Thin Solid Films 597 (2015) 7–13

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Achieving uniform layer deposition by atmospheric-pressure plasma-enhanced chemical vapor deposition

Jae-Ok Lee [a], Woo Seok Kang [a,b,*], Min Hur [a], Jin Young Lee [a], Young-Hoon Song [a,b]

[a] Department of Plasma Engineering, Korea Institute of Machinery & Materials (KIMM), Daejeon 305-343, Republic of Korea
[b] Department of Environment & Energy Mechanical Engineering, University of Science & Technology (UST), Daejeon 305-350, Republic of Korea

ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form 3 November 2015
Accepted 8 November 2015
Available online 10 November 2015

Keywords:
Plasma enhanced chemical vapor deposition (PECVD)
Atmospheric-pressure plasma
Dielectric barrier discharge
TEMAZr
Zirconium dioxide
Precursors

ABSTRACT

This work investigates the use of plasma-enhanced chemical vapor deposition under atmospheric pressure for achieving uniform layer formation. Electrical and optical measurements demonstrated that the counterbalance between oxygen and precursors maintained the homogeneous discharge mode, while creating intermediate species for layer deposition. Several steps of the deposition process of the layers, which were processed on a stationary stage, were affected by flow stream and precursor depletion. This study showed that by changing the flow streamlines using substrate stage motion uniform layer deposition under atmospheric pressure can be achieved.

1. Introduction

Atmospheric-pressure plasma-enhanced chemical vapor deposition (PECVD) is an attractive and cost-effective manufacturing technology [1–5]. Traditional low-pressure PECVD is based on a batch-type process that employs an auxiliary vacuum pump system and a complex deposition process. In contrast, atmospheric-pressure PECVD is based on an inline process that is favorable for achieving a chamberless, continuous, and large-surface-area treatment for various industrial applications [6].

One of the challenges of atmospheric-pressure PECVD is controlling the plasma state to maintain a homogeneous discharge mode, as with low-pressure plasmas. Since atmospheric-pressure glow discharge (APGD) was first studied [1,7,8], various types of plasma reactors have been proposed for the generation of uniform and homogeneous plasmas. Furthermore, these plasmas have been studied for the deposition of thin films such as SiCN:H [1], SiO_2 [9–11] and ZnO [12]. The deposition process requires precursors; however, how the additives and precursors affect plasma homogeneity is currently not well understood.

Another challenge is controlling the deposition process to obtain uniform layers. Most atmospheric-pressure plasma reactors are line sources, which enables roll-to-roll-based PECVD [4,6,10,11] for extended-area treatment. Previous studies have shown that the deposition layer quality depends on the operation parameters. Although an understanding of each deposition step is still unclear, research is being conducted on the effects of particle generation [5,9] and gas flow and recirculation [2,13] which are flow-dependent phenomena under atmospheric pressure. Precursor control under atmospheric pressure is also important because an atmospheric-pressure process consumes more precursors than are consumed in a low-pressure environment [3,14]. This is why atmospheric-pressure process poses greater challenges than low pressure processes.

The objectives of this study were to understand the mechanism of uniform layer deposition by PECVD under atmospheric pressure, determine the plasma characteristics during the deposition process, and achieve uniform layer formation by process control. In this study, we deposited a zirconium dioxide (ZrO_2) layer that exhibits excellent electrical features, suitable for a high-K dielectric material for use in electronics applications, and possesses superior mechanical properties, such as thermal stability and high wear protection [15–17].

2. Experiment

A schematic of the developed plasma reactor is presented in Fig. 1. The reactor is based on the concept of dielectric barrier discharge, and consists of two back-to-back symmetric L-shaped electrodes that are covered with dielectric material (alumina). A discharge gas passes through a gap between the electrodes, and the downstream gas flows out between the reactor and the substrate (1 mm). The reactor was

* Corresponding author at: Department of Plasma Engineering, Korea Institute of Machinery & Materials (KIMM), Daejeon 305-343, Republic of Korea.
E-mail address: kang@kimm.re.kr (W.S. Kang).

http://dx.doi.org/10.1016/j.tsf.2015.11.015
0040-6090/

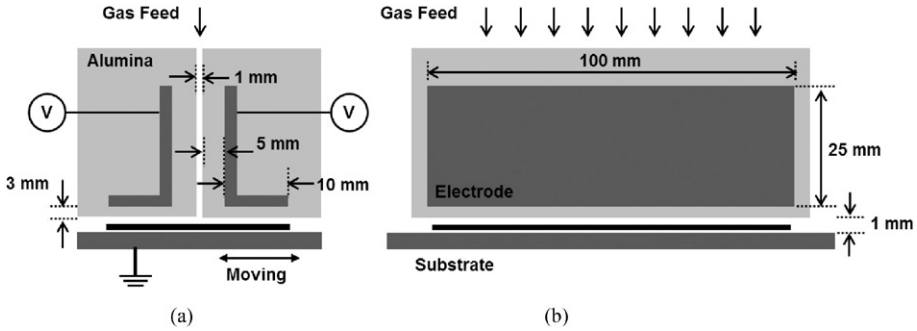

Fig. 1. Schematic diagram of the developed reactor: (a) front view and (b) side view.

operated under the maximum applied voltage of 3 kV with a 55 kHz sinusoidal wave (HPI-1600, FTLab Co. Ltd.). A detailed description of the developed reactor has been provided in our previous papers [18–21].

