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ScienceDirect
Thin Solid Films 515 (2007) 3513–3520
www.elsevier.com/locate/tsf

The relationship between chemical structure and dielectric properties of plasma-enhanced chemical vapor deposited polymer thin films

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Received 5 May 2006; received in revised form 11 October 2006; accepted 20 October 2006
Available online 14 December 2006

Abstract

Polymer dielectric films fabricated by plasma enhanced chemical vapor deposition (PECVD) have unique properties due to their dense crosslinked bulk structure. These spatially uniform films exhibit good adhesion to a variety of substrates, excellent chemical inertness, high thermal resistance, and are formed from an inexpensive, solvent-free, room temperature process. In this work, we studied the dielectric properties of plasma polymerized (PP) carbon-based polymer thin films prepared from two precursors, benzene and octafluorocyclobutane. Two different monomer feed locations, directly in the plasma zone or in the downstream region (DS) and two different pressures, 80 Pa (high pressure) or 6.7 Pa (low pressure), were used. The chemical structure of the PECVD films was examined by X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy. The dielectric constant (ε_r) and dielectric loss (tan δ) of the films were investigated over a range of frequencies up to 1 MHz and the dielectric strength (breakdown voltage) (F_b) was characterized by the current-voltage method. Spectroscopic ellipsometry was performed to determine the film thickness and refractive index. Good dielectric properties were exhibited, as PP-benzene films formed in the high pressure, DS region showed a F_b of 610 V/μm, an ε_r of 3.07, and a tan δ of 7.0×10^{-3} at 1 kHz. The PECVD processing pressure has a significant effect on final film structure and the film's physical density has a strong impact on dielectric breakdown strength. Also noted was that the residual oxygen content in the PP-benzene films significantly affected the frequency dependences of the dielectric constant and loss.
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Keywords: Plasma enhanced chemical vapor deposition (PECVD); Polymer thin films; Dielectric properties; Structure

1. Introduction

Recently, considerable work has been undertaken to fabricate polymeric dielectric and photonic thin films using plasma enhanced chemical vapor deposition techniques (PECVD) [1–8] due to its room temperature, solvent-free and versatile operation. Many organic precursors can be selected to prepare thin polymer films with a wide range of compositions and chemical functionalities. Plasma polymerized (PP-) films, exhibiting highly crosslinked structures have been targeted for optical and dielectric applications such as waveguides, anti-reflection coatings, band-gap filters for integrated optics, high performance capacitors and dielectric devices [9–13]. The focus of the current paper is the generation and evaluation of organic PECVD dielectric films with high dielectric strengths, moderately high dielectric constants and relatively low dielectric loss factors. An improved understanding of the composition/structure-property relationships is required to optimize the design and film fabrication for these various applications.

In this work, benzene and octafluorocyclobutane (OFCB) were chosen as starting precursors for exploring the relationship between structure and thin film dielectric properties. In order to study the effects of plasma-induced energetic species on the initiation and propagation of the plasma polymerization and film deposition, two monomer-feed locations and two reaction

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0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.10.126

chamber pressure regimes were investigated. The PECVD films were characterized by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Their dielectric properties were evaluated by established techniques, including measurements of dielectric constant (ε_r), loss factor ($\tan \delta$), and breakdown strength (F_b). The film thicknesses and optical refractive indices were determined by spectroscopic ellipsometry. Correlation of the composition and chemical structure with the dielectric properties of these PECVD films is discussed in detail.

2. Experimental details

Fig. 1 is a schematic of the PECVD set-up [14,15]. Briefly, 99.999% argon was used as the noble gas to flow into a 10 cm diameter glass reactor through a capacitively coupled, 13.56 MHz discharge. The diameter of the two coupling electrodes was 50 mm and the distance between them was 25 mm. The power for plasma generation could be controlled in the range of 20 to 75 W.

Two precursors were chosen for the fabrication of plasma homopolymerized thin films: benzene (C_6H_6, Aldrich Co., liquid, high performance liquid chromatography (HPLC) grade with a purity of 99.9%) and octafluorocyclobutane (C_4F_8, OFCB, SynQuest Laboratories, Inc., compressed gas, with a purity of >99%). Both of the monomers were used as received. For OFCB, the flow rate was controlled in the range of 0.5–3 cm^3/min, and for benzene the vapor flow rates were in the range of 0.05–0.3 cm^3/min (without any carrier gases). In order to keep a constant partial vapor pressure, a water-bath thermostat was used to maintain the temperature of the benzene reservoir at 19.0 ± 0.1 °C.

