Surface Morphology Engineering of Porous Thin Films by Ion Milling

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ABSTRACT

Ion milling was employed to physically modify the surface morphologies of porous thin films. Silica porous thin films, composed of arrays of vertical posts, were fabricated by glancing angle deposition. As deposited, these silica posts have rough columnar structures with numerous branching defects, and broaden while growing outward from the substrates. With ion milling, silica posts tend to become smoother and shorter, develop sharper tips, and become far more uniform in diameter. This technique may improve functionality of devices requiring large surface areas, in a wide range of applications including chromatography, sensors, photocatalysis and photovoltaics.

Keywords: glancing angle deposition, porous thin films, ion milling, surface morphology engineering

1 INTRODUCTION

Porous thin films (PTFs) have invoked a great deal of interest both from fundamental standpoints and in technical applications, due to a large surface area compared to solid films. With dimensions decreasing to the micro- or nano-scale, porous structures have an increase of surface areas, leading to a dominance of surface, rather than bulk, properties. Therefore, engineering of surface morphologies is critical to improve PTF-based device functionalities. For instance, PTFs have been developed as humidity sensors, and it was shown that smooth surfaces are required to decrease response time [1]. In chromatography, chemical species separation can be remarkably improved with uniform pore sizes [2]. In terms of substrates for solar energy conversion in photovoltaics and photocatalysis, surface roughness may be adjusted to pursue the tradeoff between the harvesting of solar energy and the effective separation of photo-induced pairs of electrons and holes [3]. In this work, we will introduce a technique to controllably modify surface morphologies and roughness of PTFs fabricated by glancing angle deposition (GLAD).

2 EXPERIMENTAL

2.1 GLAD

GLAD employs physical vapor deposition to fabricate PTFs composed of well separated columns, by taking advantage of the self-shadowing occurring at highly oblique deposition angles (>70° with respect to the substrate normal) [4]. The larger the glancing angle, the more porosity generated. With precise control of substrate movements, the morphologies of columns can be engineered over a wide range, in terms of shape, height, pitch, periodicity, chirality, inclination and surface density. The array arrangement of PTFs can be regularized by pre-patterning seed structures using electron beam lithography [5]. GLAD has been developed to generate PTFs made of a large variety of materials, including semiconductors, oxides, sulfides, fluorides, metals and organic molecules [6].

2.2 PTFs of Silica Vertical Posts

SiO_2 PTFs were deposited on p-doped Si (100) wafers by GLAD at a fixed glancing angle of 87º with respect to the substrate normal. The electron-beam accelerating voltage was 9 kV, and the emission current was 25-40 mA giving a deposition rate of roughly 0.5 nm/s. The deposition pressure was maintained in the range of 10^{-6}-10^{-5} Torr. Rapid substrate rotations of 360º per 10 nm of film growth produced vertical posts.

2.3 Ion milling

Ion milling (Ionfab 300Plus, Oxford Instruments) was performed with ions directed at a normal incidence angle to the silica-coated silicon wafers, while these wafers were rotated at 20 rpm. The ion beam voltage and current were 954 V and 120 mA, respectively, with less than 5% total variation. As an experimentally varied parameter, the duration of ion milling was controlled from 0 to 8 min in this study.

2.4 Characterization

Samples were characterized by field emission scanning electron microscopy (FESEM, JEOL 6301F). To enhance conductivity, a thin layer of chromium was deposited over samples by sputter coating.

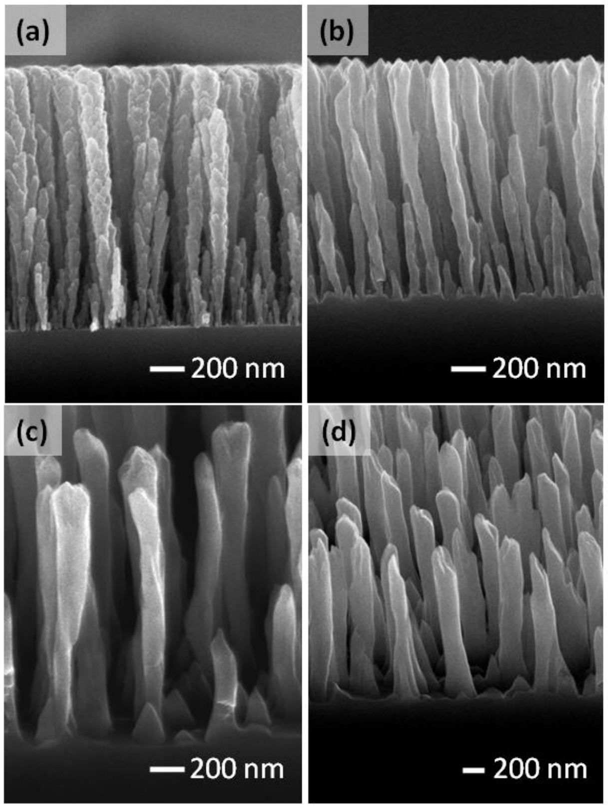

Figure 1: Surface morphology engineering of silica vertical posts by ion milling, with different duration: (a) 0 min, (b) 5 min, (c) 6 min, and (d) 8 min. (a) and (b) are SEM side views, and (c) and (d) are SEM oblique views.