A schematic of the deposition system is shown in Fig. 2. The system is composed of three modules: gas supply, process, and exhaust/after-treatment. In the gas supply module, the plasma generation gas was helium with added oxygen. After passing through a temperature-controlled canister containing a liquid precursor, some of the helium flow transported the vaporized precursor. As a chemical precursor for deposition of the zirconium dioxide layer, tetrakis[ethylmethlyamino]zirconium (TEMAZr), a precursor that is commonly used for atomic layer deposition (ALD), was used. To ensure a safe and contaminant-free process, the deposition process was conducted inside a chamber (the process module). A plasma reactor was installed in the chamber with a substrate stage unit. The process gas was exhausted to the atmosphere after passing through an external pump and a scrubber in the exhaust module.

A 6-in silicon wafer was used as the substrate in this work. The substrate was processed over a temperature-controlled stage operating in two modes: (1) stationary mode (the stage is stationary), or (2) moving mode (the stage performs a sweeping motion at a constant speed, 0.5 m/min). The deposition process was conducted for 27 cycles in the moving mode. One cycle corresponded to one sweeping motion of the substrate. The substrate temperature was set to 150 °C. The carrier gas (helium) flowed at a rate of 5 slpm with an oxygen at a rate of 50 sccm. Additional helium (500 sccm) passed through the canister, which was kept at a temperature of 80 °C to control the vapor pressure of the TEMAZr. It was then introduced into the reactor mixed with the carrier gas.

The deposition process consisted of three steps in the following order: 1) purging to reduce the number of particles remaining in the pipes and chamber, 2) deposition after the substrate temperature reached 150 °C, and 3) additional purging to eliminate residual particles.

The electrical characteristics were monitored using a digital oscilloscope equipped with voltage/current probes (P6015A and TCP0030 with DPO5054, Tektronix Inc.). The time-averaged light emission from the plasma was measured by an optical spectrometer (Maya 2000 Pro, Ocean Optics Ltd.).

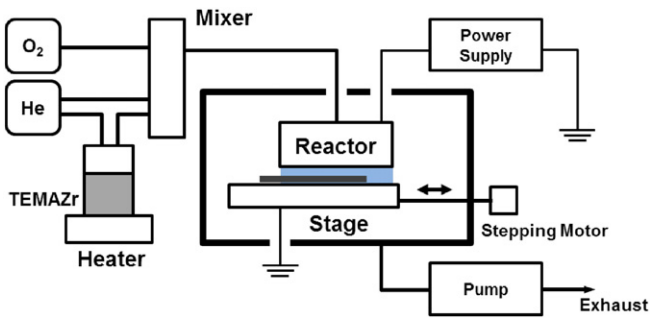

Fig. 2. Schematic diagram of atmospheric-pressure plasma-enhanced chemical vapor deposition (PECVD) system.

3. Results and discussion

3.1. Electrical and optical characteristics of the plasma

Figs. 3 and 4 show the electrical and optical characteristics of the plasma, respectively, under different gas mixture conditions. The typical characteristics of dielectric barrier discharge (Fig. 3) were observed when a phase difference was applied between the voltage (dotted lines) and the current (solid lines) waveforms. The plasma sustained by helium alone exhibited a periodic current (solid black line in Fig. 3) that confirmed homogeneous discharge, although the current pulses fluctuated owing to the displacement current components of the power supply used [18,21]. In our previous studies, optical emission images were used to verify that the helium plasma generated in this type of reactor exhibits the homogeneous mode, depending on the voltage polarity [21].

When oxygen was added, the discharge current (solid red line in Fig. 3) oscillated, indicating that the spatial distribution of the plasma became non-uniform because of localized microdischarges. However, when TEMAZr was introduced (solid blue line in Fig. 3), the current oscillation caused by the mixing of oxygen was minimized, and the current shape became periodic which indicates the homogeneous mode.

The optical measurement of the helium discharge (blue line in Fig. 4a) revealed the typical emission spectral lines, with a large helium peak ($2^3S_1 \rightarrow 2^3P_{0,1,2}$, 706.5 nm) and weak emission lines from oxygen, which may be due to the residual oxygen in the chamber. When oxygen was mixed with helium (red line in Fig. 4a), the oxygen emission lines, such as O ($3p^5P \rightarrow 3s^5S$, 777.4 nm) and O ($3p^3P \rightarrow 3s^3S$, 844.6 nm), were enhanced, whereas the helium lines were reduced, because the density of the helium metastable species decreased as a result of the quenching reaction with the oxygen-related species [22,23]. The black line in Fig. 4a shows that the introduction of TEMAZr affected the emission spectra. Specifically, the helium-related emission peaks recovered, and the oxygen emission intensities decreased. Additional emission lines that originated from TEMAZr decomposition were observed, including peaks related to nitrogen- or hydrocarbon-fragments in the range of 300 to 400 nm.

An additional emission measurement was performed by changing the flow-rate of the TEMAZr carrier gas (helium), as shown in Fig. 4b. Increasing the flow rate of the carrier gas resulted in more precursors being transported. The emission intensity ratio (777.4 nm versus 706.5 nm) was highest when the discharge gas was composed of helium mixed with oxygen. When TEMAZr was introduced, the intensity ratio decreased. When the additional helium flow rate varied from 250 to 750 sccm, the emission intensity ratio decreased (Fig. 4b). Fig. 4 highlights the importance of the counterbalance between oxygen atoms/