TRANSPARENT FILMS FOR ELECTROMAGNETIC SHIELDING OF PLASTICS

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Abstract. The interest in the development of lightweight transparent electromagnetic (EM) shields for the radio frequency range has been growing up in the last years together with the expansion of the electronic market and the increasing use of plastics. Example of industrial applications are video displays of electrical and electronic apparatus, of electromedical devices, of portable electronic equipment. Applications in the aerospace sector are also very attractive, such as in protecting the electronic systems of aircrafts from the high-intensity electromagnetic fields emitted by radio emitters, TV, radars and telecommunication systems. Moreover, the recent limits of radio frequency electromagnetic fields suggest the use of transparent shields for building windows. Thin films can provide an effective solution in EM shielding of plastic substrates or enclosures. In particular, the use of 1-D photonic band gap structures named as ‘transparent metals’ has been recently investigated and tested for EM shielding applications in the radiofrequency range, by using physical vapor deposition technique. In this work, the design method and the technological issues concerning the realization and electromagnetic testing of the shields will be described. Some recent results will be presented, and both perspectives and limits of the proposed technique will be discussed and compared with other solutions.

1. INTRODUCTION

Different technological solutions have been developed in the last years in order to make glasses or polymers to shield the electromagnetic radiation. They follow essentially two approaches: the introduction of metallic meshes or powders into the polymeric or glass matrix; the deposition of conductive coatings on the dielectric substrate.

The first solution can be cost-effective, but it induces a considerable increase in the weight and the volume of the device, due to the high amount of metal introduced (typical thickness of the metallic grid is some hundred microns).

Thin films of wide band-gap oxide semiconductors (such as indium tin oxide (ITO), zinc oxide, etc.) can be applied on either glass or plastic substrate, but their shielding ability is rather poor: a maximum shielding effectiveness (SE) of 33 dB at radio frequencies is expected from a 0.5 μm thick ITO layer with resistivity low as 1.3·10\textsuperscript{-4} Ωcm, which is the best achieved nowadays on plastic substrate [1].

It has been shown that by replacing a single metal layer with a particular metallo-dielectric multilayered structure, containing the same total thickness of metal, the transmittance in the visible range can be enhanced [2]. Indeed, metallo-dielectric coatings has been investigated for solar radiation control applications (i.e.low-emissivity filters) [3,4]. The use of such coatings as shields against electromagnetic interference in the radio frequency range has
been sometimes cited [4], but not systematically investigated and tested. Actually, very few experimental works are reported on measured EM properties of thin film shields; on the other hand, typical sheet resistance values required for a conventional low-e filter are about 10 ohms/sq., while SE values around 40 dB at radio frequency can be achieved for sheet resistance values below 2 ohms/sq., for perfect ground connection.

RF sputtering is conventionally used to deposit such coatings, and silver is usually chosen as the metallic layer, due to its high electrical conductivity and the location of its plasma frequency. This technique is suitable for industrial scale processes, but it is affected by some technological problems such as silver oxidation and agglomeration, due to the oxygen diffusion favored by the plasma radiation. Interlayer films deposition is necessary, in order to prevent coating performance degradation [3-5].

The aim of this paper is to present some recent results concerning the realization and testing of transparent thin-film EM shields. Standardized measurements of the shielding effectiveness are reported and compared, showing that a number of technical factors affect the shielding performance, beside the total metal content of the coating. The ion beam sputtering deposition technique is exploited for coating deposition on both glass and polymeric substrates and appear to present some advantages respect to conventional RF sputtering.

2. BASIC THEORY OF TRANSPARENT EM SHIELDS

The skin depth defines the thickness of material within which the electromagnetic field is attenuated of a factor $e^{-1}$. In the visible range, extending from 400 nm to 700 nm, the skin depth in highly conducting metals, like silver, varies between nearly 5 nm and 7 nm. This represents a limit in practice to the use of metals in the realization of EM shields transparent in the visible range.

In order to overcome such limit, nano-technology can be useful. In fact, inside a nano-structured material, the electromagnetic field intensity is not homogeneously distributed but is localized in some regions and depressed in others, similarly to electron density in a crystal, provided that the nano-structure size is comparable with the field wavelength. This is simply a consequence of the interference between the reflected and transmitted waves produced everywhere a discontinuity in the refractive index occurs. Such localization effect is governed by the geometry of the nano-structures. Photonic crystals are nano-structured materials in which the field localization and/or depression is induced in specific spatial regions at the optical frequencies, so that the light propagation is permitted or not in a desired frequency range. For instance, enhancement of nonlinear optical properties can be achieved in a photonic crystal containing a nonlinear material, if the field is localized in it [6].

