Flexible sol-gel coatings on polymeric and metallic materials

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\textbf{ABSTRACT}

One of the current forefront in the field of photonic are flexible photonic research and development. The desired deliverable is to adjust the mechanical properties of materials to fabricate flexible photonic systems with various applications, e.g. gratings, channel waveguides, solar cells, protective coatings. It is well known that sol-gel metal oxide coatings may find applications as flexible coatings in photonics. Moreover, these materials can be easily functionalized to obtain materials with additional special, desired properties like easy-to-clean, anti-fingerprint, anti-fogging and others, what is attractive for the potential of future commercialization of flexible photonic materials.

In this work, we present the first step of research aimed to obtain silica-based coatings with appropriate adhesion on flexible substrates as poorly wettable surface – polymer PET and Ti-6Al-4V and 316L metallic thin foil as active oxide surface. The use of various types of substrates was aimed at presenting diversity in the possibilities of using the proposed coating materials. Nanoindentation, tensile test and scratch test of the investigated samples were studied. Measuring the mechanical properties of thin oxide films is difficult because it is usually impossible to detach of coating, not destroying its, from substrates. The thickness of coatings can range from a dozen to a few hundred nanometres, so complete methodology to determine a full set of mechanical properties is still lacking. In literature, the surface of samples is measured without a clear indication on coating properties, but on features which are the results of substrate-coating combinations.

\textbf{Keywords}: mechanical properties, silica, hybrids, adhesion, thin coating, scratch resistance, nanoindentation, tensile test

1. \textbf{INTRODUCTION}

The combination of metal oxides with silica allows obtaining materials with changed mechanical properties\textsuperscript{1,2}. Moreover, creation of hybrids with silica leads to materials with improved stability and/or enhanced properties\textsuperscript{3}. Researchers in the recent studies of inorganic metal oxide-silica hybrids observed dependencies between optical properties and the contribution of particular oxides in materials\textsuperscript{4,5}. Research on materials obtained in low temperature are the additional value, because most of recent works consider high temperature treated materials applied on glass. There are many scientific publications which determine mechanical properties at the nano- or submicron scale for selected engineering materials\textsuperscript{6,7}. What is more, there are also publications aimed at systematizing the information collected so far in the field of research methods and obtained values in mechanical tests of various thin layers\textsuperscript{8}. However, there is still a lack of clear data in definition of mechanical parameters for materials which at least one dimension is in nano- or submicron scale.

What is more, it is still challenging to relate the results obtained at the nano and submicron level to the results obtained at the macro scale. The data to unambiguously describe the mechanical properties for nanometric and submicron objects, i.e. in the area between quantum mechanics and classical mechanics, are still insufficient.

1.1. The potential of the sol-gel method in the field of flexible coatings for photonic application

Thin layers obtained by the sol-gel method are increasingly used as functional coatings for getting active feature, e.g. sensor, anti-reflective, polarizing surfaces. Thin sol-gel multilayer coatings may additionally have a protective character, obtained as a result of composition modification, e.g. by using organosilanes or admixtures such as fibres, powders. Modifications may result in increased coating resistance to scratches or abrasion resistance, but also increased adhesion or tensile strength. The aim of the study was to determine the basic mechanical properties of thin layers or the layer-substrate...
sample and to determine the effect of the substrate on the mechanical properties of the samples. This publication presents a set of preliminary results for simple and hybrid silica coatings on metallic and polymeric substrates. The authors aimed to illustrate the potential of new-synthesized sol-gel coatings on elastic substrates in terms of resistance to deformation. Indeed, materials for applications in flexible photonics must be able to easily bend without breaking/destroying.

2. EXPERIMENTAL METHOD

2.1. Coatings types

Under the sol-gel experiment the silica coatings based on different precursors were obtained in variants as presented in Table 1. The used precursors are as follows: TEOS (tetraethoxyorthosilicate), DEMS (diethylidimethoxysilane), MtEOS (methyltriethoxysilane), n-PtEOS (n-propyltriethoxysilane), iBtMOS (iso-butyltrimethoxysilane), DMES (dimethyldiethoxysilane), AliP (aluminiumizopropoxide), di-secBAltES (di-sec-butoksylaluminoksytrietoksysilan), TBOT (titanium(IV) butoxide).

