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Liquid assisted plasma enhanced chemical vapour deposition with a non-thermal plasma jet at atmospheric pressure

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ABSTRACT

The present study introduces a process for the synthesis of functional films onto substrates directly from the liquid phase. The reported method is based on the initialization of the synthesis by means of an atmospheric pressure plasma jet operating with argon above a thin liquid film of the starting material. The process is demonstrated by the formation of a thin, solid SiO_x film from siloxane-based liquid precursors. Changes in the chemical properties of the precursor were studied in-situ during the polymerization process on the diamond crystal by using Fourier transform infrared spectroscopy The elemental composition of the SiO_xC_y films was analyzed by X-ray photoelectron spectroscopy (XPS). Furthermore, XPS was applied to study the effect of post-annealing processes on the composition of the films. The obtained deposits exhibit a low concentration of carbon groups. The amount of hydroxyl groups and interstitial water can be reduced significantly by post-process annealing of the films.

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1. Introduction

The preparation of thin functional films using chemical vapour deposition (CVD) has been established as one of the standard coating technologies today. This method allows the formation of various thin films differentiated by their chemical composition, resulting in diverse chemical, mechanical, optical and electrical properties. CVD is described by heterogeneous chemical reactions of gaseous reactants at the surface leading to formation of solid films on the substrate [1]. If the gas mixture is activated using plasma, this process is called plasma assisted or plasma enhanced chemical vapour deposition (PACVD or PECVD). An essential advantage of PECVD with respect to CVD is the lower substrate temperature and hence the minimized thermal stress of substrates. The application of atmospheric pressure CVD technology has been demonstrated on the industrial scale already in 1969 [2]. However, PECVD processes were until recently dominated by vacuum technologies because suitable plasma sources have been available predominantly for low pressure processing. Several publications dealing with atmospheric pressure PECVD appeared in early investigations of dielectric barrier discharges for plasma polymerization from 1979 onwards [3,4]. Later, non-thermal plasma jets [5,6] served as plasma sources for thin film deposition experiments, e.g. [7,8]. However, despite recent progress regarding film homogeneity and chemical composition under atmospheric pressure conditions, e.g. from [9,10], it is generally supposed that low pressure methods yield films with superior qualities (e.g. spatial morphological homogeneity). This is attributed to several reasons of intrinsic and of technological nature. Whereas the latter are linked merely to their technological maturity level, the former are related to plasma physical constraints that may have a negative influence on the film properties. We name here e.g. (i) the steep spatial parameter gradients observed in most filamentary discharges which may translate into spatially inhomogeneous film chemistry or (ii) the absence of a steady flux of kinetic (ionic) species to the growing film which plays an essential role in many low pressure PECVD processes by contributing to the formation of denser and pinhole-free films [11]. O'Neill et al. propose a route to barrier coatings using atmospheric pressure plasma liquid deposition in which precursors are introduced into the plasma using an ultrasonic nozzle atomizer [12]. It enables atmospheric pressure PECVD also for liquid precursors with vapour pressures insufficient for evaporation.

There exist several other techniques for the deposition of films operating with liquids. Wet chemistry for surface treatment in general represents a well-established field that is related to the long history which the polymer chemistry has been writing already for more than 100 years [13]. In chemical solution deposition methods, the solution is transferred onto substrates by spin, dip, and spray coating. Its curing and cross-linking are initiated by subsequent exposure to thermal

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energy, vacuum ultraviolet radiation [14,15] or plasma [16]. The latter process is known as plasma-induced polymerization [17]. Several methods employ the electric field to disperse and/or transport a liquid to be processed, e.g. electrospray or electrospinning, and they can be combined with plasma techniques [18,19,20].

Numerous approaches exist towards the plasma treatment of liquids for the synthesis of materials within the solution. However, to our knowledge, the synthesis of a compact solid thin film which exhibits a stoichiometry close to SiO_2 by direct plasma treatment of an organosilicon liquid has not been published yet. Therefore, efforts have been made to develop promising approaches for deposition processes at atmospheric pressure. In this study we present a method for the production of thin solid films from the liquid phase referred to as liquid assisted PECVD (LA-PECVD) which is particularly suited for materials with low vapour pressure that are difficult to transfer into the gas phase and furthermore, it facilitates using mixtures of different raw materials.

For the pilot study here, we demonstrate LA-PECVD by comparing three liquid compounds, hexamethyldisiloxane (HMDSO), octamethyltetrasiloxane (OMCTS), and tetrakis(trimethylsilyloxy)silane (TTMS), that are approved precursors for the formation of organosilicon films using PECVD. Indeed, molecular properties of HMDSO have been described already in 1950 [21]. The compound has been used in coating technology for more than 40 years [22]. The usage of OMCTS for PECVD dates back to 1992 and was motivated by demands for improved chemical functionality [23]. According to our recent results, the distinguished steric molecular structure of TTMS offers prospects for the deposition of thin films based on these structures [24].