The simplest case of photonic crystal, the one-dimensional one, is a multi-layer coating, consisting in the alternation of two different materials having high and low refractive indices, such that the layer thickness is of the order of a reference wavelength in free-space.

The so-called ‘transparent metals’ [2] consist in metallo-dielectric one-dimensional photonic crystals in which one of the alternating materials is a metal. By choosing opportunately the optical thickness of each layer, the field intensity at the optical frequencies can be localized in the transparent material and forced to propagate trough the overall structure, thanks to a ‘resonant tunneling’ mechanism trough the thin metal layers. This mechanism increases the transmittivity of the structures of several magnitude orders thus allowing the use of metals in optical devices.

In particular, transparent metals can provide an efficient solution for transparent EM shields: for all those frequencies outside the visible range, the metal absorption combined with the multiple reflections inside the structure lead to a drastic decreasing of transmission, while a transmission band is present in the visible range, tunable by varying the structural parameters of the sample.

The details of the design criteria and procedure of EM shields based on transparent metals have been described elsewhere [7,8]. Commercial optimization programs based on the standard matrix transfer method are usually employed [9], which are of common use in the coatings community.

The interest in considering such structures from the point of view of the photonic crystal theory is the possibility to extend the basic physical principles of the ‘resonant tunneling’ to two or three-dimensional nano-structure, increasing the number of degree of freedom of the system and then the number of different requirements the can be obtained from the device.

3. EXPERIMENTAL
3.1. Ion Beam Sputtering

The multi-layered metallo-dielectric coatings have been deposited on polycarbonate (PC) and glass
Table 1. Deposition parameters for the different thin film materials.

<table>
<thead>
<tr>
<th>Layer material</th>
<th>Target material</th>
<th>(O_2) partial pressure (mbar)</th>
<th>Rate (Å/s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Ag</td>
<td>–</td>
<td>4.72</td>
<td>&lt; 35</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti</td>
<td>–</td>
<td>1.24</td>
<td>&lt; 35</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>Ti</td>
<td>5x10(^{-5})</td>
<td>1.56</td>
<td>&lt; 35</td>
</tr>
<tr>
<td>ZnO</td>
<td>ZnO</td>
<td>4x10(^{-5})</td>
<td>0.72</td>
<td>&lt; 35</td>
</tr>
</tbody>
</table>

substrates by a dual ion beam sputtering (DIBS) system, well described elsewhere [10]. A 2.5 cm grid aperture Kaufman ion source (Ion Tech Instruments) is directed towards the target at an angle of 45° with respect to the target surface. A rotating holder can accommodate two targets, allowing sequential sputtering of different materials without breaking the high vacuum. A blank position is also available, in order to avoid target contamination during substrate etching. A second ion source allows the ion bombardment of the rotating substrate before the film growth. A plasma bridge neutralizer emits electrons for space charge neutralization at the substrate surface, during the pre-deposition etching process, as well as at the target surface, when an insulating target is used.

In the present work, silver and titanium targets have been used to deposit respectively Ag/TiO\(_2\) multilayers, with or without the Ti interlayer, while a zinc oxide target has been used for ZnO layers deposition. In all cases space charge neutralization has not been necessary, because all the targets are conductive. Such configuration has been preferred in order to eliminate the additional heating from the neutralizing electrons. In fact, thermal stress is crucial when depositing films with very different expansion coefficient as in the case of metals and oxides, and also when dealing with plastic substrates [11]. Furthermore, heating drastically affects silver thin films quality, due to enhanced oxidation and migration [5]. For all the above reasons, the substrate was not intentionally heated. All coatings have been deposited on both glass (1 mm thick) and Lexan polycarbonate (3 mm thick) substrates. They have been chemically cleaned in order to remove dust and organic contaminants, by washing in ethylic alcohol and dry air fluxing. Then, they have been etched by Ar ions in an oxygen atmosphere, in order to improve film/substrate adhesion [12].

Single layer films of silver, zinc oxide, titanium and titanium dioxide have been optimized and characterized [13]. The correspondent deposition parameters are summarized in Table 1. A high rate was selected for silver, to minimize metal oxidation [14].

