Barrier SiO_2-like coatings for archaeological artefacts preservation

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Barrier SiO_2-like coatings for archaeological artefacts preservation

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Abstract. Thin film chemical vapour deposition technique has been used for more than 50 years. Introducing organo¬silicones as precursors, e.g. hexamethyldisiloxane (HMDSO) or tetraethyl orthosilicate (TEOS), brought new possibilities to this method. Barrier properties of thin films have become an important issue, especially for army and emergency services as well as for food and drink manufacturers. Our work is focused on protective HMDSO thin films for encapsulating cleaned archaeological artefacts, preventing the corrosion from destroying these historical items.Thin films are deposited via plasma enhanced chemical vapour deposition (PECVD) technique using low pressure capacitively coupled pasma in flow regime. Oxygen transmission rate (OTR) measurement was chosen as the most important one for characterization of barrier properties of deposited thin films. Lowest OTR reached for 50 nm thin film thickness was 120 cm3 m-2 atm-1 day-1. Samples were also analyzed by Fourier Transform Infrared spectrometry (FTIR) to determine their composition. Optical emission spectra and thin film thickness were measured during the deposition process. We optimized the deposition parameters for barrier layers by implementation of pulsed mode of plasma and argon plasma pre-treatment into the process.

1. Introduction

Chemical vapour deposition has been used for thin film production for more than 50 years. We can find many successful applications in different industry branches, e.g. in automotive, food industry or in medicine. During 1980's, this deposition technique has been improved by adding plasma to the process. Plasma enhanced chemical vapour deposition (PECVD) or plasma assisted chemical vapour deposition (PACVD) allow using many new types of precursors, especially organosilicones.

Organosilicones offer several advantages. Organic groups have nearly infinite options for proper control of deposited layers. Additionally, they are compatible with other organic compounds and provide elasticity, preventing the layer to crack. Silicon atoms support binding to inorganic substrates including glass [1]. Hexamethyldisiloxane (HMDSO) and tetraethyl orthosilicate (TEOS) are used as PECVD precursors very often [2,3]. Main applications of organosilicone precursors are in microelectronics [4], automotive and food industry [5].

There are also other fields which can benefit from this type of precursors. Archaeology is one of them. Some organosilicone thin films have good barrier properties which make them suitable candidates for archaeological artefacts preservation. The aim of this work is to examine thin films based on HMDSO for possible application in archaeology. There are thousands of artefacts in museum depositories waiting for conservation. Their price is invaluable and they are being destroyed over time

due to the lack of conservation capacity of museums. Thus there is a need for a new high capacity technique which is relatively cheap.

When conserving an artefact, several criteria have to be met:

1. Conserving layer has to provide sufficient corrosion protection.
2. Layer must not change the appearance of treated item.
3. Temperature of treatment process must not cause any changes to the item.
4. Layer must be removable by simple technological procedure.

Barrier properties are the most important parameter of all. They can be tested in corrosion chamber where salt fog and increased temperature simulate most frequent factors causing corrosion. However, the results are evaluated visuallyand cannot be quantified easily. Another approach is to measure the permeability of deposited layers. Oxygen transmission rate (OTR) measurement is a standard method for gas permeability determination [6]. In principle, it measures the amount of oxygen gone through the thin film over time. It allows us to quantify barrier properties of a thin film in few hours while single corrosion chamber test takes several days or weeks.

Second criterion demands no visible changes in appearance of the artefact. Optical changes are usually determined by colorimetry. This technique works with colour spaces using coordinates for each colour. CIE $L^*a^*b^*$ system of coordinates is currently used as the standard. Colour difference is calculated from the change of coordinates in colour space [7]:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{1}$$

where ΔE^* is colour difference and L^*, a^* and b^* are coordinates in CIE $L^*a^*b^*$ colour space. Distinguished changes in appearance occur for $\Delta E > 0.5$.

Next, no changes can be caused thermally. Temperature may have significant influence on the artefact. PECVD is a low-temperature technique. When the setup for the deposition is correct, the temperature of the substrate does not exceed 100°C. Metallic artefacts withstand relatively high temperature without any harm. However, metallurgical changes can occur in certain metals (e.g. brass) at the temperature higher than 150°C. Non-metallic items must be treated more carefully. Material of these items can usually withstand only much lower temperatures (e.g. t < 80-100°C for plastic artefacts). PECVD offers an excellent option for this purpose: application of pulsed mode. Recent studies proved pulsed mode can decrease thermal stress down to about 60% in comparison with continuous discharge [8].

