Growth of thin films via atmospheric UVC-driven syngas PICVD

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Abstract: Oligomeric thin films were deposited in an atmospheric chemical vapour deposition reactor by photo-initiation of syngas in the presence of iron pentacarbonyl as a photo-catalyst and UVC lamps as an excitation source. Morphology of the deposits showed island growth synthesis representative of a Volmer–Weber growth mode. Moreover, chemical analysis shows film is composed of ketones, aldehydes and aliphatic groups. Films are stable up to 700 °C.

Keywords: Photo-initiated chemical vapour deposition, syngas, organometallic, thin film, island growth.

1. Introduction

Photo-initiated chemical vapour deposition has recently gained significant attention due to its simple reactor design, suitability for the synthesis of nanometer size films, low-cost scale-up as well as decreased environmental impact compared to solvent-based approaches [1-6]. It makes use of one key component of plasma processing – UV light, without the need to necessarily have the process operate under plasma conditions (low pressure, etc.). Despite the existence of this technology for several decades, several elements have remained elusive, including precursor development, nucleation and film growth processes, as well as reaction mechanisms [7-9]. Most studies performed in this area used VUV light (emitting at wavelengths $\leq$200 nm), which require specialized reactor window such as MgF_2, and LiF [8, 10-14]. Little attention has been devoted to UVC light (200-280 nm) [15, 16]. Moreover, most researchers have focused mainly on film thickness and deposition rates, without a comprehensive understanding of the deposition mechanism or growth [8, 10-14]. Previously, our group investigated the use of UVC-driven syngas PICVD for different substrates [16-19]. In this study, we investigate the effect of treatment duration on the epitaxial growth of deposited films, as well as their chemistry and thermal stability.

2. Experimental Methods

Deposition of Syngas PICVD Films

A semi-plug flow quartz tube housed within a UV cabinet was used as PICVD reactor for these experiments. The cabinet consisted of 28 UVC low-pressure mercury lamps, with a main emission peak at 253.7 nm and a total light intensity of 0.012 W/cm^2. Films were deposited on 110 orientation N-type silicon wafers substrates cut into 1 cm × 1 cm coupons. The substrates were sonicated first in deionized water and then in isopropanol for 10 minutes prior to the experiments and dried with compressed air. Part of the substrates were masked with Kapton tape as a reference. The reactor was first purged with argon gas; then 0.2 L/min of CO and 0.2 L/min of H_2 gas streams were fed to the reactor as reactive precursors while the reactor was maintained at atmospheric pressure. UVC lamps were then turned on and treatment duration was set to 30 min, 60 min, 120 min, and 180 min for experiments 1 to 4, respectively. Treatment duration was the main experimental parameter varied to control film thickness and investigate the growth mode. Over the course of UV treatment, reactor temperature linearly increases from ~22 °C (room temperature) to ~ 62 °C due to heat generation from the UVC lamps. Each experiment was repeated 3 times to ensure reproducibility.

Characterization Techniques

CytoViva Microscope Imaging: CytoViva Enhanced Darkfield Hyperspectral Microscopy has been used to study the texture and morphology of films.

Scanning Electron Microscopy (SEM): Texture and morphology of films was further examined using a Hitachi ultrahigh-resolution cold field emission scanning electron microscope (Hitachi SU8230), equipped with an X-ray energy-dispersive spectroscope (EDS) (Bruker® Quad detector-Bruker® 4SD Argus system) operated at an accelerating voltage of 1-2.5 kV.

Profilometer: A Veeco Dektak 150 surface profiler was used to measure films thickness

X-ray Photoelectron Spectroscopy: A VG ESCALAB 3 MKII X-ray photoelectron spectroscope (XPS) equipped with a non-monochromatic Mg-Kα radiation source was used for elemental analysis of the films. Analysis was performed at 300 W (15 kV, 20 mA) and survey and high high-resolution spectra were acquired at a pass energy of 100 eV and 20 eV, respectively. Corrections were applied by referencing all peaks with respect to the C1s signal at a binding energy of 285.0 eV. The full width at half maximum (FWHM) of 1.6, 1.8, 2.2, 2.7 eV were selected for C, O, Si, and Fe respectively.

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR): Chemical analysis of the samples was carried on KBr coated disks using a Perkin Elmer 65 FTIR-ATR instrument. FTIR spectra were recorded over a wavenumber range of 650-4000 cm^{-1} (total of 128 accumulated scans) and a 4 cm^{-1} resolution.

Thermogravimetric Analysis (TGA): The amount of grafted film samples was determined using a TGA-METTLER TOLEDO apparatus operating from 25 to 800 °C with a heating rate of 10 °C /min under a nitrogen gas flow.

3. Results and Discussion

Fig.1 shows optical images of islands formed on the treated substrates. These are further detailed in the SEM micrographs shown in Fig.2.

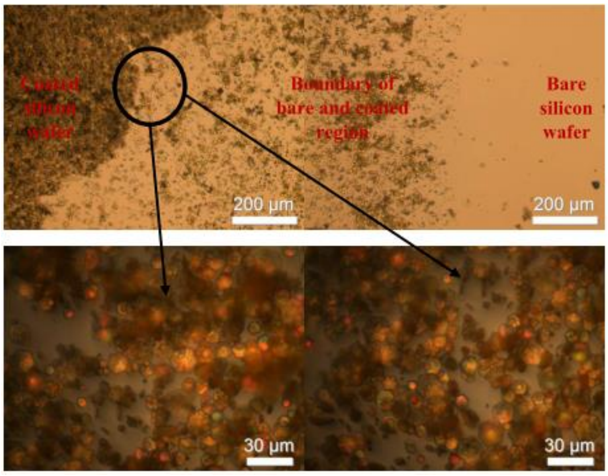

Fig. 1. Optical microscopy showing island growth (120 min sample)