In some of the specimens realized a mask has been inserted before the deposition of the top layer, covering the areas through which the electrical contact occurs with the guiding structure of the shielding effectiveness measurement setup. This bonding configuration has been found to strongly enhance the SE of samples having an insulating layer on the top [15]. We refer to such samples as ‘masked’.

3.2. Optical and electrical characterization

Specular transmittance and reflectance spectra at normal incidence have been recorded in the visible-NIR range by standard spectrophotometric technique (Lambda 19 Spectrophotometer by Perkin-Elmer).

The dielectric constants of each material have been derived from the spectro-photometric measurements of the single layer coatings and used in the design (by TFCalc from Software Spectra Inc.) of the multilayers.

Similarly, the sheet resistance has been measured by the standard four probe technique (Napson Corporation) and the layer thickness by a profilometer (P10 by Tencor Inc.), in order to calculate the experimental electrical conductivity values.

3.3. EM shielding tests at radiofrequency

The shielding effectiveness of an infinite planar screen is defined as the ratio in decibel between the incident \((E)\) and transmitted \((E)\) field intensities \((SE = 20 \log(E/E_i))\).

The measurements of the SE of planar samples of transparent metal have been performed by using the coaxial waveguide set-up, according to the ASTM-D4935-89 standard [16] for shielding effec-
### Table 2. Relevant parameters of the realized samples. The 'average SE' values reported correspond to the mean value of the frequency spectrum calculated on the whole frequency range (from 30 kHz to 1.2 GHz); the 'average' transmittance values reported correspond to the integral of the transmittance spectrum in the range 320-1100 nm, weighted by the sensitivity curve of the human eye [22].

<table>
<thead>
<tr>
<th>Sample Layer sequence and thickness (nm)</th>
<th>SE av. (dB)</th>
<th>R sheet ohms/sq.</th>
<th>Masked</th>
<th>T av. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 [TiO₂/Ag/TiO₂]_1 [32/17/32]_1</td>
<td>1.34</td>
<td>Yes</td>
<td>63.1</td>
<td></td>
</tr>
<tr>
<td>#2 [TiO₂/Ag/Ti/TiO₂]_1 [32/17/1/32]_1</td>
<td>1.29</td>
<td>Yes</td>
<td>66.4</td>
<td></td>
</tr>
<tr>
<td>#3 [TiO₂/Ti/Ag/Ti/TiO₂]_3 [32/17/17/1/32]_3</td>
<td>41.5</td>
<td>1.3</td>
<td>Yes</td>
<td>64.6</td>
</tr>
<tr>
<td>#4 [ZnO/Ag]_4/ZnO [109/17]_4/109</td>
<td>37.2</td>
<td>Yes</td>
<td>42.86</td>
<td></td>
</tr>
<tr>
<td>#5 [ZnO/Ag]_5/ZnO [109/17]_5/109</td>
<td>28.5</td>
<td>No</td>
<td>51.2</td>
<td></td>
</tr>
<tr>
<td>#6 [Ag/ZnO/Ag]_6 [11.3/81]_6</td>
<td>39.4</td>
<td>No</td>
<td>39.4</td>
<td></td>
</tr>
<tr>
<td>#Ag Ag/Ag 63/9</td>
<td>41.8</td>
<td>1.24</td>
<td>No</td>
<td>0.62</td>
</tr>
</tbody>
</table>

The thickness measurement of planar samples from 30 kHz to 1.2 GHz.

The test setup is described in details elsewhere [7]. The SE test is performed by inserting the test specimen between two coaxial transitions (having characteristic impedance of 50 Ω and internal diameter of 76.8 mm) and measuring the scattering parameter S₂₁. The effect of the contact impedance between the material sample and the guiding structure is corrected by using as reference the scattering parameter S₂₁ measured when the two coaxial transitions are coupled through the 'reference' specimen, which covers only the contact areas of the waveguide with the 'test specimen'.

### 3.4. Durability tests

Practical adhesion was evaluated by the standard Scotch test (according to the normative MIL-A-413 Rev C) and damp heat test (according to the normative ISO 9211-3:1994(E) for optical coatings). Samples were stored at 55 °C and 95% humidity for 16 h. Then they were inspected by unaided eye and their specular transmittance spectra have been measured and compared with the ones recorded before the aging test.

