SYNTHESIS OF SiO$_2$ NANOFIBRES BY UTILIZATION OF DCSBD ATMOSPHERIC PRESSURE PLASMA

Jana HANUSOVÁ$^1$, Dušan KOVÁČIK$^{1,2}$, Jitka BĚLÍKOVÁ$^1$, Mirko ČERNÁK$^{1,2}$, Pavel ŠTAHEL$^1$

$^1$Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

$^2$Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovak republic

email: hanusova@sci.muni.cz

Abstract

The objective of this study was to investigate the plasma calcination of SiO$_2$ nanofibres as an alternative to the conventional thermal calcination. Typically, the thermal calcination is an energy consuming and slow process limiting the potential in-line production of SiO$_2$ inorganic nanofibres. An additional problem is that the high calcination temperature is prohibitive in the preparation of inorganic nanofibres films on heat-sensitive substrates and problematic in adhesion of the nanofibres to metal substrates. In this work we present the results on the fabrication of SiO$_2$ nanofibres using an open air Diffuse coplanar surface barrier discharge (DCSBD) plasma. The experiments were conducted to determine the potential of DCSBD technique for in-line continuous calcination of nonwoven films of the electrospun nanofibres. Very short plasma exposure times of several minutes indicate that the DCSBD plasma calcination is from in-line processing point of view compatible with the typical line speed of several tens of centimeters per minute. The removing of polyvinylpyrrolidone (PVP) used as a “base polymer” in electrospinning procedure was after plasma assisted calcinations verified by weight loss and FTIR measurement.

Keywords:
SiO$_2$ nanofibres, calcination, atmospheric pressure plasma, dielectric barrier discharge

1. INTRODUCTION

Nowadays nanofibres are getting increased attention through wide range of industries. Inorganic SiO$_2$ nanofibres, which are the main topic of this contribution, are applicable in microelectronics, catalysis and metal or ceramics nanocomposites. Nanofibres are prepared by electrospinning technique, which consist of two steps. First nanofibres are deposited onto a substrate, subsequently nanofibres are transformed to ceramics by calcination at high temperatures. The aim of calcination is to remove organic “base polymer”, which is used to ensure sufficient viscosity of solution appropriate to electrospinning process. Normally, the calcination, which is crucial to control the performance of the resulting nanofibres, takes place in air for several hours at the temperatures up to 700°C [1]. This means that the thermal calcination is much slower process than the first step and limits the potential in-line production of such inorganic nanofibres. In our study we focused on investigation of the plasma calcination of electrospun SiO$_2$ nanofibres as an alternative to the conventional thermal calcination. As a source of atmospheric pressure plasma a reactor based on Diffuse Coplanar Surface Barrier Discharge (DCSBD) was used.
EXPERIMENTAL DETAILS

1.1. Materials
In all experiments as a tested material the commercial electrospun inorganic SiO₂ nanofibres on the small glass plates supplied by Kertak Nanotechnology s.r.o. (Czech Republic) were used. Polymer solution for electrospinning procedure consisted of Dimethylether (C₂H₆O) with 2% Toluene (C₆H₅(CH₃)), Polyvinylpyrrolidone (PVP), (C₆H₉NO)n used as base polymer, Acetylacetone (C₅H₈O₂) and Tetraethyl orthosilicate abbreviated TEOS (Si(OC₂H₅)₄).

1.2. Plasma source
For the plasma treatment of SiO₂ nanofibres the DCSBD source housed in small reactor was used (Fig. 1 - left). DCSBD is a type of dielectric barrier discharge generated on the surface of the dielectric barrier with the embedded metallic electrodes. Its primary feature is ability to generate a thin layer of non-equilibrium macroscopically uniform diffuse atmospheric pressure plasma of high power density in any working gas including ambient air (Fig. 1 - right). More detailed description of the DCSBD electrode design with explanation of its principle and pointing out the possible applications of DCSBD are given in [2-4].

Fig. 1: Experimental apparatus (left) and the detailed view of DCSBD plasma with the sample of SiO₂ nanofibres on the glass plate placed in the plasma field (right)

1.3. Plasma treatment – plasma assisted calcination
During plasma surface modification of SiO₂ nanofibres the samples were placed in plasma of DCSBD in the distance 0.18 mm from ceramics, as working gas an ambient air was used and input power was set to 300 W and 400 W. SiO₂ nanofibres were exposed to DCSBD plasma for different treatment times 1, 3, 5 and 10 minutes.

1.4. Analytical methods
For the verification of PVP removing effect two qualitative methods – the weight loss and ATR-FTIR measurements were used. The weight loss (G) was calculated according formula:

\[ G = \frac{M - m}{m} * 100\% \]  

where \( M \) is the weight of SiO₂ nanofibres sample after and \( m \) before plasma treatment. ATR-FTIR method was realized using Bruker, Vertex 80v spectrometer with the range 4500 – 500 cm⁻¹ and resolution 4 cm⁻¹. For ATR measurement technique diamond crystal was used. Each sample of nanofibres was scanned on three different spots and subsequently the obtained spectra were averaged.
2. RESULTS
Tab. 1 and 2 summarize the results of SiO$_2$ nanofibres weight loss measurement for the samples treated by DCSBD plasma for different treatment times at input powers 300 and 400 W. As it can be seen the results confirmed our assumption that atmospheric pressure DCSBD plasma removed some components of nanofibres. Excepting the samples exposed to plasma for 1 and 5 min at power 300 W for all studied samples the weight loss of SiO$_2$ was observed. ATR-FTIR spectra (detailed in the range 1750-500 cm$^{-1}$) for SiO$_2$ nanofibres treated by plasma at input powers 300 and 400 W can be seen in Fig. 2 and 3. From the spectra it is evident that intensity of the characteristic peak for functional group C=O at wave number 1650 cm$^{-1}$ that confirms the presence of organic PVP in SiO$_2$ nanofibres samples has tendency to go down with increasing exposure time of nanofibres in plasma. This fact indicates removing of PVP from the SiO$_2$ nanofibres substrate due to DCSBD plasma treatment with increasing exposure time. Moreover, the growing intensity of peak corresponding to Si-O-Si functional group at 903 and 1054 cm$^{-1}$ wave number can be understood as a proof of creating silicon nanofibres.

<table>
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<tr>
<th>t[min]</th>
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3. CONCLUSIONS
Based on the presented preliminary results it can be concluded that DCSBD operating in ambient air at atmospheric pressure has the potential to become an efficient tool for the plasma assisted calcination of inorganic SiO$_2$ nanofibres. Due to plasma exposure in the order of minutes the organic components can be removed as it was confirmed by the weight loss and ATR-FTIR measurement. Short plasma treatment times indicate that DCSBD plasma calcinations could be from in-line processing point of view compatible with the typical line speed of several tens of centimeters per minute. Our future work will be focused on the detailed study of the elementary composition changes of SiO$_2$ nanofibres using XPS method as well as the determination of the optimal plasma treatment conditions.
Fig. 2: ATR-FTIR spectra of SiO$_2$ nanofibres, plasma input power 300 W

Fig. 3: ATR-FTIR spectra of SiO$_2$ nanofibres, plasma input power 400 W
ACKNOWLEDGEMENT

The presented work has been supported by the project R&D center for low-cost plasma and nanotechnology surface modifications CZ.1.05/2.1.00/03.0086 funded by European Regional Development Fund (ERDF), and further partly by project 26240220042 - the Research & Development Operational Programme funded also by the ERDF.

REFERENCES