<table>
<thead>
<tr>
<th>No.</th>
<th>COATING NAME</th>
<th>TYPE of COATING and USED PRECURSOR/-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>coating A</td>
<td>SiO$_2$ based on TEOS</td>
</tr>
<tr>
<td>2</td>
<td>coating B</td>
<td>SiO$_2$ based on TEOS and DEMS mixture</td>
</tr>
<tr>
<td>3</td>
<td>coating C</td>
<td>SiO$_2$ based on TEOS and MtEOS mixture</td>
</tr>
<tr>
<td>4</td>
<td>coating D</td>
<td>SiO$_2$ based on n-PtEOS</td>
</tr>
<tr>
<td>5</td>
<td>coating E</td>
<td>Al$_2$O$_3$ based on AliP</td>
</tr>
<tr>
<td>6</td>
<td>coating F</td>
<td>SiO$_2$/TiO$_2$ based on iBtMOS and TBOT mixture</td>
</tr>
<tr>
<td>7</td>
<td>coating G</td>
<td>SiO$_2$/Al$_2$O$_3$ based on DMES and TEOS and di-secBAltEOS mixture</td>
</tr>
</tbody>
</table>

All precursors were used as received without further purification. The hydrolysis and condensation reactions were conducted under the acid conditions, in room temperature and ambient pressure. The reagents were homogenised by the mechanical stirrer. The obtained hydrolysates were applied to substrates by the dip-coating method.

2.2. Substrate preparation

Metallic substrates were used in the form of thin foil (thickness=50μm) and rectangular plates (thickness=1mm). The substrate thickness plays a significant role due to the manner of conducting mechanical research. The surfaces of metallic substrates as 316L stainless steel and Ti-6Al-4V titanium alloy, have been prepared by grinding and polishing. The surface of the polymer substrate as PET, have not been treated by any mechanical treatment. To increase the adhesion of hydrolysates to poorly wettable polymer substrates, the UV-ozone-cleaning have been used for 10 minutes for PET substrates. Each type of substrate was washed directly before the coating process or in case of polymeric substrate before surface activation. On fig. 1a-1c, examples of changing the texture of the metallic substrate (316L SS) by mechanical treatment were presented.

![Figure 1](https://journals.spiedigitallibrary.org/conference-proceedings-of-spie)

Silica layers were deposited on each type of substrate by the dip-coating method. In the case of metallic substrates, the process was repeated ten times to form 10-layers coatings. Then samples were stabilized at 250°C. In the case of the PET substrate, the coating process was repeated three times to form 3-layers coatings. These coatings were stabilized at 90°C.
The sample surfaces without and with particular coating are shown in Fig. 2. The distribution of silicon was presented for coating on both metallic substrates in Fig. 3..

2.3. Characterization

2.3.1. Nanoindentation
The nanoindentation tests of coatings on metallic substrates were performed using nanoindentation tester NHT² (CSM Instruments) with maximum load 0.1 mN. For examination of coatings on polymeric substrate ultrananoindentation tester UNHT (Anton Paar) was used, applying a maximum load of 0.01 mN.

2.3.2. Tensile test
The tensile curve was determined in the process of static tensile test. The test was performed on an MTS Bionix testing machine equipped with a specialized force sensor with a range of 250N. The deformation of the samples was conducted at a velocity of 1 mm/min.

2.3.3. Scratch test on polymeric substrates
The scratch tests of coatings on polymeric substrates were conducted with Micro Combi Tester (CSM Instruments) using Rockwell diamond indenter with a diameter of 200 µm. The scratch speed was 10 mm/min and loading speed 10 N/min starting at 0.03 N up to 15 N.

Figure 2. SEM micrograph of (a) 316L SS substrate; (b) Ti-6Al-4V titanium alloy substrate; (c) PET substrate; (d) SiO₂ (coating B) on 316L SS; (e) SiO₂ (coating B) on Ti-6Al-4V; (f) SiO₂ (coating D) on PET, mag. 5000x

Figure 3. EDX maps of the silicon atom distribution (yellow) of the SiO₂ (coating B) on the 316L SS (a), and on the Ti-6Al-4V (b).
3. RESULTS AND DISCUSSION

3.1. Nanoindentation

As results of nanoindentation measurements, Young’s modulus ($E_{\text{inst}}$) and hardness ($H_{\text{inst}}$) for coated substrates were received. In general, any of obtained thin coating did not affect global mechanical properties of substrate both for metallic and polymeric. These results are presented in section 3.2. Tensile tests. However, the nanoindentation studies have shown that significant changes were obtained in the measured parameters on the surface of each tested samples. The representative examples of obtained results for each type of substrates are presented below.