### 4. RESULTS AND DISCUSSION

Six different metallo-dielectric multi-layer coatings have been realized having the same total thickness of metal. Silver has been used for the metallic layers while zinc oxide or titanium dioxide for the dielectric ones. The same thickness of the silver layer has been chosen for all samples, in order to have the same electrical conductivity. In fact, the dependence of the metal layer electrical conductivity on its thickness has been proven for different multi-layer combinations and deposition techniques [4, 7, 17]. In Table 2 are reported the measured electrical conductivity values of the silver single layers deposited in our DIBS plant.

A thick layer of silver with the same theoretical sheet resistance has been also deposited for comparison. It has been protected with a thin nickel top layer to prevent SE degradation due to oxidation and wear [10], so that it has been used for comparison with all the multi-layer samples deposited also at different times. The relevant parameters of all samples are resumed in Table 3. In Fig. 1 are compared the experimental shielding effectiveness spectra, showing differences from one sample to the other higher than 10 dB, despite the identical amount of silver contained in each sample.

#### 4.1. TiO₂/Ag coating

Titanium dioxide is a good candidate material for dielectric layers in "transparent metals", due to its high refractive index and low absorption in the visible range. Actually, higher maximum transmittance and color neutrality can be theoretically achieved if the refractive index of the dielectric is higher [3]. Furthermore, titanium dioxide has recently been shown to possess self cleaning catalytic properties [18], which can be transferred to the multi-layer coating if the top layer is made of this material, increasing the multi-functionality of the EM shield and its appeal especially in the building and automotive field. A critical issue in Ag/TiO₂ multi-layer coatings real-
ized by conventional RF sputtering technique is the silver oxidation and agglomeration, due to the oxygen diffusion favored by the heat and ions bombardment from the plasma [3-5]. The use of blocking layers is necessary in that case, which anyway lower a bit the optical transparency.

In order to investigate the effect of silver oxidation and interface mixing in our ion beam sputtered coatings, some samples have been realized by inserting a titanium interlayer on the top side (sample #2) or on both sides (sample #3) of the silver layer. The titanium interlayer on the top side of the silver layer is finalized to protect the metal from the oxygen exposure during the adjacent oxide layer deposition. A double interlayer is indeed necessary if oxygen diffusion from the oxide to the metal occurs at the interfaces. Actually, the measured sheet resistance values of the samples with and without Ti inter-layers are both very similar to that of the thick Ag film (see Table 2), suggesting that oxygen diffusion is marginal.

As concerning the optical performance (see Fig. 2), a bit higher transparency is observed in sample #2 having only 1 Ti interlayer on the top side of the silver layer, thus indicating that the main responsible for silver oxidation is the oxygen adsorption from the reactive atmosphere during the first layers of TiO₂ growth. In particular, the titanium blocking layer on the top side of the silver is likely fully oxidized after the adjacent oxide layer deposition, due to the very low formation enthalpy of the titanium oxide [19].

Finally, the environmental damp heat test has been performed on both samples and the transmittance spectra (see Fig. 2) and sheet resistance values (see Table 2) have been compared after and before aging, showing no evidence of coating degradation on both samples, with and without inter-layers, either on glass and polycarbonate substrate.

In Fig. 1 the measured SE spectra of one of the TiO₂/Ag samples is compared with that of the thick silver layer, showing no differences out of the experimental error (1-2dB).

### 4.2. ZnO/Ag system

A bit lower SE is observed in the zinc oxide/silver multi-layer coating, coherently with a higher value

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**Table 3.** Measured electrical conductivity values for silver single layers deposited by DIBS with different thicknesses. The values reported in literature for the bulk specimen is reported for comparison.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>17</th>
<th>63</th>
<th>400</th>
<th>bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Conductivity (10⁸ S/m)</td>
<td>7.75</td>
<td>12.8</td>
<td>15.6</td>
<td>66.7</td>
</tr>
</tbody>
</table>
of the sheet resistance. The EM shielding effectiveness spectrum remains 2-3 dB below that of other samples containing TiO$_2$, despite the identical silver content, which theoretically determines the sheet resistance and then the SE performance. Actually, the influence of the dielectric constant (which is about two orders of magnitude higher for TiO$_2$ respect to ZnO) is negligible in the studied frequency range [20]. On the other hand, the DC electrical conductivity of our deposited ZnO is too low to have any effect on the shielding performance [20]. Then, a more pronounced silver oxidation should be accounted for the observed lower electrical conductivity. Indeed, in the case of zinc oxide, the material is sputtered from an oxide target (see Table 1). Consequently, neutral atomic oxygen is also present inside the vacuum chamber during the oxide deposition, while only molecular oxygen is flowing during titanium oxide deposition. Actually, neutral oxygen radicals have been shown to be effective in silver film oxidation, differently from oxygen bi-atomic molecules and, obviously, to a less extent than energetic oxygen ions [21].

