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ScienceDirect

Vacuum 82 (2008) 50–55

VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY

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Optical constants of silicone-like ($Si:O_x:C_y:H_z$) thin films deposited on quartz using hexamethyldisiloxane in a remote RF hollow cathode discharge plasma

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Received 18 January 2007; received in revised form 19 March 2007; accepted 29 March 2007

Abstract

Deposition of amorphous silicone-like ($Si:O_x:C_y:H_z$) thin films in a remote RF hollow cathode discharge plasma using hexamethyldisoloxane as monomer and Ar as feed gas has been investigated for films optical constants and plasma diagnostic as a function of RF power (100–300 W) and precursor flow rate (1–10 sccm). Plasma diagnostic has been performed using Optical Emission Spectroscopy (OES). The optical constants (refractive index, extinction coefficient and dielectric constant) have been obtained by reflection/transmission measurements in the range 300–700 nm. It is found that the refractive index increases from 1.92 to 1.97 with increasing power from 100 to 300 W, and from 1.70 to 1.92 with increasing precursor flow rate from 1 to 10 sccm. The optical energy band gap E_g and the optical-absorption tail ΔE have been estimated from optical absorption spectra, it is found that E_g decreases from 3.28 to 3.14 eV with power increase from 100 to 300 W, and from 3.54 to 3.28 eV with precursor flow rate increase from 1 to 10 sccm. ΔE is found to increase with applied RF power and precursor flow rate increase. The dependence of optical constants on deposition parameters has been correlated to plasma OES.

Keywords: Hexamethyldisiloxane; Optical emission spectroscopy; Optical constants; PECVD; RF hollow cathode discharges

1. Introduction

Plasma-enhanced chemical vapor deposition (PECVD) is widely used to prepare plasma polymers of silicone-like ($Si:O_x:C_y:H_z$) thin films based on organosilicone monomers such as hexamethyldisiloxane (HMDSO: $(CH_3)_6$-Si_2-O) [1–6]. The prepared films were found to be amorphous and pinhole free [5], and they provide good optical and mechanical properties [6–9], such as scratch-resistant films [1], protective coating [6,10] and optical filters [5]. They can be deposited on glass and silicon substrates [11,12].

This paper is devoted to study the optical constants (refractive index, absorption coefficient, extinction coefficient, dielectric constant and energy gap) of plasma polymer thins films deposited on microslides quartz substrates, using a low pressure 13.56 MHz Hollow Cathode Discharge (Plasma Consult GmbH PlasCon HCD-L 300 System). This system is a very attractive device for plasma-aided materials processing and synthesis. It generates intense primary plasma with density approaching $10^{11}\,cm^{-3}$ [13], allowing plasma jets to form and create remote plasma with a very homogeneous plasma density distribution [14]. The deposition of films has been performed using HMDSO as precursor and Ar as feed gas; the latter is introduced into the primary hollow cathode discharge. The HMDSO is introduced in the remote discharge. The plasma polymer thin films are deposited by a process called plasma polymerization [4,5,11], through the reaction between the active species, present in the plasma phase and the surface of the sample [12]. Optical Emission Spectroscopy (OES) is used as an *in situ* tool for plasma monitoring during the deposition process. The optical constants of the films, as a function of processing conditions, have been deduced from reflectance/transmittance measurements and they are correlated with

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0042-207X/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2007.03.007

OES results. The effect of power on the optical constants of the films has been investigated in the range (100–300 W), at fixed precursor flow rate $Q_{HMDSO} = 10$ sccm. In addition, the effect of precursor flow rate has been studied in the range (1–10 sccm), at 100 W deposition power.