Two reaction chamber pressures were applied during the study: 6.7 Pa labeled as the low pressure regime (L-) and 80 Pa labeled as the high pressure regime (H-). The chamber pressure described here was due both to the noble gas (argon) and monomer (OFCB or benzene vapor). A two-stage pumping system was used. In the first stage, a diaphragm vacuum pump (Model MD4C, Vacumbrand) was used instead of a rotary oil pump, in order to avoid oil contamination from back-streaming. In the second stage, a turbo-molecular pump (Model Turbo-V301 Navigator Pump, Varian) was used to keep the chamber vacuum close to 10^{-4} Pa.

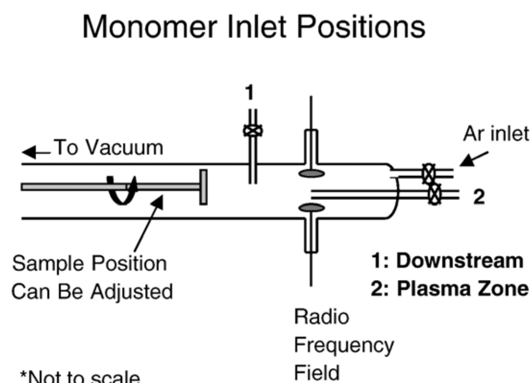

Fig. 1. Schematic of the PECVD set-up showing the two monomer inlet positions.

Processing conditions for this work included a plasma power of 45 W, argon flow rates of 20 cm^3/min (for the low pressure regime) or 100 cm^3/min (for the high pressure regime), with monomer feed locations either in the center of the plasma zone (PZ) or in the downstream region (DS), about 7 cm from the center of the plasma zone. The substrates for film deposition were placed 1.5 cm further downstream from the DS inlet.

PECVD films were deposited directly on potassium bromide (KBr) disks for FTIR analysis, which was performed on a Perkin Elmer Spectrum 2000 FTIR spectrometer in the transmission mode, with a scanning range of 400 to 4000 cm^{-1} in 1 cm^{-1} increments.

For both XPS and spectroscopic ellipsometry measurements, the PECVD films were deposited on 5 cm diameter silicon wafers. The XPS analysis was carried out in a Surface Science Instruments M-Probe using monochromatic Al Kα X-rays. The surface composition and component atomic ratios were measured from survey scans taken with an analyzer pass energy of 150 eV, and X-ray power of 200 W. Measurements were also taken for individual components' line-shapes, such as C 1s, at a pass energy of 100 eV (higher energy resolution) in order to distinguish between chemistries related to different species in the films. A low energy electron flood source was used to reduce and stabilize electrical charging during analysis [16]. The ellipsometry measurements were carried out with a Woollam variable-angle spectroscopic ellipsometry system with detailed procedures reported elsewhere [14].

For the dielectric and electrical property examinations, the PECVD films were deposited either on 8 μm thick polyester (Mylar™) substrate films with one surface coated with 20 nm (±3 nm) thick Al, or 25 μm Mylar™ substrate films with both surfaces coated with 20 nm (±3 nm) thick Al, both supplied by Steinerfilm, Inc. After the PECVD film deposition, another Al layer (50 nm ± 5 nm) was sputtered onto the surface of the PECVD films to make a metal–insulator–metal (M-I-M) sandwich structure for all the dielectric/electrical measurements. The whole preparation process of the M–I–M components was performed in a standard clean room (Class 10,000). The loss factor and the capacitance as well as the derived dielectric constant of the metallized PECVD films were measured with a 4284A precision LCR Meter (Agilent Technologies) in the range of 20 Hz to 1 MHz. The dielectric breakdown strength of the PECVD thin films is defined as the maximum electric field strength that the films can withstand intrinsically without experiencing failure of their insulating properties. In our experiment, the dielectric strength of the films was evaluated using a precision-regulated high voltage power supply (Model 210-05R, Bertran, or Model SR6, Spellman) by gradually increasing the voltage and monitoring the current variation through the films. The voltage was increased in 5 V steps and the duration of each step was 5 s. The breakdown threshold was set at a DC current of 10^{-7} A (the corresponding resistance reading, $10^8 \sim 10^9$ Ω, was also used as a reference). For high strength films, 10 V/step was also tested, but no significant difference was observed. All the dielectric properties were measured under ambient conditions with a temperature of 21 ± 1.5 °C and humidity in the range of 50 to 70%.

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