A rough estimate of the number of neutral oxygen atoms impinging on the silver surface before it is completely covered by the zinc oxide can be obtained from the sputtering yields, current density and rate (see Appendix). The estimate indicates that $2.5 \times 10^{15}$ atoms/cm$^2$ with an energy of about 20 eV impinge on the silver surface before it has been covered by the zinc oxide. This number is comparable with that of the atoms staying on the silver surface ($2.4 \times 10^{15}$ atoms/cm$^2$ for bulk material), suggesting that neutral atomic oxygen uptake is likely.

4.3. The effect of bonding configuration

An accurate study of the effect of the contact impedance between the shield and the reference ground on the SE performance has been carried out in previous publications [7,8,15]. Design solutions and bonding configurations have been considered and successfully realized in order to overcome the problem. Here, we want just to mention for completeness such technological issue, because it is really crucial in order to achieve a good shielding performance.

Sample #4 and #5 have been realized with the same structure, differing only in the bonding configuration (#4 is "masked", then is bonded to ground through the metallic layer, while #5 is not, then it is bonded to ground through dielectric layer). Then, the considerable difference in the SE spectra (see Fig. 1) accounts for the effect of the contact impedance between the shield and the reference ground on the SE performance. On the other hand, sample #6, having a structure completely different from sample #4, but being grounded through the metallic layer (not due to the ‘masked’ configuration but be-

Fig. 2. Measured frequency spectra of the SE. Sample names are explained in Table 2.
cause of the silver top layer), shows an identical SE spectrum, within the experimental error.

5. CONCLUSION
In this paper we have presented some results concerning the realization and testing of transparent EM shields, based on metallo-dielectric multilayered coatings on both glass and plastic substrate. The theory of photonic crystals has been usefully applied in order to design transparent electromagnetic shields. The ion beam sputtering technique has been exploited, which is not conventional for the present typology of coatings investigated, but it seems to be well performing on both glass and polymeric substrates. In particular, thanks to the low temperature at which the whole process can be carried out, and to the absence of direct oxygen ion bombardment of the growing film from the reactive plasma, the oxidation of the metallic interfaces is very limited, and good adhesion also to plastic substrates can be achieved.

Anyway, some practical aspects, as the bonding configuration of the shields have to be carefully considered to achieve optimum shielding performance. Finally, EM shields with SE average values higher than 40 dB at radio-frequency and maximum transmittance in the visible of 69% have been realized and tested.

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APPENDIX
The flow of oxygen atoms sputtered from the ZnO target and directed to the film surface is:

\[ \Phi_o = Y_o \cdot J^{ion}/e = 3.45 \times 10^{15} \text{ cm}^{-2} \cdot \text{s}^{-1} \]

where \( Y_o \) is the sputtering yield (calculated by the TRIM code, by J.F. Ziegler and J.P. Biersack) of oxygen bound in a ZnO target from a positive argon ion impinging with 1200 eV kinetic energy and at an angle of 45° respect to the target plane; \( J^{ion} \) is the ion current density hitting the target (\( J^{ion}=40 \mu\text{A/cm}^2 \)); \( e \) is the electron charge. The sputtered oxygen atoms bombard the silver surface for a time \( \Delta t \), which a monolayer of ZnO takes to be deposited:

\[ \Delta t = c/R_{ZnO} = 7.2 \text{ s} \]

where \( c \) and \( R_{ZnO} \) are respectively the lattice constant [19] and the deposition rate (see Table 1) of zinc oxide. Then, the total number of neutral oxygen atoms impinging on the silver surface before it is completely covered is:

\[ n_o = \Phi_o \cdot \Delta t = 2.50 \times 10^{15} \text{ cm}^{-2}. \]

REFERENCES


[17] M. Bender, W. Seelig, C. Daube, H. Frankenberger, B. Ocker and

F. Sarto, M. S. Sarto, M. C. Larciprete and C. Sibilia


[20] From calculation of the SE performed by using the transfer matrix method, as described in details in ref. [8].