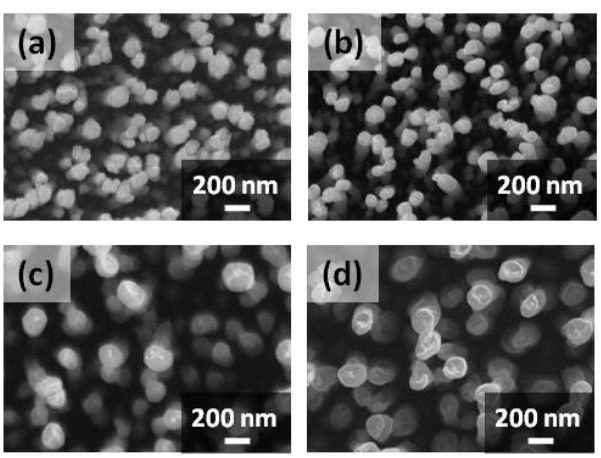

Figure 2: SEM top views of ion milled silica PTFs, with duration of (a) 0 min, (b) 5 min, (c) 6 min, and (d) 8 min.

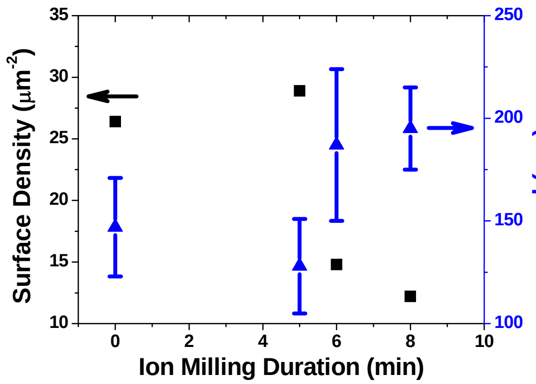

Figure 3: Plots of surface density (black squares) and column diameters at the top of posts (blue triangles) of silica PTFs with ion milling duration.

3 RESULTS AND DISCUSSIONS

Silica vertical posts generated by GLAD broaden while growing outward from the substrates, displaying branching features (Fig. 1a). The total thickness of PTFs in this work was ~1.6 µm. Within these films, however, many individual posts stop growing at positions much less than the full 1.6 µm, due to shadowing from adjacent posts.

With exposure to ion milling for 5 minutes, the PTFs shrink as thin as ~1.4 µm, and the cylindrical columns develop sharp tips (Fig. 1b). The columns tend to become far smoother, though still have wavy profiles. The column diameters tend to become more uniform with longer exposure time, as shown in Fig. 1c and 1d for 6 and 8 minutes, respectively. Note that the sharp tips created within 5 minutes are anisotropically milled during prolonged ion bombardment, as shown in Fig. 1d. Fig. 2 shows the change of column diameters and surface density of PTFs with ion milling, and these results are plotted in Fig. 3. With ion milling, the diameters at the top of posts decrease from 147±24 nm to 128±23 nm after 5 minutes, but then increase to 187±37 nm at 6 minutes and 195±20 nm at 8 minutes. The surface density changes in an opposite trend. The unmilled film has 26.4 posts per μm^2, reaches the maximum of 28.9 μm^{-2} after 5 minutes, and then the surface density diminishes more than 50% to 12.2 μm^{-2} with ion bombardment for 8 minutes.

These results indicate that engineering of surface morphology by ion milling has two distinct steps. Within 5 minutes, ion milling makes cylindrical columns smoother and shorter, and the sharp tips develop, with little change in the arrangement of individual columns within the array. Beyond 5 minutes, the milled silica redistributes from the top to the bottom of the posts, making diameters increase and improving post uniformity. Shorter columns tend to be completely etched away, resulting in a decrease of surface density in the PTFs.

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4 CONCLUSIONS AND PERSPECTIVES

GLAD fabricated PTFs of silica vertical posts tend to have rough architectures and broaden while growing. Ion milling was employed to smooth the posts, develop sharper tips, homogenize column diameters by redistributing milled silica, and increase the post to post separation in the arrays resulting from the complete milling of short posts.

Ion milling introduces a great deal of freedom to tune surface morphologies of PTFs, and may enhance device operation. For instance, the ion-milled PTFs may be employed as scaffolds to uniformly immobilize probe molecules, to improve detection reproducibility and reliability in bio-diagnostics. Furthermore, PTFs may act as templates to direct the fabrication of tubular structures, using a sequential set of processes including shell-material coating on core-PTFs, and core-PTFs exposure and extraction. Defects in tubular structures may be eliminated, due to uniform coating of shell-material on the smooth PTF surfaces created by ion milling. These studies are currently underway.

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