Plasma Enhanced Chemical Vapour Deposition of SiO_2-like Films: Monitoring and Optimization of the Process

Michal Procházka
Lucie Blahová, František Krčma, Radek Přikryl

Brno University of Technology
Faculty of Chemistry
Institute of Physical and Applied Chemistry
Purkyňova 118, 612 00 Brno, Czech Republic
xcprochazkam@fch.vutbr.cz

1 Introduction

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, organosilicons 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], Tetramethoxysilane (TMOS)[2] or Tetraethoxysilane (TEOS)[3] are the most common organosilicone 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_x layers for low carbon content and oxygenproof coatings with possible application as protection layers of archaeological artefacts. Similar technique has been used successfully for permeation barrier coatings in PET bottles[4].

2 Experimental

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.

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_2 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 polyethylenevinyl-acetate (PEVA) foil. Optical emission spectra were measured during the deposition process. Oxygen transmission rate was measured for PEVA foils after the deposition.

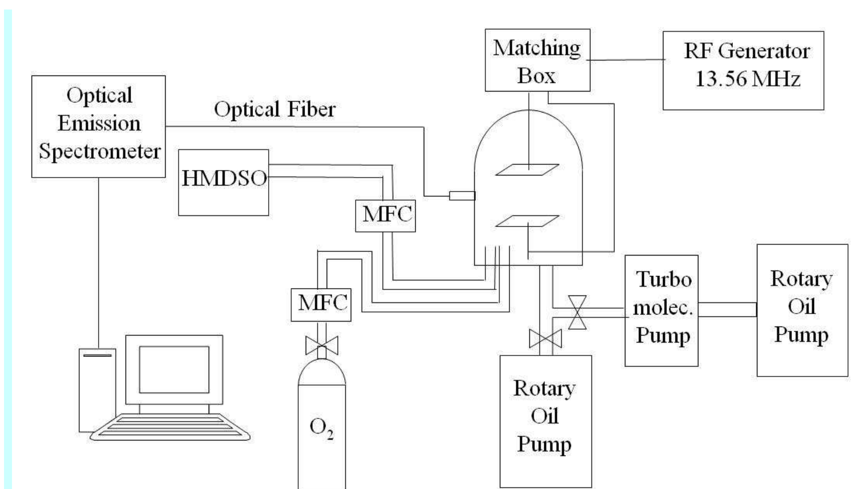

Fig. 1: Scheme of apparatus for PECVD of SiO_x layers from hexamethyldisiloxane/O_2 gas mixture.

3 Results and Discussion

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

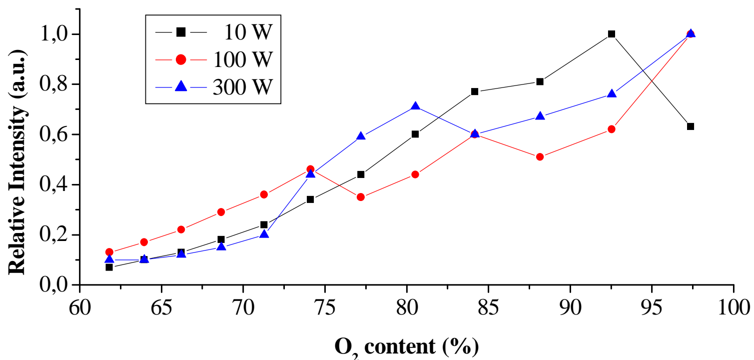

Fig. 2: Dependence of intensities of CO fragment on O_2 content in gas mixture. Measured by OES.

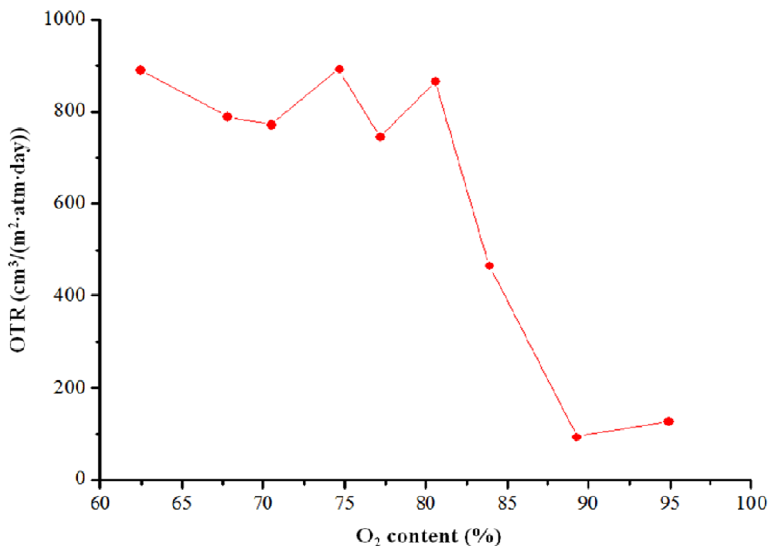

Fig. 3: Dependence of oxygen transmission rate of samples on O_2 content in gas mixture.

intensities of CO on HMDSO/O_2 ratio expressed as percentage content of oxygen in the mixture. It is obvious that most CO is created when there is over 90 % 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 shown in Fig. 3 indicate that thin films deposited

at 90 % of oxygen in the mixture have better barrier properties than those deposited at lower or higher oxygen contents. Layers with incorporated carbon atoms have holes in their structure caused by spatial arrangement of organic groups. On the other side SiO_2-like layers with nearly no organic content crack after the deposition when the substrate cools down. This effect occurs due to different thermal expansion of the layer and the substrate.

4 Conclusion

Plasma enhanced chemical vapour deposition of hexamethyldisiloxane was used to prepare SiO_x thin films with good barrier properties. Optical emission spectra measured during the deposition process show the decrease of CO fragment concentration with increasing O_2 content in gas mixture. Thin films prepared from HMDSO/O_2 mixture with more 90 % of O_2 do not contain carbon atoms in their structure. However, preliminary results of oxygen transmission rate measurements indicate that thin films deposited at 90 % of oxygen in the mixture have better barrier properties than those deposited at lower or higher 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.

5 References

1. GOUJON, M., BELMONTE, T., HENRION, G. OES and FTIR diagnostics of HMDSO/O_2 gas mixtures for SiO_x deposition assisted by RF plasma. *Surf. Coat. Tech.*, November-December 2004, vol. 189-190, p. 756-761.
2. BANG, S. B., CHUNG, T. H., KIM, Y. Plasma enhanced chemical vapor deposition of silicon oxide films using TMOS/O_2 gas and plasma diagnostics. *Thin Solid Films*, August 2003, vol. 444, p. 125–131.
3. MAHAJAN, A. M., PATIL, L. S., BANGE, J. P., GAUTAM, D. K. TEOS-PECVD system for high growth rate deposition of SiO_2 films. *Vacuum*, March 2005, vol. 79, p. 194–202.
4. DEILMANN, M. *Silicon oxide permeation barrier coating and sterilization of PET bottles by pulsed low-pressure microwave plasmas.* Bochum, 2008. 142 p. Dissertation supervisor: Prof. Dr.-Ing. Peter Awakowicz.

Acknowledgement: This work has been supported by the Ministry of Culture of the Czech Republic, project No. DF11P01OVV004.