

## In-situ monitoring of thin film deposition process using optical emission spectroscopy

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Plasma enhanced chemical vapour deposition (PECVD) has become more and more popular for thin film deposition, especially using organosilicon precursors. This work focuses on high density films deposited by PECVD using hexamethyldisiloxane precursor. Optical emission spectroscopy was used for plasma diagnostics. Oxygen transmission rate and infrared spectra of deposited layers were measured. Optimal experimental conditions for low carbon content layers and layers with good barrier properties were determined.

Plasma enhanced chemical vapour deposition (PECVD) has been used successfully in many industrial applications. Chemical sensors or computer chips can be fabricated using this technique. Recently, organosilicon become more and more popular as PECVD precursors [1,2]. Thanks to silicon atom inside, they can form various thin films capable to bind to glass and other inorganic substrates. Additionally, organic parts of the precursor ensure flexibility and versatility of functional groups leading to practically limitless possibilities of substitutions. Hexamethyldisiloxane (HMDSO) [1] or Tetramethoxysilane (TMOS) [2] are the most common organosilicon precursors in PECVD. The interest of experts is focussed especially on precursors forming low carbon-content layers regarding their high density and consequently their barrier properties.

Optical emission spectroscopy (OES) was chosen for plasma diagnostics. It allows determination of various radiating species as well as consequent calculation of some plasma parameters as rotational, vibrational and electron temperatures. The biggest advantage of this method is that it can be used during the plasma deposition without affecting it so it is perfectly suitable for monitoring of the deposition process.

The aim of this work was to monitor a thin film deposition process and to determine optimal conditions for SiO<sub>x</sub> layers for oxygenproof coatings with possible application as protection layers of archaeological artefacts. All experiments were done in a glass bell jar reactor with capacitively coupled plasma using a RF generator (Cesar, 13.56 MHz). The scheme of the apparatus is showed in Fig. 1.

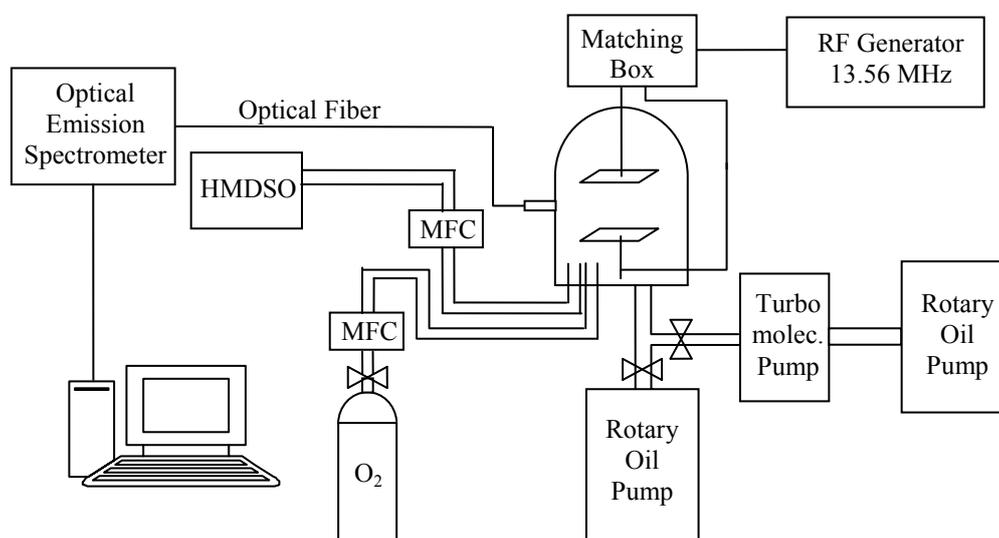


Fig. 1: Scheme of plasma deposition systeme.

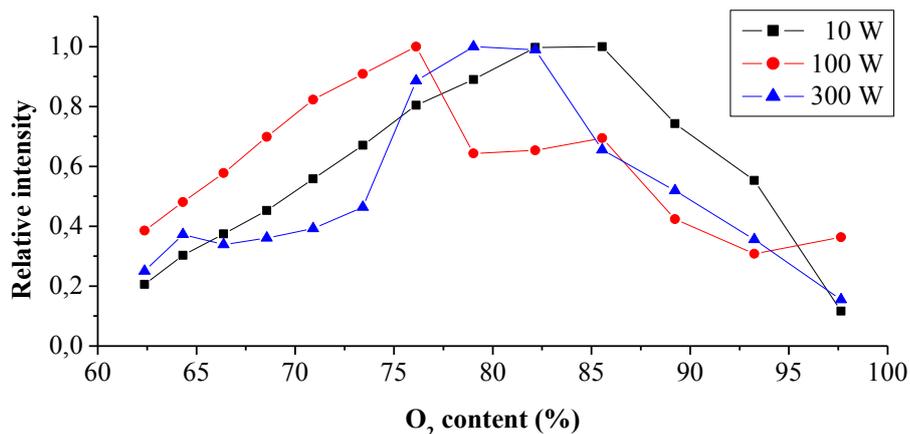


Fig. 2: CO intensities dependence on the amount of oxygen in reactor.

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. The flow of oxygen (10 sccm) and the flow of precursor (0.2 to 6 sccm) were controlled by Bronkhorst mass flow controllers. Whole device was continuously pumped 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 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. 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 protected by a metallic mesh which prevents coating of the window during the depositions.

Supplied power and HMDSO/O<sub>2</sub> ratio 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 on pure silicon substrate and polyethylevinylacetate (PEVA) foil. Optical emission spectra were measured during the deposition process. Oxygen transmission rate was measured for PEVA foils after the deposition.

In optical emission spectra, we focused on CO fragment providing the information about carbon content in the deposited layer. The more CO is created, the less organic parts remain in the layer and the higher density film is formed. Fig. 2 shows the dependence of intensities of CO on HMDSO/O<sub>2</sub> ratio expressed as percentage content of oxygen in the mixture. It is obvious that most CO is created when there is 75-85 % of oxygen in the mixture (the rest is HMDSO). The content of oxygen varies for different values of supplied power and other parameters (total pressure, duty cycle, flow rate). The layer deposited at these conditions should have the lowest organic content. This corresponds to results gained from infrared spectra of deposited layers. However, the thin film with the least organic content has not necessarily the best barrier properties. Preliminary results of oxygen transmission rate measurements indicate that thin films deposited at 95 % of oxygen in the mixture have better barrier properties than those deposited at lower oxygen contents. More detailed measurements will be held on this topic in order to improve gas protection of the substrate. If the protection is sufficient, this method will be used for conservation of archaeological metallic artefacts.

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## References

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