Deposition and characterization of SiO_x-like thin films from HMDSO mixtures plasmas

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Plasma polymerization of organosilanes is a valuable method for depositing both inorganic SiO_2-like films, which have found many applications in microelectronics and optics, and polymer-like SiO_x films, suitable for barrier films in food packaging and corrosion protection layers.
In this work, SiO_x-like films were deposited on silicon and on aluminum substrates starting from HMDSO as precursor with different reactive gases (O_2 and/or Ar) . Thin film morphology depends on growth process, two different chemical vapour deposition techniques has been employed: Plasma Assisted Supersonic Jet Deposition (PASJD) and Plasma Enhanced CVD (PECVD). Correlation between different operating conditions (such as the effect of HMDSO/O_2 ratio, total treatment pressure and growth time) and the resulting surface properties were also discussed. The structure and bondings in the deposited films were studied by means of Fourier Transform Infrared (FTIR) spectroscopy. Films morphology and nano-structures were analyzed by Scanning Electron Microscopy (SEM). Thermal annealing was also performed and the effects induced on film composition and chemical structure were therefore evaluated.
The capability of controlling the film composition by varying operating conditions opens interesting perspectives. A potential research direction of this study worth exploring is to electrochemically reduce the SiO_x-like films to obtain a nano- or fine micro-structured surface layer, providing a novel Black-Silicon fabrication process.

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Silicon oxides or organosilicone thin films deposited by plasma assisted deposition have attracted great interest for a variety of technological and industrial applications, such as protective coatings[1], optical filters, chemical barrier coatings, scratch resistance coatings and humidity and chemicals sensors [2]. HMDSO precursor is non-toxic, non-explosive and has a high vapor pressure (48 hPa), which provides easier use in vapor deposition processes [3]. The use of this monomer is therefore advantageous and it also contains the Si-O bonds needed for silicon oxides thin films formation.
The aim of this work is to characterize thin films obtained from hexamethyldisiloxane (HMDSO) and O_2/Ar plasmas [4].

Two different chemical vapour deposition techniques have been employed: Plasma Assisted Supersonic Jet Deposition (PASJD) [5] and Plasma Enhanced CVD (PECVD). The former is a technique which splits the deposition process into two steps: the precursor dissociation by a radio frequency (RF) inductively coupled plasma (ICP) and the nanoparticles acceleration and assembly on a substrate by means of a supersonic inseminated jet. The latter is one of the techniques allowing industrial-scale deposition of high-quality coatings. The reacting gases are also ionized by an RF inductively coupled discharge and the substrate is placed within a diffuse plasma region. Since PASJD is discussed also in another contribution, we will focus on the discussion of our PECVD experiments.

A cubic chamber with size 40x40x40 cm was used for deposition. An ICP antenna, annular in shape, is placed inside a top cap above the chamber. The source gases were flowed through micrometer valves into the vacuum deposition system and the partial pressures were controlled by a capacitive and a Penning gauge. Inside the plasma chamber an inductively coupled plasma is generated by a 13.56 MHz-RF power supplier. The chamber is grounded and the RF generator powers the ICP antenna through an RF manual matching network [6]. The RF power of 300 W is unvaried for all depositions. Aluminum foils and silicon wafers (100), used as substrates, have been placed within the visible glow, downstream and facing the plasma source region.