Fourth criterion is for PECVD the most challenging one. PECVD products can be prepared with excellent adhesion to the substrate and most researchers have been trying to find a way how to improve adhesion on their substrates. On the other hand, we need to control the adhesion quite accurately for the purposes described. The deposited layer must have sufficient adhesion to maintain idle state and protect the substrate but there must be a way how to overcome adhesion or to reduce it subsequently. We can use adhesion "demoters" to control the adhesion. Other approach is to deposit an interlayer which is compatible with both substrate (artefact) and barrier thin film and can be removed easily. This interlayer may or may not have barrier properties. Anyway it must meet the other preservation criteria. Special photoresins as well as different thin films (e.g. parylene) may meet them.

2. Experimental

PECVD was carried out in a glass bell-jar type reactor (volume of 60 L). Capacitively coupled plasma was generated by a radiofrequency source (Cesar, 13.56 MHz). The scheme of the apparatus is shown in Figure 1. Plasma discharge was formed between two disc electrodes (diameter of 14 cm). The upper electrode with substrate holder was supplied through automatic matching network by a RF source with frequency 13.56 MHz up to the power of 500 W. HMDSO was used as the precursor. Liquid precursor was transformed into vapour phase and mixed with oxygen before it entered the reactor. Oxygen and precursor flow rates (0.2 to 6 sccm) were controlled by Bronkhorst mass flow controllers to maintain total constant flow rate of 10 sccm. Whole device was pumped continuously by rotary oil pump as a primary pumping. Secondary pumping system including another rotary oil pump and a turbomolecular

pump was used to clean the reactor from all impurities before each deposition. Secondary pumping was separated from the reaction chamber by a gate valve during the deposition in order to prevent the thin film deposition inside the turbomolecular pump. The precursor pressure and the total pressure in the reactor were monitored by Penning, Pirani and Capacitance gauges. Total pressure of 15 Pa remained constant during the deposition process. The optical emission spectrometer Jobin Yvon Triax 550 with a 1200 gr/mm grating and CCD detector was used for the plasma diagnostics. Optical fibre was installed at a quartz window on a long flange protected by a metallic mesh which prevents coating of the window during the deposition.

Supplied power, reaction mixture composition and duty cycle of pulsed plasma were chosen as main parameters for the deposition control. Only one parameter was varied at a time, the others remained constant. Thin films were deposited simultaneously on pure silicon substrate, iron plates, glass, polyethylenevynilacetate (PEVA, 100 μm) and polypropylene foil (PP, 20 μm). Optical emission spectra were measured during the deposition process. Oxygen transmission rate was measured for PP foils after the deposition. Infrared (IR) spectra were obtained after the deposition, as well. Thin film thickness was monitored in situ by quartz crystal monitor and verified on finished thin film by interference microscopy. Thickness of all films was 40-50 nm. It is known that thinner films do not form compact layers reliably. Thicker films crack on these substrates due to different thermal expansion coefficients.

Some substrates were cleaned by plasma before thin film deposition. Argon plasma and oxygen plasma was used for the cleaning (treatment time 15 minutes; 50 W continual regime; argon/oxygen flow rate of 10 sccm).

To decrease substrate temperature and improve barrier properties of thin films, we managed to implement duty cycle into the deposition process. In pulsed mode, both supplied power and duty cycle were varied to maintain mean power in plasma discharge (mean power 50 W, supplied power 50-500 W, duty cycle 10-100%).

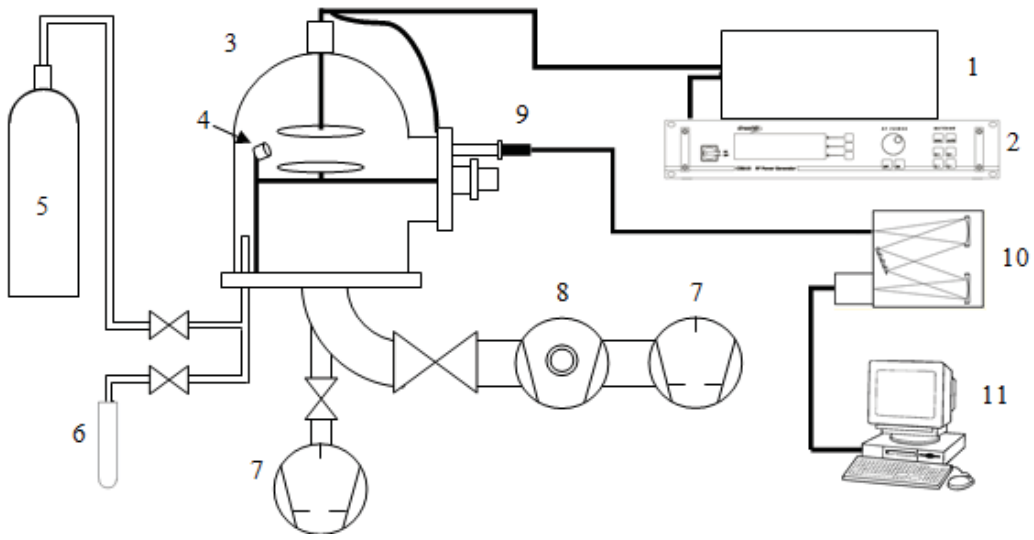

Figure 1. Apparatus for PECVD with HMDSO precursor.
1. Matching Box; 2. RF generator (13.56 MHz); 3. Deposition chamber; 4. Crystal oscillator; 5. Oxygen bottle; 6. HMDSO precursor; 7. Rotary oil pump; 8. Turbomolecular pump; 9. Optical fibre; 10. Optical emission spectrometer; 11. PC.