2. Experimental

Fig. 1 shows a schematic block diagram of the used experimental set-up for deposition process and plasma diagnostic. The HCD-L 300 source consists of two coaxial tubes of 30 cm length. The inner tube is the hollow cathode and the outer-grounded tube forms the anode. Both cathode and anode are supplied with two rows of coaxial holes aligned to each other resulting in 30 plasma jets. RF power (300 W maximum) at 13.56 MHz is applied to the cathode. Prior to deposition process, the processing chamber ($50 \times 50 \times 50\,cm^3$) was evacuated to a base pressure of 10^{-4} mbar using a primary pump (Alcatel 2063 C2) and a roots pump (Alcatel RSV 301B). The evaporation system of HMDSO consists of a liquid mass flow meter (Lintec-LM-2100A) and a vaporizer (Lintec-VU 410), heated to 50 °C. The HMDSO vapor is carried by helium gas to the plasma chamber, through 50 °C heated line. Inside the chamber, the precursor line is situated at a distance of 5 cm below the source holes. A spectrograph (Jobin Yvon, Triax 550) allows us to measure the lines and bands emission intensities, through the collected light from the plasma via a lens and an optical fiber. A double langmuir probe system (Plasma Consult GmbH, L2P system) is used to measure the electronic temperature T_e and the plasma density. A Jobin–Yvon, Triax 550, UV/vis/NIR computerized spectrophotometer is used for measuring optical refection and transmission of the deposited films, in the condition of near normal incidence (angle of incidence $\cong 1.5°$), the measurements have been carried out within the spectral range 300–700 nm with as step of 1 nm. The thicknesses of films have been measured by an Aplha-Step IQ surface profiler.

Commercial argon and helium gases with 99.999% purity and HMDSO (from Sigma-Aldrich) with 98% purity grade have been used. The films have been deposited on microslides quartz substrates for the reflectance and transmittance measurements and on n-type Si(1 1 1) wafers for thickness measurements. The samples are placed on a substrate holder, positioned at 4.5 cm below the source. The deposition has been performed for 15 min at room temperature, at constant flow rates of Ar (35 sccm) and He (70 sccm) and at constant total pressure of about 0.03 mbar.

3. Results and discussion

3.1. Plasma diagnostic

The fragmentation of the monomer of HMDSO gives rise to a complex mixture of active species, such as ions and radicals. Granier et al. [14] mentioned that the emissions of excited Si, SiO and SiH are characteristics of HMDSO plasma OES. As it is well known, the emitting light by the activated species is a function of the excited states and not directly of the densities of species in their fundamental state. OES can be utilized for a measure of relative concentrations, using the actinometry method [11]. This method suggests that all excited species are produced by direct electron impact from ground state. In our conditions Ar is the actinometer, the emission of the detected species divided by the actinometer emission can be assumed representative of the species concentration trends in the ground state [15]. Each line or band intensity is normalized by the intensity of a neutral argon line [16] (e.g., argon line at 415.85 nm is employed for the SiH band). The information about electronic temperature (T_e) and plasma density (n_i) has been obtained by using double Langmuir

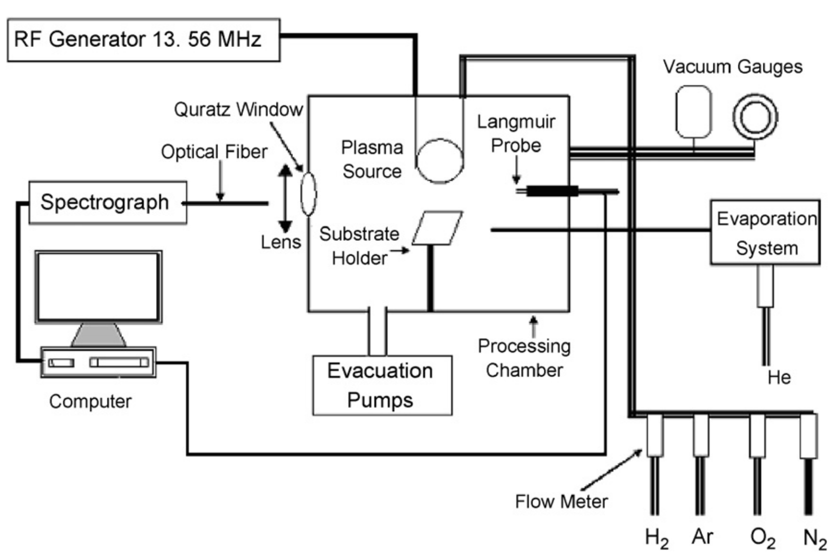

Fig. 1. Schematic block diagram of the plasma system, the deposition system and the plasma diagnostic set-up.