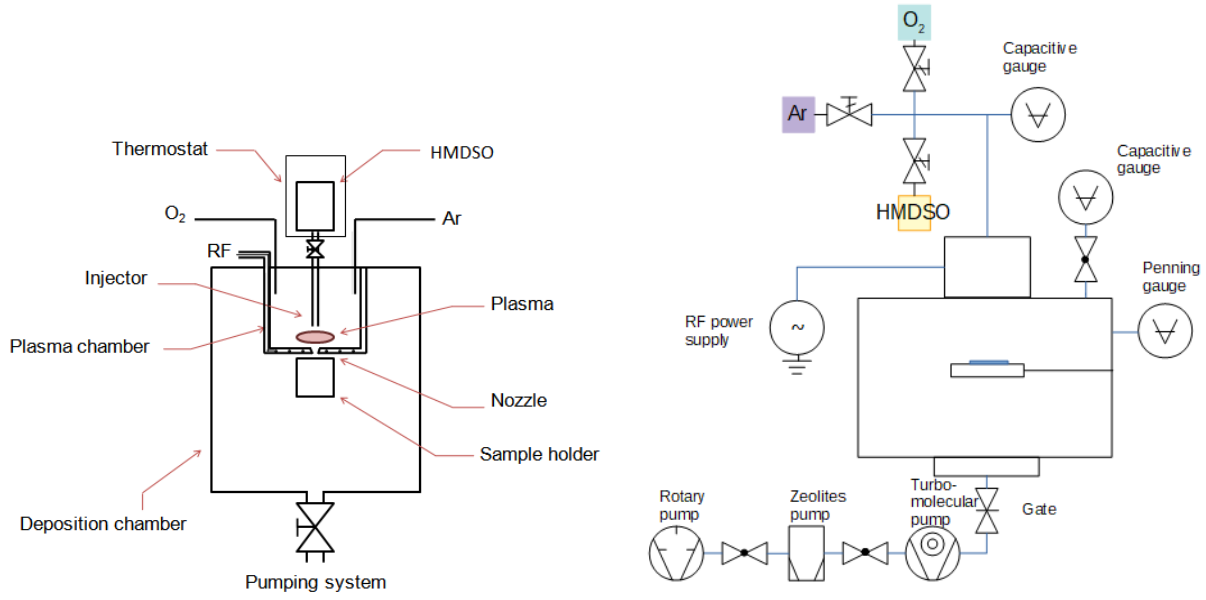


Figure 1: Schematic representation of the two deposition systems. The PASJD reactor, Piuma, on the left and the PECVD reactor, Copra, on the right.

Operating parameters, such as the gas feed mixture composition and the total treatment pressure have been varied in order to evaluate the films composition and morphology.

The deposition processes have been performed in two different pressure regimes, high ($\sim$ 1 x 10^{-1} mbar) and low ($<$ 5 x 10^{-2} mbar) total pressure. The HMDSO ratio in the mixture has been varied from 0 to 30 % and from 20 to 40 %, respectively. Argon and oxygen mixture was chosen as processing gas because oxygen enables the oxidation of the precursor and it is involved in the fragmentation of the monomer while argon ensures a stable high density plasma. A ratio around 1 : 2 was usually employed. Increasing the HMDSO concentration the deposition rate grows whereas the plasma state remained stable and diffuse.

The substrates have been partially masked and the average deposition rate was evaluated by measuring the films thickness by means of a mechanical profilometer. The thickness of some films has been evaluated also by cross-section SEM images, resulting in broad agreement with the measured rates. To have a reference, we estimated a deposition rate of about 1 nm/s for the 30% HMDSO plasma at high pressure.

FTIR absorption spectra of films were collected in attenuated total reflection (ATR) by the Varian 670-IR spectrometer equipped with a nitrogen-cooled mercury cadmium telluride detector. The spectra were recorded in the range 4000-650 cm^{-1} and under the following conditions: 2 cm^{-1} spectral resolution, 25 kHz scan speed, 512 scan coadditions. Decomposition of the spectra was undertaken using the GRAMS/Al 32 software suite.