3. Results and Discussion

First, barrier properties of deposited thin films were tested. Gas permeability of organosilicone-based thin films is highly dependent on deposition parameters. This was confirmed by preliminary experiments. We prepared thin films with very different barrier properties. Oxygen transmission rate varied from 120 to 1500 cm^3 m^{-2} atm^{-1} day^{-1}. We focused on films with low OTR only, optimizing the parameters of the experiment to obtain as low OTR as possible. Dependence of oxygen transmission rate on supplied power and on composition of reaction mixture (O_2 content in gas mixture of HMDSO+O_2) is shown in Figure 2. Both dependences show minima corresponding to the best barrier properties achieved. Several reasons led to these results:

- Low supplied power does not enable sufficient ionization and fragmentation of the precursor.
- Too high power causes excessive fragmentation. Composition of thin films was analysed by X-ray photoelectron spectroscopy and infrared spectroscopy. Both techniques indicate composition similar to SiO_2. Because Si-O bonds are required, destroying these bonds by high power leads to lower SiO_x layer formation. Additionally, defects in the thin film occur.
- Infrared spectra (Figure 3) show decreasing carbon content in the thin film with increasing O_2 content in reaction mixture. This also corresponds to the decrease of CH fragment concentration in optical emission spectra. All that means less and less carbon incorporated in deposited thin film. The lower the carbon content, the better barrier properties can be achieved. However, certain amount of carbon is needed. When the carbon content in the thin film was too low, thin films lost their elasticity and started to crack. Incorporated carbon provides elasticity which is vital for deposition on flexible substrates.

Implementation of pulsed mode into the deposition process brought new interesting results. Dependence of OTR on duty cycle (Figure 4) showed a minimum between 20% and 30%. High power in a pulse created particles with high kinetic energy responsible for more intensive bombardment of the substrate surface. Bombardment removes solitary particles jutting out over the created thin film. It makes thin film denser with better barrier properties. Bombardment is influenced by bias, too. Bias (or self-bias, in our case) enhances particle bombardment and therefore improves barrier properties of thin film. Significant dependence of self-bias on total pressure was observed. Standard working pressure for our apparatus is about 15 Pa. When increasing the pressure over 30 Pa, the electrode with substrate holder ceases to bias self.

Barrier properties of deposited films depend on surface morphology, as well. The smoother the surface, the better barrier properties of the thin film. Several tests were run to explore the option of cleaning of the substrate by argon and oxygen plasma before thin film deposition. Argon pre-treatment decreased OTR of deposited film from 120 cm^3 m^{-2} atm^{-1} day^{-1} to 80 cm^3 m^{-2} atm^{-1} day^{-1}.Oxygen pre-treatment caused OTR to increase to about 160 cm^3 m^{-2} atm^{-1} day^{-1}. Oxygen plasma probably grafted reactive species (e.g. radicals of atomic oxygen, O_2, OH) to the surface of the substrate instead of cleaning it by simple particle bombardment. Oxygen plasma did not improve barrier properties; argon plasma pre-treatment is suitable for deposition of better barrier layers.

During preparation of thicker thin films, it is necessary to pay attention to thin film appearance and transparency. Thick SiO_x films (film thickness more than 10 μm) have white or light yellow colour and their transparency decreases. Certain thicknesses cause light diffraction. These cases must be avoided. To evaluate the change of artefact's optical appearance, colorimetry was used. Colour difference (ΔE) did not exceed 0.3 for every deposited thin film. Higher values of ΔE are expected for thicker films. Finding an optimum for film thickness and ΔE will be the subject of further research.

Temperature of the substrate was monitored during the deposition. It did not exceed 100°C in all cases. No change was observed for metallic and glass substrates. Substrates made of polymers can deform depending on polymer type. We tested PEVA and PP substrates. PEVA substrates were corrugated during depositions lasting more than 5 minutes. The temperature of these substrates was close to their melting point (105°C) causing the deformation. PP substrates (melting point 120°C) are more suitable for depositions and OTR measurement. Other types of substrates (e.g. polyethylene, ceramics) will be tested soon.