2. Experimental part

2.1. Plasma source

The experiments were conducted using the cold atmospheric pressure plasma jet kINPen 11 (neoplas tools, Greifswald, Germany). The plasma jet consists of a high-voltage (HV) needle electrode centred inside a ceramic capillary (∅1.6 mm) and a grounded outer ring electrode [25]. The central electrode is powered with 2 W at a frequency of 1.1 MHz in this study. The operating rare gas or gas mixture flows through the ceramic capillary. The scheme of the source with experimental conditions is shown in Fig. 1.

2.2. Materials

The experiments in this study have been performed using three liquid organosilicon compounds: HMDSO, OMCTS and TTMS (delivered by Sigma-Aldrich Chemie GmbH, Germany, purity 98%). The specification of the compounds is given in Table 1. The same amount of HMDSO and OMCTS liquid ($V_p = 100$ μl) was prepared on a circular area S = 26 mm^2 on the substrate. It resulted in a droplet height of 3.8 mm. For the TTMS the amount was smaller (60 μl) because of lower evaporation loses compared to the aforementioned liquids. The corresponding droplet height was 2.3 mm.

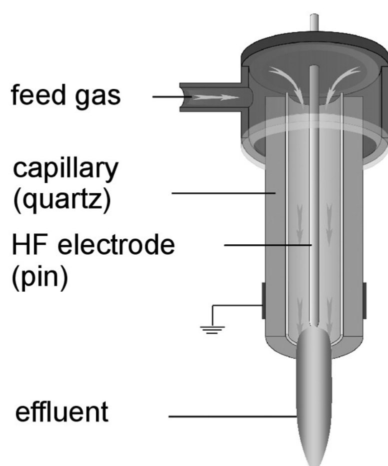

Fig. 1. Plasma source: atmospheric pressure plasma jet kINPen 11 (neoplas tools GmbH) operating at 1.1 MHz, power 2 W, argon flow rate 4.7 slm.

A polished diamond crystal of the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometer (Spectrum One, Bruker) was used as the substrate for the in situ monitoring of material changes and a double-sided polished silicon wafer (thickness 0.2 mm) was used for the comparative ex situ analyses. The plasma source was operated with argon (Linde, purity 5.0) at 4.7 slm.

2.3. Process: liquid assisted PECVD (LA-PECVD)

The material synthesis in form of thin solid films proposed here combines the principles of wet-chemical polymerization with plasma enhanced chemical vapour deposition (PECVD). The main difference of LA-PECVD to traditional PECVD is the temporal separation of the coating process into two consecutive steps, which enables to initiate additional chemical reactions. In the first step the precursor liquid is applied to the surface to be coated. In the second step synthesis of the liquid film occurs by exposing the prepared surface to the plasma jet. The interaction of the plasma effluent above the liquid surface adopts characteristics from PECVD, where the active species generated by the jet react with the organic substances. In the case of LA-PECVD additional reactions develop below the liquid – plasma interface and contribute to a more complex material synthesis. The amount of reacting precursor molecules is defined by preparation of the liquid film in the first step.

During the second step, the synthesis of solid products consumes the precursor molecules. In parallel, light volatile molecules evaporate and are in part redeposited back on the surface where they form a solid film material in a process similar to PECVD. An important mechanism of step two relates to the polarisation of the liquid layer by charging of the liquid surface by plasma. This represents also a substantial difference of LA-PECVD to those seemingly similar CVD processes where the liquid raw material is supplied by continuous spraying and its transport to the surface is assisted by means of discharges or applied electric fields (e.g. electrospraying [18]). In particular, during LA-PECVD, the established electric field in the liquid film wetting the substrate contributes to a higher efficiency of the solidification process and hence a higher film production yield. The sequential procedure of LA-PECVD consolidates the effect: at the beginning, the interface substrate – liquid conserves the initial neutral charge and only after the discharge is ignited, the additional electric charge polarises the liquid film and accelerates the mechanisms of LA-PECVD.

After completion of step two, the process can be repeated in order to achieve the desired film thickness. The methodology of LA-PECVD is shown in Fig. 2 and the process conditions are summarized in the figure caption. For films polymerized from OMCTS and TTMS the 'plasma ON' time was 5 min per cycle. Due to the higher vapour pressure of HMDSO, 10 cycles with the 'plasma ON' time of 10 min were needed to obtain the coating appropriate for the purpose of surface diagnostics. For the analytical purpose, the films were deposited on silicon wafers at normal laboratory environmental conditions: 30% humidity, 25 °C.

2.4. Methods

A complex film analysis that couples a number of complementary surface diagnostics methods allows drawing more profound conclusions with regard to film deposition processes. The chemical surface composition was determined by high-resolution scanning X-ray photoelectron spectroscopy (XPS) using the Axis DLD electron spectrometer (Kratos Analytical, Manchester, UK) with a monochromatic Al Kα

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