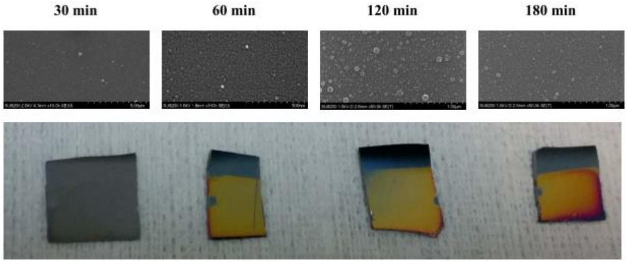

Fig. 2. SEM micrographs showing island growth and their corresponding sample

Film thickness increases linearly as a function of treatment duration, from 20 nm at 30 min to 120 nm at 180 min. This corresponds to a deposition rate of roughly 0.7 nm/min.

The surface concentration of deposited carbon compared to silicon (from the substrate) increased significantly in the coated samples compared to the bare samples (Fig. 3). Moreover, this XPS analysis shows the presence of iron in the deposits. This is the result of $Fe(CO)_5$ contamination in the CO cylinder [20, 21]. This compound play a photocatalytic role in the deposition process and accelerates the formation of oligomeric films. By increasing the treatment duration, more substrate surface will be covered and thus the ratio of elements representing the film (C, O, Fe) increase too (Table 1).

Table 1. Elemental atomic ratio of coated samples.

Elemental ratio (%)	Bare	30 min	60 min	120 min	180 min
C/Si	0.3	3.2	6.6	18.8	11.9
O/Si	2.4	3.9	9.3	33.7	22.1
Fe/Si	0.0	0.8	2.9	14.6	9.5

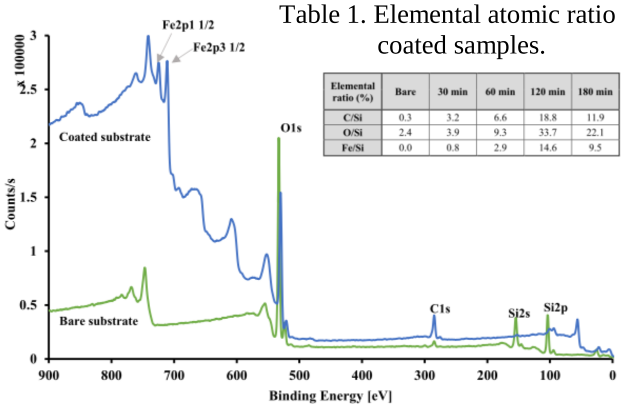

Fig. 3. XPS survey of bare and coated samples.

To define the chemical groups representing the deposited film, we prepared a KBr pellet and treated for 120 min using the same PICVD protocol. Fig. 4 shows the FTIR spectra and their corresponding chemical groups.

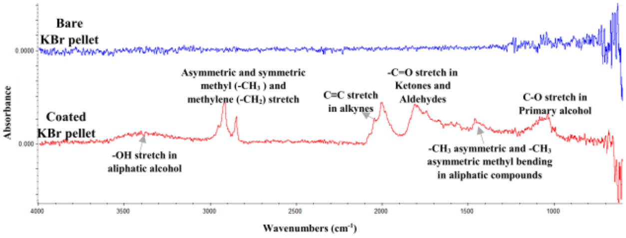

Fig. 4. ATR-FTIR spectra of bare and coated KBr samples

The film mainly consists of $–CH_2$ and $–CH_3$ groups in aliphatic form, along with –C≡C in alkynes, –C=O in ketones and aldehydes as well as –OH groups in aliphatic primary alcohols.

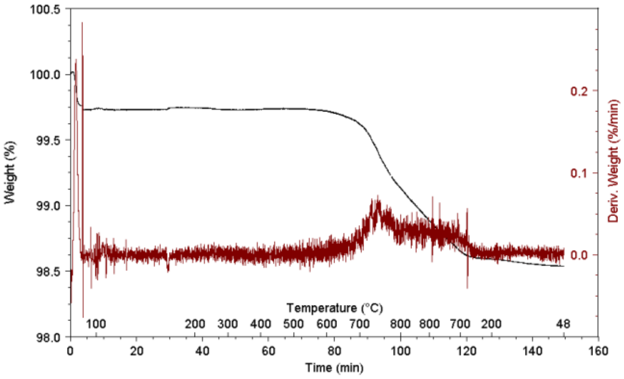

Fig. 5. Thermogravimetric analysis of a coated sample (120 min treatment)

TGA analysis (Fig. 5) is carried out on 120 min coated samples to define the thermal stability of deposited film. The film started to decompose at 700 °C, demonstrating high thermal stability. Moreover, 0.5% mass lost corresponds to the humidity and water content while the other 1% corresponds to the oligomeric deposited film, which decomposes in 700-800°C.

4. Conclusion

We have shown that a UVC-driven syngas PICVD process produces an oligomeric film through island-like growth. By increasing treatment duration, films tend to have a more compact morphology. This type of film morphology was previously observed during plasma deposition of other organic compounds [22] and is representative of a Volmer–Weber (VW) growth mode (3D morphology, island growth). This type of deposition occurs by growth of islands that eventually merge, instead of layer by layer deposition.

By increasing the treatment duration, thicker film with higher amounts of chemical elements (C, O, and Fe) are produced. The organic content of the deposits is mostly in the form of aliphatic groups, along with ketones, alcohols, aldehydes and alkynes. The film shows strong thermal stability and it starts to decompose only at 700 °C. It is therefore expected that the coatings presented and characterized in this study will be useful in the development of surfaces that need high thermal stability.

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