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Preparation of micropatterned poly(silsesquioxane) thin films using adamantylphenol molecules

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Abstract

Poly(methyl silsesquioxane) (PMSSQ) thin films with micropatterned surface structures have been prepared by use of adamantylphenol molecules as a photo-thermal sensitive moiety together with UV lithographic technique and mild heating process. Initially, PMSSQ films form positive patterns of micronscale due to the film densification triggered by photooxidation and photopolymerization of doped moieties within UV exposed region. With thermal treatment, negative patterns from these pre-patterned films are formed by the difference of polycondensation rates between non-exposed regions and irradiated areas without additional developing or etching steps. This structural transformation of PMSSQ thin films was investigated using Fourier-transformed infrared spectroscopy, ultraviolet visible spectroscopy, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and field emission scanning electron microscopy.

Keywords: Silsesquioxane; Photooxidation; Structural properties; Surface structure

1. Introduction

Polysilsesquioxane (PSSQ) materials represented by empirical formula $(RSiO_{3/2})_n$ recently receive an increasing attention in both fundamental and applied science. Potential application for these materials includes use in nanocomposites as reinforcing fillers, low dielectric (low-*k*) insulators in microelectronic devices, and micro-optical waveguides [1–3].

In addition to such promising fields, patterning of PSSQ has considerably been interested for their practical applications to copper interconnect of low-dielectric materials, anti-reflective films, and surface relief gratings [4–6]. Since it is well known that PSSQ can be crosslinked or polymerized by heat or irradiation source such as X-ray and electron beam, selective irradiation or heating within the confined film surface can make the formation of diverse patterned structures possible [7–9]. Patterning of nanoporous poly(methyl silsesquioxane) (PMSSQ) films was also introduced using a typical UV lithographic technique combined with aid of photoacid/base generators and ozone generation [10–12]. Together with these versatile methods to prepare patterned PMSSQ structures, there is still a need to control patterned structures using simpler efficient process. Moreover, for successful implementation of PMSSQ as low-*k* materials into advanced integration devices, the development of technique without etching or developing step is required to fulfill the practical advantages such as a direct formation of via or trench.

Adamantylphenol grafted to PMSSQ matrix was previously employed to prepare the nanoporous PMSSQ thin films using only thermal treatment for low-*k* application. As was previously mentioned, the decomposition temperature of adamantylphenol was observed to shift to higher temperature compared to pristine adamantylphenol due to the chemical bonds of adamantylphenol into the PMSSQ matrix [13,14]. This suggests that the introduction of covalently bonded adamantylphenol is not suitable for realizing the diverse patterned structure under the condition of mild heating. In present study, we described a simple approach for micropatterning, where positive patterns formed on PMSSQ films are transformed to negatively patterned structures without additional developing or etching steps. This method employs adamantylphenol molecules

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without covalent bond as photo-thermal sensitive moiety together with UV irradiation as well as mild thermal treatment. In addition, the detailed mechanism for formation of patterned structures was discussed.

2. Experimental details

2.1. Preparation of PMSSQ and adamantylphenol

All the reagents used in present study were purchased from Aldrich and were used as received unless otherwise specified.

In this study, PMSSQ polymers were synthesized with 1,2-bis-trimethoxysilylethane and methyltrimethoxysilane by carefully controlled hydrolysis-condensation reaction. A detailed synthesis procedure of PMSSQ polymer was previously published as well as adamantylphenol moiety [13,14]. The prepared PMSSQ and adamantylphenol characterized by ^{1}H nuclear magnetic resonance (^{1}H NMR) measurement (Bruker, AVANCE 500 MHz) are in a good agreement with the results reported previously [13,14]. From ^{1}H NMR spectrum, the Si-OH content in polymer was 19.3 mol% and number average molecular weight of polymer measured by Gel Permeation Chromatography was 7400.