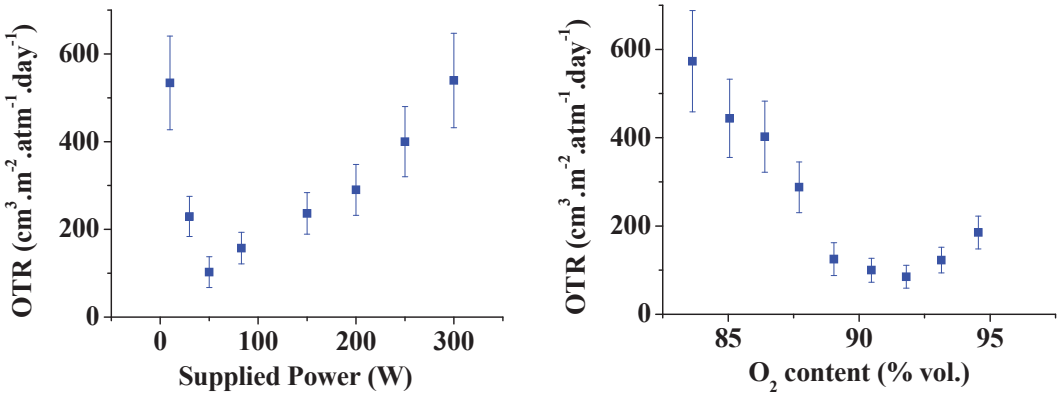

Figure 2. Dependence of oxygen transmission rate on supplied power (left) and O_2 content in reaction mixture (HMDSO+O_2) (right).

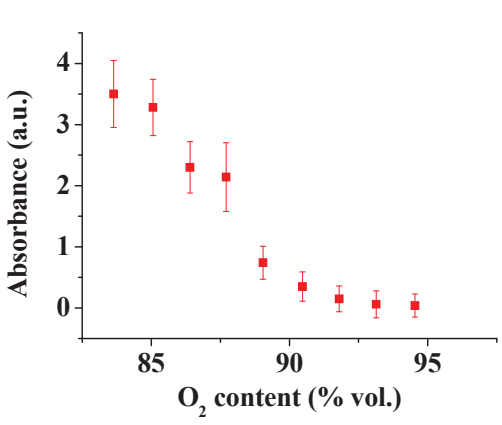

Figure 3. Dependence of IR absorbance of Si-$(CH_3)_x$ on O_2 content in reaction mixture (HMDSO+O_2).

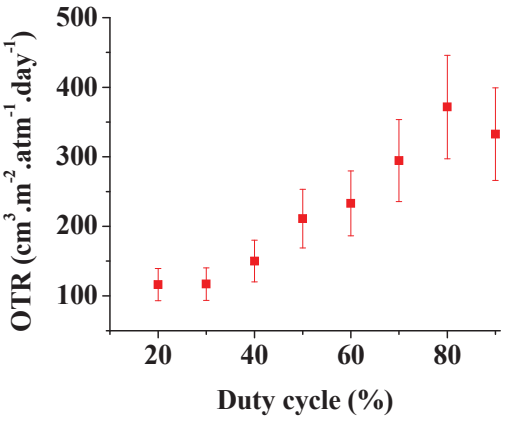

Figure 4. Dependence of oxygen transmission rate on duty cycle (mean power 50 W).

Finally, removability of thin films was tested. SiO_x layers have excellent chemical resistance so all attempts to remove these films chemically failed. Mechanical removal is quite complicate, as well. SiO_x films are very thin (40-50 nm) and have very good adhesion to the substrate surface. It is difficult to scratch them off without causing any harm to the substrate. Best solution is to use an intermediate layer which can be removed easily and that is compatible with both substrate and SiO_x thin films.

4. Conclusion

SiO_2-like thin films were tested for possible application in archaeology artefacts conservation. Thin films were deposited via low pressure PECVD using HMDSO as a precursor. They were examined whether they meet the criteria for proper conservation of artefacts.

Deposited films have good barrier properties. Best barrier properties were achieved for 50 W mean supplied power, pulsed mode of plasma with 20-30% duty cycle and 92% of O_2 in reaction mixture (O_2+HMDSO). Oxygen transmission rate of these films was approximately 120 cm^3 m^{-2} atm^{-1} day^{-1}. Argon plasma pre-treatment before the thin film deposition decreased oxygen transmission rate of thin

film to 80 cm^3 m^{-2} atm^{-1} day^{-1}. Thin films have very low carbon content determined by infrared spectrometry. Colorimetric measurements proved that colour difference caused by deposition of a thin film on an item is very low. Prepared thin films do not change the appearance of the substrate.

SiO_x layer removal is complicated due to low thickness, high adhesion and excellent chemical resistance. This will be solved by an interlayer which will be removable easily. Several types are tested. Further research will focus on multi-layer systems for cultural heritage items protection as well as on temperature influence on substrates made of different materials.

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