3.1.1. Coatings on metallic substrates (316L SS, Ti-6Al-4V)

Significant changes in Young’s modulus and hardness for the surfaces of metallic substrates were obtained after they were coated with silica coatings. In Fig. 4 and Table 2 results for 10-layers SiO$_2$ (coating B) on both metallic substrates were presented.

Table 2. Instrumental values of Young's modulus ($E_{\text{inst}}$) and hardness ($H_{\text{inst}}$) for metallic substrates and SiO$_2$ coating

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{\text{inst}}$ [GPa]</th>
<th>$H_{\text{inst}}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L substrate</td>
<td>167 ± 11</td>
<td>3.8 ± 0.3</td>
</tr>
<tr>
<td>10-layers coating B (SiO$_2$) on 316L substrate</td>
<td>43 ± 5</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>Ti-6Al-4V substrate</td>
<td>168 ± 14</td>
<td>11.6 ± 1.3</td>
</tr>
<tr>
<td>10-layers coating B (SiO$_2$) on Ti-6Al-4V substrate</td>
<td>37 ± 7</td>
<td>0.8 ± 0.2</td>
</tr>
</tbody>
</table>

$E_{\text{inst}}$ – Young’s modulus (instrumental), $H_{\text{inst}}$ – Hardness (instrumental)

The multilayers coating were synthesized because of low layer thickness and measurement parameters of the used device, i.e. to eliminate the coating-substrate interaction the depth of sample penetration should not be higher than 10% of coating thickness [8,9]. From measurements we know that 3-layer coating thickness is ~250nm, so we estimated that at a load of 0.1mN, the thickness of a 10-layer coating (about 800nm) is enough not to exceed 10% of its thickness.

![Figure 4. Load-displacement curves for the SiO$_2$ coatings and metallic substrates](image)

It has been observed that SiO$_2$ (coatings B) on metallic substrates reduce the surface mechanical parameters. However, the coating on 316L SS has a higher Young’s modulus and hardness than the coating on Ti-6Al-4V substrate. Since both types of substrates have the same type of layer (coating B), it can be assumed that despite increasing the thickness of the
layer, the impact from the substrate has not been eliminated. In the case of coating on the Ti6Al4V substrate, the penetration depth of 0.1 mN was obtained ~ 60nm. Probably, the obtained results were influenced by the interactions occurring at the coating-substrate interface, for one of two reasons: (1) the coating has a thickness of approx. 600 nm or less, and we did not avoid the influence of interface interaction, or (2) in the case of the tested coating-substrate system, penetration depth not exceeding 10% of the coating thickness should be obtained.

### 3.1.2. Coatings on polymer substrate (PET)

Young’s modulus (E\textsubscript{inst}) and hardness (H\textsubscript{inst}) of SiO\textsubscript{2} and SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} coatings on PET substrate are presented in Table 3. Contrary to coatings on metallic substrates, the coating materials on PET substrate have a varied effect on the measured parameters.

**Table 3. Instrumental values of Young’s modulus (E\textsubscript{inst}) and hardness (H\textsubscript{inst}) for PET substrate and SiO\textsubscript{2} and SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} hybrid coatings**

<table>
<thead>
<tr>
<th>Material</th>
<th>E\textsubscript{inst} [MPa]</th>
<th>H\textsubscript{inst} [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET substrate</td>
<td>236±33</td>
<td>3.4±0.2</td>
</tr>
<tr>
<td>SiO\textsubscript{2} on PET substrate, ie. 3-layers coating D</td>
<td>197±39</td>
<td>3.9±0.6</td>
</tr>
<tr>
<td>SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} on PET substrate, ie. 1-layer coating C + 3-layers coating E</td>
<td>466±16</td>
<td>4.5±0.4</td>
</tr>
</tbody>
</table>

\(E_{\text{inst}}\) – Young’s modulus (instrumental), \(H_{\text{inst}}\) – Hardness (instrumental)

The results presented in Table 3 and Fig. 5 show that depending on used coating material, it can increase or decrease the final Young’s modulus in relation to the initial \(E_{\text{PET}}\). By applying the simple silica coating (SiO\textsubscript{2}) it is possible to decrease Young’s modulus of the sample surface, and by applying the hybrid silica-alumina coating (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}), it is possible to increase Young’s modulus of the sample surface. Regarding the initial values of Hardness and Young’s modulus we may also be tempted to make assumptions about yield strength, i.e. according to [10], the hardness (H) of a material tends to increase with an increase in the elastic modulus (E) and yield strength (\(\sigma_y\)). So, to maintain this assumption, in case of simple silica (coating D), a decrease in Young’s modulus must be associated with an increase in yield strength.