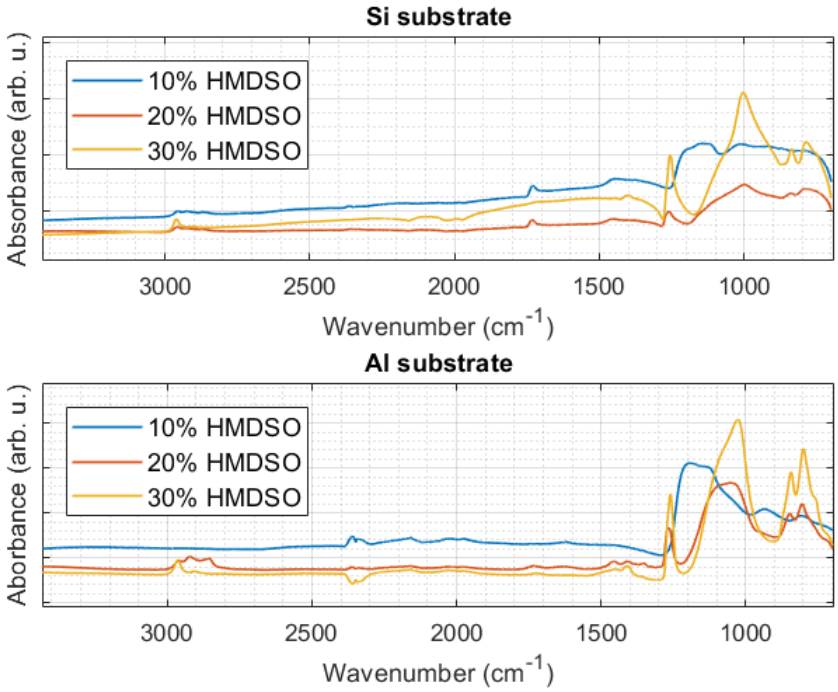
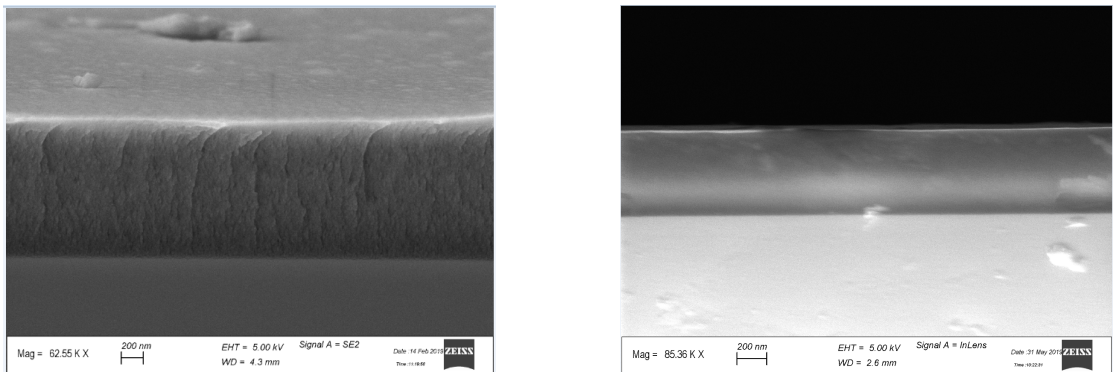


Figure 2: Examples of FTIR absorption spectra under the following conditions: high total pressure, 10' treatment time, different HMDSO ratios and substrates.

According to literature [4, 7], the stronger absorption band in the range 1000-1150 cm^{-1} can be assigned to the Si-O-Si asymmetric stretching mode, the CH_3 symmetric bending in Si- CH_3 at 1260 cm^{-1}, the CH_x symmetric and asymmetric stretching at 2800-2960 cm^{-1}. Of particular interest is the deconvolution of the SiO_2 absorption band into Gaussian peaks, which gives rise to four vibrational modes assigned to different environments for silicon atoms [7, 8]. This is affected especially by annealing process. It has been performed at 500°C for 30'. As assessed by FTIR, the film desorbed several compounds: hydrocarbon content of the film is reduced and a significant increase in absorption by SiO_2 has been observed [9].
SEM analysis revealed that the films are homogeneous and the thickness is uniform. As it could be grasped from figure 3, a higher thickness can be obtained with the PASDJ technique.



(a) (b)

Figure 3: Cross-section SEM images of films deposited by PASDJ (a) and PECVD (b).

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