Developments In Tarnish Resistant Silver Alloys

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ABSTRACT

Several silver based alloys have been developed to improve tarnish resistance in multi-layer stacks. These alloys traditionally have had 80 – 95% silver and employed gold or platinum group metals as alloying elements to stabilize the properties of the silver when exposed to moisture or mildly acidic environments. New, lower cost alloys have been developed that represent a favorable balance between cost and performance. These new alloys tend to be more complex than the standard binary or ternary alloys currently in use, but they can be produced using readily available production equipment.

INTRODUCTION

Silver and some of its alloys have been employed for many years as reflectors in thick or thin film applications. In thick film applications such as paints, they were applied to the back side of the substrate and normally laminated into an assembly. In thin films, silver has been used on both the front and back side of substrates and has been employed as a mirroring material for IR, laser and visual light applications.

In all applications, pure silver thin films required protective layers on top, or in some cases, below to prevent degradation of the film. Silver also requires edgewise protection to inhibit corrosion at the edges in the film that slowly creep into the working surface area of the film.

Historically adding gold or platinum group metals such as palladium or platinum have been added as a means of adding nobility to the silver. This has worked for many applications, but the added cost of gold or platinum group metals can increase the intrinsic raw material component of the cost by an order of magnitude or more.

Therefore any improvements made would have to give due consideration to metal costs and the attendant handling issues.

NEW ALLOY DEVELOPMENT

Practical Approach

As a means of addressing the issues of improving performance, lowering cost, ease of manufacturing and flexibility in application, it was important to take a practical approach to selecting the alloying elements. As was mentioned, the traditional alloying elements of gold, platinum and palladium, are very expensive and are difficult to recover from spent targets and associated scrap. Selecting common elements that would alloy well with silver, be readily available in the purities required and provide technical benefits in passivation or inertness to the operating environment.

Development

Tests were initiated using a proprietary, patent pending, combination of several common elements alloyed in a silver matrix. Based upon previous experience, the amount of each was varied slightly in an effort to optimize the ability to cast and work the material in a normal manner. Several casts were made and a suitable combination of elements was determined to warrant further tests. A bar was cast, rolled and finished machined to a size of 5” x 18”. This size was chosen to evaluate the uniformity over a target footprint similar to a target segment in a web or large glass coating machine.

TESTING

Optical Properties - Reflectivity

The principle application of this alloy would be as a replacement for silver and/or gold and their alloys in visible or infrared reflecting thin films. Therefore the focus would be to compare the reflectivity against these materials. Table 1. compares the reflectivity properties of the alloys tested against both silver and gold standards. The sputtering tests were carried out on standard quartz medical slides and on PET web plastic. The coatings were made in a 27” wide web coater using an Advanced Energy MDX 10 kW power supply. The slides were placed upon the cooling drum and sputtered in a static position. Reflectivity in the ultraviolet, visible and near infrared ranges was measured with a Perkin Elmer model Lambda 19 spectrophotometer. Far infrared testing was conducted using a Perkin Elmer model 1310 infrared spectrophotometer. All measurements made are in reference to aluminum standards.

Table 1. Comparison Of Reflectivity Percent – Compared To Aluminum

Wavelength (nm)	Opti-Sil 592	99.95% Pure Ag	99.95% Pure Au	85%Ag-15% Au	93%Ag-7%Pd
304	9.94	10	42	-	-
404	80	105	42	96	93
504	97	108	64	104	101
604	102	110	102	107	106
704	107	112	109	110	111
804	114	117	116	115	117
904	107	110	110	106	108
1004	103	106	104	102	104
1104	102	104	103	101	103
1204	101	103	102	100	102
1304	101	103	102	100	102
1404	101	102	101	99	102
1504	100	102	101	99	102
1604	100	102	101	99	102
1704	100	102	101	99	101
1804	100	102	101	99	101
1904	100	101	101	99	101
2004	100	101	101	99	101
2104	100	101	101	99	101
2194	100	101	101	99	101

Optical Properties – Absorptance & Emittance

Each of the sputtered films were evaluated for absorptance and emittance properties for comparison versus pure silver and pure gold. Pure silver and pure gold are employed in architectural, aerospace and automotive glass applications, so these properties would be of interest. The tests were conducted using standard ASTM tests on unprotected films in the as-sputtered and after environmental testing. The results are shown in Tables 2 and 3. The following standards were used:

Solar absorptance measurements: E903
Emittance measurements: E408
Environmental aging tests: D1735
Adhesion tests: D3359

Table 2. - Absorptance, Emittance & Adhesion

Metal/Alloy (weight %)	Solar Absorptance	Emittance	Adhesion
Opti-Sil^{TM} 592	.10	.04	Good very slight removal
85%Ag-15%Au	.07	.04	Good
93%Ag-7%Pd	.06	.05	Good
Pure Au 99.95%	.19	.06	Good
Pure Ag 99.95%	.03	.03	OK

Table 3.
Absorptance, Emittance & Adhesion After Aging

Metal/Alloy (weight %)	Solar Absorptance	Emittance	Adhesion
Opti-Sil^{TM} 592	.11	.05	Good very slight removal
85%Ag-15%Au	.06	.04	Good
93%Ag-7%Pd	.09	.05	Good
Pure Au 99.95%	.20	.06	Good
Pure Ag 99.95%	.05	.03	OK

Electrical Properties
Sputter Rate and Sheet Resistance

Silver alloys are employed in transparent conductive films due to their excellent conductivity. Typically the silver layers are part of an oxide-metal-oxide film stack to optimize the optical properties and isolate the metal film. Table 4. provides the sheet **r**esistance values for each of alloys tested and compares them to gold and silver standards. The targets were sputtered with a 4 kW power supply that provided an average power density of 44 W/in^2. All materials were sputtered in an argon atmosphere with a flow rate of 250 sccm at a sputtering pressure of 1.0 x 10^{-3} torr. Note that the films are rather thick; on the order of 1500 Å. This was done to provide good average sputter rates and also to eliminate substrate effect for sheet resistance measurements. A thicker coating would also provide more interfacial stress in the film and make the adhesion test more relevant.

Table 4. Sputter Rate And Sheet Resistance

Metal/Alloy (weight %)	Nominal Thickness (Å)	Sputter Rate (Å/sec.)	Sheet Resistance (Ω/□)
Opti-Sil™ 592	1425	194	.55
85%Ag-15%Au	1454	215	.60
93%Ag-7%Pd	1533	233	.45
Pure Au 99.95%	1584	174	.60
Pure Ag 99.95%	1344	232	.32

CONCLUSION

The results show that Opti-Sil™ 592 is a good candidate material to replace more expensive or less corrosion resistant materials in some applications. The properties for Opti-Sil™ 592 in several key areas of interest to the thin film engineer, show good concurrence with the ranges of the more expensive materials. Optical properties, sheet resistance, adhesion and sputter rate demonstrated or derived from the test data show significant technical promise. Work on this and other similar alloys is ongoing.

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