![Figure 5. Load-displacement curves for PET, SiO\textsubscript{2} on PET and SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} on PET](image)

**3.2. Tensile test**

The nanoindentation test allowed to measure the surface mechanical properties of samples (substrate + coating). How the measurement results corresponds to the coating parameters, we discussed above.
The tensile test method allows to measure the parameters of the whole sample, and it is challenging to determine the properties of a surface or thin coating in such measurement. This chapter tests the coating effect on the mechanical properties of the sample. As substrates, thin foils were used: 50μm of Ti6Al4V, and 150μm of PET.

### 3.2.1. Coatings on metallic substrates

In order to determine the contribution of the layer to strengthening the metallic sample, the Ti-6Al-4V substrate in the form of a thin foil (50μm thickness) and shape of dog-bone (Fig.6) were coated with multilayer silica coating, i.e. coating A.

#### Table 4. Próba wyznaczenia właściwości mechanicznych cienkich warstw krzemionkowych

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>PARAMETER</th>
<th>Rm [MPa]</th>
<th>Rₑ [MPa]</th>
<th>Ru [MPa]</th>
<th>E [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al4V</td>
<td>Rm</td>
<td>514</td>
<td>407</td>
<td>446</td>
<td>109,97 *10³</td>
</tr>
<tr>
<td>Ti6Al4V + 3-layers-SiO₂ (coating A)</td>
<td>Rm</td>
<td>515</td>
<td>408</td>
<td>455</td>
<td>111,82 *10³</td>
</tr>
<tr>
<td>Ti6Al4V + 10-layers-SiO₂ (coating A)</td>
<td>Rm</td>
<td>518</td>
<td>412</td>
<td>452</td>
<td>112,97 *10³</td>
</tr>
</tbody>
</table>

Where, Rₘ = tensile strength [MPa], Rₑ = upper yield point [MPa], Rᵤ = breaking stress [MPa], E = Young’s modulus [MPa]

In each case, the standard deviation of measured parameters was at least 10%. In Fig. 7, the stress-strain relationship is presented. The results show that, according to the assumption, the analysed silica coatings do not affect the mechanical parameters of the substrate.

![Graph of tensile strength test of Ti-6Al-4V substrate with SiO₂ coating](image)

Another point of analysis was to check the quality of the coating after the tensile test. Fig. 8 presents the SEM images of coating on Ti6Al4V foil after the tensile test. The furrows in the coating are visible - marked in Fig. 8 (a) in red. The furrows are denser, the closer the sample breaks, what may mean that the coating loses continuity in these areas.
detachment or peeling of coating was observed, what indicating its good adhesion to the substrate, even after the tensile test.

Figure 8. SEM microphotographs of titanium alloy with silica layers after tensile test, mag. 2000x (a) and mag. 6000x (b)

3.2.2. Coatings on polymer substrate
In order to determine the contribution of the layer to strengthening the polymer sample, the PET substrate in the form of a thin foil (150um thickness) and shape of dog-bone were coated with silica (coating D) and multilayer silica-titania hybrid (coating F).

The dog-bone shaped samples had the following dimensions: length 24mm, medium width 6mm, thickness 0.15mm. As a result of static tensile tests, the data to calculate the mechanical parameters were obtained. Averaged values are presented in Tab. 5.

Table 5. Average results of tensile strength of PET and SiO₂ coatings

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>PARAMETER</th>
<th>Rₘ [MPa]</th>
<th>RₑU [MPa]</th>
<th>Rᵤ [MPa]</th>
<th>E [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td></td>
<td>128</td>
<td>125</td>
<td>104</td>
<td>3 534</td>
</tr>
<tr>
<td>PET + SiO₂ interlayer (D)</td>
<td></td>
<td>128</td>
<td>114</td>
<td>122</td>
<td>3 726</td>
</tr>
<tr>
<td>PET + SiO₂ (coating D) – SiO₂/TiO₂ (1-layer coating F)</td>
<td></td>
<td>134</td>
<td>118</td>
<td>106</td>
<td>3 801</td>
</tr>
<tr>
<td>PET + SiO₂ (coating D) – SiO₂/TiO₂ (3-layers coating F)</td>
<td></td>
<td>110</td>
<td>117</td>
<td>71</td>
<td>3 185</td>
</tr>
</tbody>
</table>

