Optical Emission Spectroscopy of Plasma Deposition Processes Using Dimethylphenylsilane Precursor

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Abstract
The inductively coupled low pressure plasma operating in continuous as well as in pulsed mode was used for the experiments. The aim of the presented experiment was to study the dimethylphenylsilane (DMPS) fragmentation, and the influence of set-up parameters on the deposition process. Fragments of DMPS were identified by optical emission spectroscopy. Dependences of fragment populations on supplied power as well as on DMPS pressure were determined, and consequently, the electron and rotational temperatures were calculated. Some optimal values of set-up parameters as DMPS pressure and duty cycle were found.

Keywords: Optical emission spectroscopy, organosilicons, thin film deposition, plasma diagnostics.

Introduction

Plasma polymerization is a modern technique used for deposition of thin film layers for various purposes. Although this is a kind of polymerization, it differs from conventional polymerizations essentially. In conventional polymerization, the first reactive particle is created that reacts with a molecule of monomer and starts a chain reaction. In plasma polymerization, energy in the form of plasma causes fragmentation of monomer, and then these fragments react with each other to form three-dimensional cross-linked net. Plasma serves here as a source of energy that is needed for fragmentation [1].

Different types of organosilicon precursors have been used in plasma polymerization recently. Some of them showed good properties to be used in plasma polymerization technologies, e.g. HMDSO (hexamethyldisiloxane) [2], TEOS (tetraethylsilane), TMOS (tetramethoxysilane) [3], TVS (tetravinylsilane) [4]. As their properties are pretty well described, the attention of both scientists and investors was turned to new options to improve the production process, such as searching for new precursors with similar structure and/or properties.

DMPS (dimethylphenylsilane) is an isomer of TVS. Its properties make it very suitable to serve as a precursor in plasma polymerization. This compound is in the liquid state at laboratory temperature, it has low boiling point (157 °C at 99.192 kPa) [5], but the most important of all is its structure. Silicon enables to bind to glass surface. Organic groups assure chemical resistance and thanks to spatial arrangement they have a low density (0.899 $g.cm^{-3}$) [5]. Additionally, the aromatic group influences the distribution of the charge in the molecule, and partially allows also the further classical polymerization.

The 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 [6]. The presented results extend our recent knowledge of deposition plasmas using various precursors [7–9].

Experimental

Plasma reactor was designed for thin film deposition with inductively coupled plasma using a RF generator (Cesar, 13.56 MHz). Its schematic drawing is presented in Fig. 1. The Quartz tube (i.d. of 40 mm, lenght of 60 cm) was used as the reactor body. The copper coil was supplied through automatic matching network by an RF source with frequency of 13.56 MHz up to power of 500 W. Flow of argon (used for the experimental device cleaning and surface activation before deposition) was controlled by Bronkhorst mass flow controller. DMPS was stored in thermostatic box fixing its pressure, and it was introduced into the reactor using Pfeiffer dosing valve. The whole device was

continuously pumped by the diffusion pump connected to the rotary oil pump. DMPS pressure and the total pressure in the reactor were monitored by Penning and Pirani manometers. The optical emission spectrometer Jobin Yvon Triax 550 with a 1200 gr/mm grid and a CCD detector was used for the diagnostics. Optical probe was installed at the reactor axis. A metallic mesh was installed between plasma and quartz OES window to protect window against coating during the experiments.

The whole apparatus was pumped down to the ultimate pressure of 10^{-3} Pa, and after that, the argon discharge at pressure of a few Pa was applied for 5 minutes at the argon flow rate of 10 Sccm . The same procedure was applied before the deposition. Thus, the deposition process was carried out in pure DMPS atmosphere at pressure of a few Pa.

