticed that for the optimization of such tonalities, computer simulation shows that a relatively high number of layers with a total thickness between 150 and 225 nm, is required. As found in the simulations shown in Fig. 1, the calculated reflectivity peaks of coated Mg substrates are rather wide. Such behavior results in rather iridescent and undefined colors. From additional simulation attempts performed on white metals (Al, Mg), it can be stated that such metals are not easily "painted" with intense colors. On the other hand, gray metals (Fe, steels) respond much better to such treatments, as can be seen in the following section.
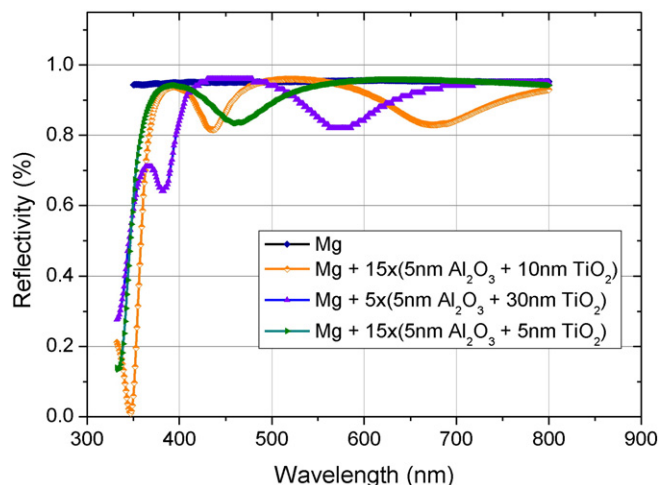

Fig. 1. Computer simulation of some colorations to be conferred to Mg.