Rₘ – tensile strength [MPa], RₑU – upper yield point [MPa], Rᵤ – breaking stress [MPa], E – Young’s modulus [MPa]

The standard deviation in all cases was at least 10%, so in the most, no significant effect of the multilayers coatings on the strength properties of the substrate was observed. However, for multilayer hybrid coating (3-layers coating F, the stress-strain relationship in Fig. 9 marked in pink) a slight effect of lowering the values of the measured parameters was noticed. The lowering of parameters values may be caused by higher coating thickness and coating material properties. It means that the obtained hybrid coating is easier deformable than PET substrate. Further investigation needs to be done.
It should also be added, that after the tensile test, the sample surface was observed with optical microscopy. The result of this microscopic measurement was present in Fig. 10, below.

After the tensile test, the tested coating lost the continuity, what is visible in the Fig. 10 on the left. In the next step, the point of start to lose continuity will be searching and analysed.

Figure 9. Graph of tensile strength test of PET substrate with particular coatings.

Figure 10. Example of breaking of multilayer silica-titania hybrid coating (1-layer coating D and 3-layers coating F) deposited on polymer before and after tensile test.
3.3. Scratch tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lc1</th>
<th>Lc2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating D on PET</td>
<td>1.09N</td>
<td>2.35N</td>
</tr>
<tr>
<td>2 layers of coating G on PET</td>
<td>0.66N</td>
<td>3.83N</td>
</tr>
<tr>
<td>4 layers of coating G on PET</td>
<td>0.67N</td>
<td>2.11N</td>
</tr>
</tbody>
</table>

$Lc1$ – coating cracking (cohesion damage), $Lc2$ – coating chipping (adhesion damage)

The scratch test measurements of sol-gel coatings on PET substrate showed that adhesion of coatings to the polymeric substrate after its activation is satisfactory – total detachment of coatings is not observed up to the force causing substrate damage. SiO$_2$/Al$_2$O$_3$ hybrid coatings are more fragile than SiO$_2$ simple coatings, and decohesion occurs at lower load - about 0.66 N for 2 layered coating and 0.67 N for 4 layered coating, what also indicate that coatings thickness do not influence the cohesion in this case. The cohesion damage ($Lc1$) type is identified as extensible Hertz cracks which then evolve in connection of extensible Hertz cracks with v-shape cracking inside the scratch track, what is visible in pictures of $Lc2$ damage. For organically functionalized silica coating only single small cracks are observed from 1.09 N of load, what indicates higher flexibility of this coating in comparison to a hybrid one. The adhesion damage in the form of discontinuous plastic perforation occurs at 2.35 N for SiO$_2$ coating and in the form of chipping for 2-layered hybrid
coating at 3.83 N and 4-layered at 2.11 N, what shows that increase of thickness significantly deteriorate the coatings’ adhesion to PET substrate.

4. CONCLUSION

Presented results indicate the high dependence of the obtained mechanical parameters on the interactions between the coating and the substrate. Close attention should also be paid to the preparation of the substrate topography. Due to the thickness of the final coating (submicron), the value of the roughness parameter must be maintained max at the thickness of the coating. Otherwise, the thickness of the coating is not homogeneous, thus the obtained results are subject to a significant error, which can affect the reliability of measurements and prevent from competent conclusions when the measurement error is high.

The silica coated surface of 316L SS is less deformable (higher Young’s modulus) then the silica coated surface of Ti-6Al-4V titanium alloy (lower Young’s modulus). The same is with hardness – higher hardness was recorded for the modified steel surface than for modified surface of titanium alloy. Both, the type of used substrate (shown on the example of a coating on metallic substrates) and the type of coating material (shown on the example of coatings on a polymeric substrate) influence the change of the mechanical parameters of the modified surface layer. Type of interactions occurring at the coating-substrate interface affect the mechanical properties of the modified surface regardless of the type of layer and type of substrate.

By applying the sol-gel oxide coating, we are able to modulate the ability to the surface deformation from more deformable to less deformable in relation to the polymer substrate.

It can be said that a thin film does not affect the strength properties of a bulk metallic substrate. Whereby the coating itself, depending on the composition and synthesis conditions, can be continuous as long as the substrate remains continuous or it can be more fragile and crack, peeling, break away mainly in the plastic area of the substrate.

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