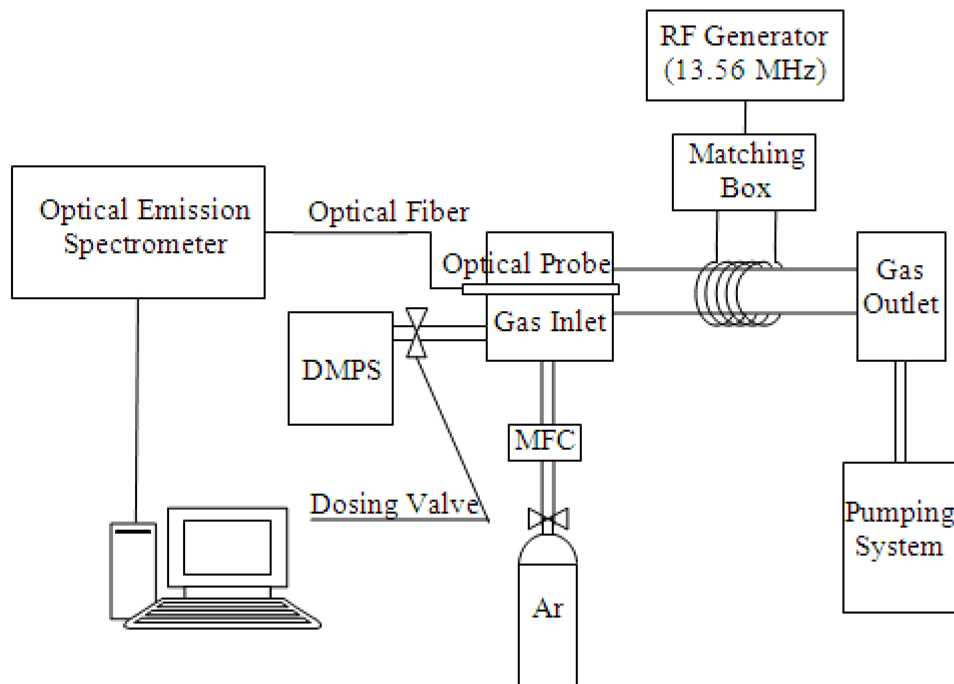

Fig. 1: Scheme of apparatus for ICP plasma polymerization

Results and discussion

The aim of the presented experiment was to make a series of measurements with different setup, and determine the best conditions for the deposition of desired thin film layer. Our attention was concentrated at two main parameters: amount of energy supplied by the RF generator expressed by the power, and the monomer pressure.

First, we decided to change the applied power. The amount of energy affects the fragmentation of the precursor. In other words, it determines what species are created during the fragmentation, and how much of them are created. It destines the content of the deposited thin film layer. We must also consider the economical point of view. The use of energetically demanding processes should give nice results but they are too expensive for wide application in technology.

Although the range of supplied power might be vast, there are some limitations we have to keep in mind. Every discharge needs a certain minimum amount of energy to be lit, and this energy is expressed by the minimum of supplied power. On the other side, we are limited by the apparatus. It can be supplied by the power of about 500 W, but it has its own electrical resistance which reflects a part of supplied energy back. This decrease is called “reflected power”, and it appears mainly due to the construction of the apparatus.

The study of supplied power influence was held at two different DMPS pressures of 1 Pa and 2 Pa. After the discharge was ignited, the pressure decreased in both cases to the half of its starting value and then, increased linearly with increasing power. However, it didn’t reach its starting value until the discharge was switched off. Due to the internal apparatus resistance, a part of the supplied power was reflected back. We kept the increasing supplied power up to 200 W when the reflected power value reached 25 % of the supplied power value.

The optical emission spectra were recorded in the spectral interval of 320–780 nm. Species identified in spectra were atomic hydrogen (Balmer series), molecular hydrogen, CH radical, atomic carbon (in the spectrum of second order), and atomic silicon. No C_2 bands were found in the spectra, neither the SiH peak that are usually observed during similar deposition processes. The fragmentation degree was probably very high at the given conditions and thus dominantly small fragments were created. Fig. 2 a) and b) show intensities of selected species. It can be seen that intensities of nearly all fragments increased more or less linearly with increasing effective power. Atomic hydrogen seemed to grow exponentially, only. We can observe small decrease of all intensities at 100 W at the pressure of 1 Pa. The discharge turned its mode from the type localised inside the coil to the type outside the coil at these conditions. After this breaking point, intensities of all signals started to rise again.