2.2. Preparation of thin films

As a typical example, PMSSQ thin films containing adamantylphenol were prepared by spin-coating from polymer solutions dissolved in methylisobutylketone (MIBK) with concentration of 30 wt.% adamantylphenol. The silicon wafer pre-treated with *piranha* solution (H_2SO_4/H_2O_2=7/3 v/v) was spun at 2000 rpm for 30 s to give film thickness ranging from 550 nm to 650 nm. Subsequently coated films were dried under vacuum for 3 days to remove residual MIBK at 50 °C. The dried films were irradiated through copper grid (100 or 400 mesh, GLIDER) with UV light (wavelength; 254 nm) of 3.9 mW/cm^2 for exposure time of 12 h in air, as can be seen Fig. 1. Some non-irradiated films were thermally treated as well as irradiated films with home-made furnace under N_2 flow at 300 °C for 2 h at a heating rate of 3 °C/min, respectively.

2.3. Characterization

The Fourier-transformed infrared spectroscopic (FT-IR) measurements were performed on a JASCO FT/IR 200 spectrometer. Ten accumulations were signal-averaged at a resolution of 4 cm^{-1}. Baseline corrected infrared spectra were obtained for films on silicon wafer in absorbance mode at room temperature. The ultraviolet-visible (UV-VIS) spectra were collected for film coated on quartz plate using Perkin-Elmer UV-VIS spectrometer (model 2287) with an operational wavelength range of 190–400 nm. Auger electron depth profiles were obtained on a Physical Electronics scanning Auger microprobe systems (model 660) by etching the film surface with an argon ion beam (2 keV, 20 μA/cm^2). X-ray photoelectron spectra (XPS) were collected on a SIGMA PROBE (ThermoVG, UK) equipped with a monochromatic Al-

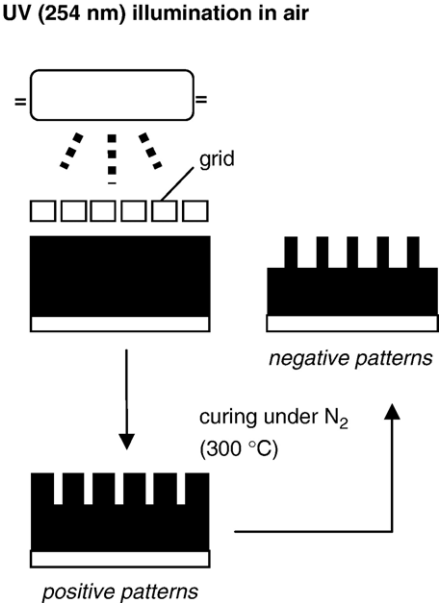

Fig. 1. Schematic procedure to prepare the PMSSQ films with positive and negative patterns.

Kα X-ray source (1486.6 eV). Spectra were recorded for a takeoff angle of 90° and the peaks were corrected to the C 1s peak at 284.6 eV. Optical microscopic measurements were carried out using a Nikon OPTIPHOT-2POL in reflection mode. Atomic force microscopy (AFM) was performed using a Digital Instruments Nanoscope IIIa in a tapping mode with a Si_3N_4 tip. The field emission scanning electron microscopy (FE-SEM) (JEOL 6330F) was employed to investigate the surface texture of the thin films. Spin coated films were cut into small pieces and fixed on a sampling holder to analyze the surface structure. In order to minimize the film damage due to the electron beam and also to obtain clear images, gold was sputtered onto the thin films.

3. Results and discussion

Previous studies presented the feasibility of employing covalently bonded adamantylphenol as a porogen (pore generating material) in the preparation of nanoporous low-*k* films [13,14]. When adamantylphenol was chemically incorporated into the PMSSQ matrix, the decomposition temperature of adamantylphenol significantly increased to 450 °C, which is higher than that of pristine adamantylphenol without the presence of a covalent bond. This suggests that chemically linked adamantylphenol is a good pore forming agent leading to the formation of nanoporous films. In order to form the porous films, adamantylphenol should be decomposed after the vitrification of the PMSSQ matrix. On the other hand, adamantylphenol without chemical bond can decompose below 300 °C, which indicates that there are no nanopores in the film owing to the sublimation of adamantylphenol before the condensation of PMSSQ. In this study, the adamantylphenol molecules without the chemical bond are used as photo-thermally active dopant because it can sublime at relatively low