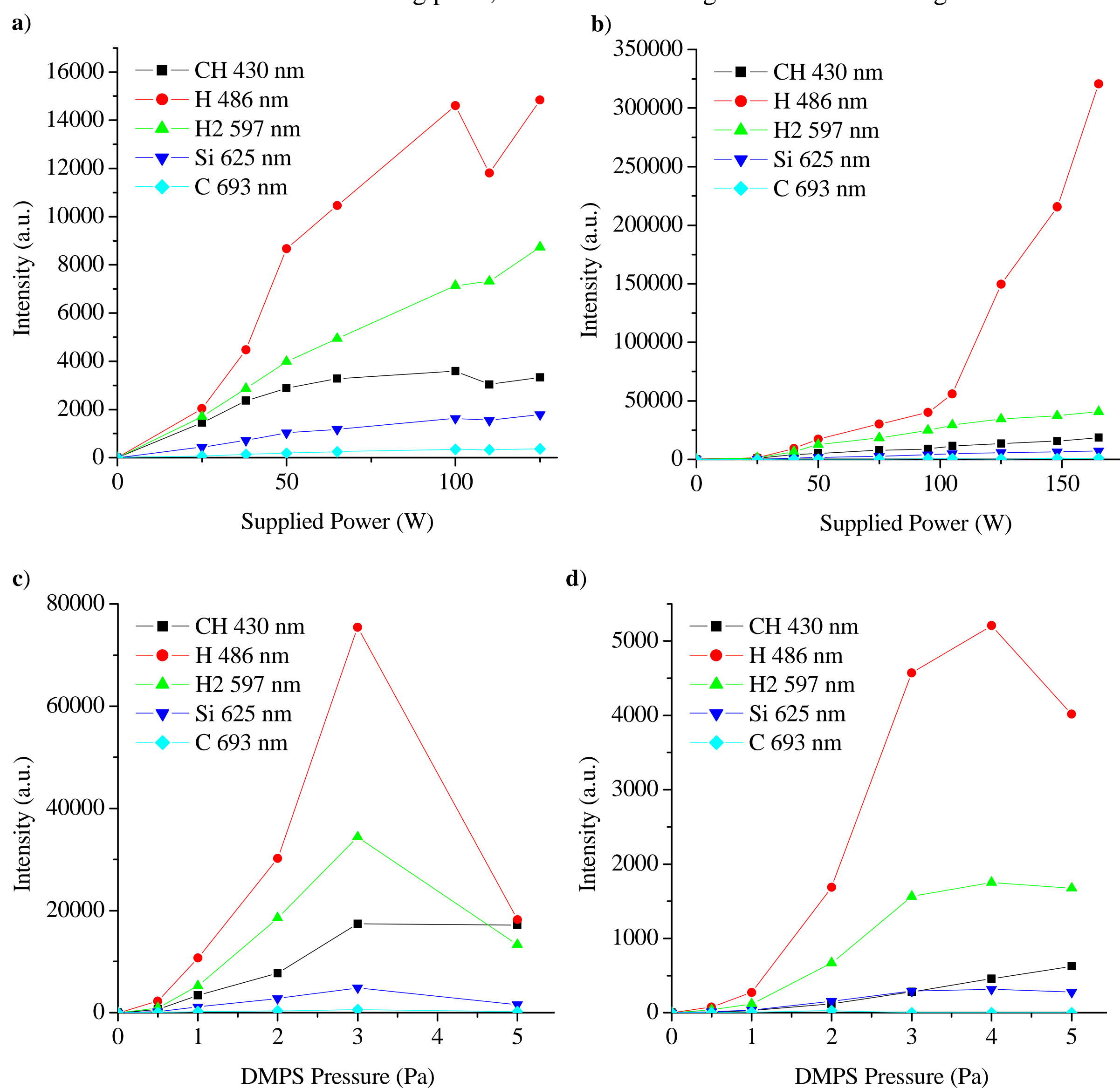

Fig. 2: Intensities of selected fragments:

a) at 1 Pa of DMPS, **b)** at 2 Pa of DMPS, **c)** at 100 W, **d)** at 200 W

The second parameter which influences the deposition process significantly is the pressure of monomer. By the amount of monomer, expressed by the partial pressure of the monomer, we can control both the content of plasma, and the content of the deposited thin film. Also the degree of fragmentation is dependent on the amount of monomer. The higher the pressure is, the greater fragments are created, and the lower their populations are. If we determine pressure optima for particular fragments, we might be able to establish the right conditions of the deposition process in

order to achieve the desired product – a thin film of required composition. However, plasma processes are dependent on many factors, e.g. fragmentation depends on supplied power, too. So we must look for pressure optima in combination with optima of other parameters, in this case with optimal supplied power.

The second part of experiments was carried out at two fixed applied powers (100, and 200 W), and the DMPS pressure was varied in the range of 0.5–5 Pa. Unfortunately, the apparatus construction did not allow achieving lower or greater pressure of DMPS.

Figs. 2 c) and d) show the dependences of selected fragments intensities on the DMPS pressure. When supplied power of 100 W was used, the most of fragments reached their maximal intensities at pressure of 3 Pa. The best reply of CH radical was estimated at 4 Pa. Similar dependencies were obtained also at the higher applied power, only the maximal intensities (except the intensity of CH radical) were obtained at 4 Pa. Intensity of CH radical increased in the whole studied pressure range, but based on results obtained at lower pressure, we can expect that the maximal CH intensity should be at about 5-6 Pa, i.e. out of the measurable pressure range.

The measured spectra allowed determination of rotational and electron temperatures. The rotational temperature was calculated from CH $^2\Delta \rightarrow ^2\Sigma$ 0-0 band at 431.5 nm using classical pyrrometric procedure. Rotational lines assignement as well as rotational constant of the upper state was taken from LifBase software [10]. Electron temperature was calculated from line intensities of hydrogen Balmer series using constants given by NIST [11]. The spectrometer response function was obtained using Oriel standard lamp. Figs. 3 and 4 show the dependences of both temperatures on the experimental conditions. Considering the 15–20% deviation, we can assume that rotational temperature was independent on supplied power or DMPS pressure. Electron temperature was slightly decreasing with increasing supplied power. When pressure of monomer was increasing, electron temperature was decreasing significantly. Vibrational temperature couldn't be determined because any convenient particle for calculation wasn't found in the spectra [12].

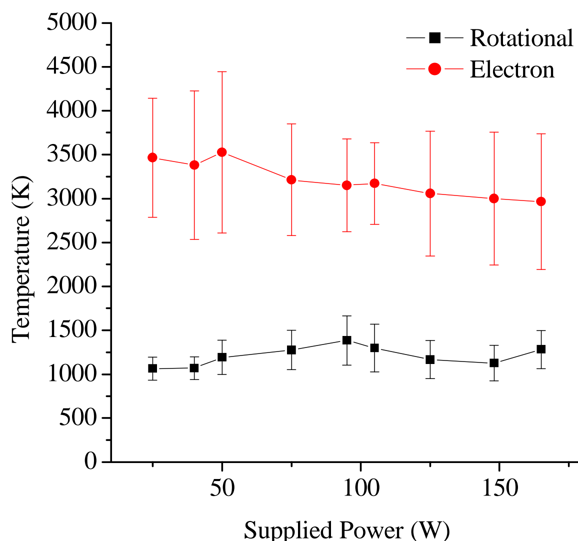

Fig. 3: Temperatures at 2 Pa of DMPS

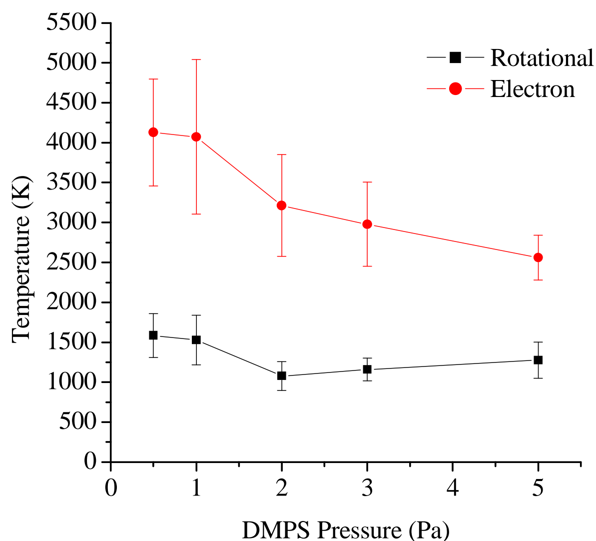

Fig. 4: Temperatures at 200 W

Conclusions

Evaluation of different parameters was investigated during RF inductively coupled plasma polymerization of dimethylphenylsilane monomer using optical emission spectroscopy. Results show high degree of fragmentation leading to the creation of many small fragments. Dependence of fragments concentration on supplied power was proven to be linear in the most cases. When changing pressure of monomer at constant supplied power, some optima for particular fragments were determined. To get more precise optimal values of DMPS pressure, it is necessary to make more detailed measurements also at higher pressures of DMPS. Rotational and electron temperatures were determined, too. Rotational temperature was nearly independent on the supplied power as well as on the DMPS pressure. Electron temperature decreased in both cases with the increasing adjusted

parameter. However, it decreased significantly with increasing DMPS pressure.

The presented results showed possibility to change the DMPS fragmentation level by varying the plasma parameters. The more detail study of the other setup parameters as well as the detailed exploration of current ones is necessary to complete in the future. Other diagnostics might be performed including in-situ mass spectroscopy or infrared spectroscopy to achieve more precise report about plasma content. These results may be compared to thin film analysis results of the deposited layers. By this way, we would be able to optimize plasma polymerization process in order to predict the composition of thin film layer, and set up the process to produce it.

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