Surface patterning by nanosphere lithography for layer growth with ordered pores

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Received 24 February 2007; accepted 28 May 2007
Available online 9 June 2007

Abstract

Porous Ta layers were grown by glancing angle deposition (GLAD) onto two types of regular surface patterns: honeycomb nanodot arrays and pyramidal hole arrays. The patterning technique employs colloidal self-assembly of 260- to 700-nm-diameter SiO2 nanospheres that form hexagonal close packed monolayers on Si(001) surfaces. Directional evaporation through the holes between the nanospheres yields honeycomb nanodot patterns, while sputter deposition through the nanospheres leads to a thin film mesh that acts as a mask during subsequent anisotropic etching, resulting in an array of inverted pyramid holes. GLAD on nanodot patterns results in honeycomb nanopillar arrays containing a regular array of 450-nm-wide pores that are each surrounded by six 286-nm-wide pillars. GLAD on inverted pyramid hole patterns leads to porous layers with arrays of 280-nm-wide vertical nanochannels separated by 60–130 nm wide Ta nanorod walls. These results demonstrate that substrate patterning by nanosphere lithography is effective in controlling both the size and the arrangement of pores during GLAD.

Keywords: Nanosphere lithography; Glancing angle deposition; Porous layers; Ta

1. Introduction

Glancing Angle Deposition (GLAD) [1], also known as oblique angle deposition, is a physical vapor deposition technique in which the incident flux impinges onto the substrate from a glancing angle \( \alpha \geq 80^\circ \), resulting in porous, highly under-dense thin films with columnar microstructures due to atomic shadowing. GLAD films can be sculptured, by manipulation of both the deposition angle \( \alpha \) and the substrate rotation angle \( \varphi \), into vertical columns [2–4], zigzags [5,6], spirals [7,8] and branched pillars [9,10], with potential applications as photonic crystals [7,8], sensors [6,11], catalyst supports [12], magnetic storage media [13–16], and field emitters [17,18]. Controlling the porosity is desired for various chemical and biological applications [19]. Both experiments and simulations on Ta2O5, WO3 and Ge films have shown that the deposition angle strongly affects the porosity [19–21], which increases moderately to 30% when \( \alpha \) is raised from 0 to 60°, but increases more dramatically with \( \alpha > 60^\circ \) and reaches, for the case of GLAD with \( \alpha > 80^\circ \), values ranging from 60% to 80% for Al, Cr, Cu, Si, Ti, SiO2 and even up to 90% for CaF2 [1,22]. That is, the deposition angle is a very effective parameter to control the overall porosity. However, it does not control the pore arrangement and its size distribution.

Various patterning techniques have been employed to grow periodic GLAD nanostructures, including colloidal self-assembly [7,23], e-beam lithography [3,24] and laser interference lithography [25]. While the former is cost effective but limited to hexagonal close packing with a high packing density, the latter two techniques are capable of creating regular sub-100-nm patterns with various lattice geometries, but are limited by low processing speed, high cost, and incompatibility with large-area processing. Nanosphere lithography (NSL) is, as demonstrated in this article, a promising patterning technique for growing GLAD layers with regular pores. It is an inexpensive high throughput process that employs a self-assembled close-packed monolayer of mono-disperse nanospheres as a lithographic mask during PVD [26,27], and has emerged as a versatile patterning technique to create various nanostructures such as nanodots and nanorings [28].

In this article, we present the fabrication of novel ordered high-porosity nanostructured films by combining GLAD and NSL. Honeycomb nanodot patterns are deposited through the
holes between nanospheres by evaporation normal to the substrate surface. Subsequent GLAD yields nanopillars with a highly porous honeycomb arrangement, with potential applications in sensors and optical devices including 2D photonic band gap structures [29]. Cr deposition through the holes of the nanosphere array by sputtering yields, due to the large angular distribution in the deposition flux, Cr network films with periodic pores which are subsequently used as protective mask for anisotropic etching, leading to inverted pyramid hole arrays. GLAD on such hole patterns results in two-level porous layers consisting of vertical nanochannel arrays separated by porous Ta nanorod walls. Both types of layers, honeycomb nanopillar and vertical nanochannel arrays, exhibit ordered, highly porous structures which are promising for potential optical [30,31], chemical [32,33] and biological [34] applications that require a controlled pore arrangement and/or size distribution.

2. Experimental procedures

Fig. 1a illustrates the nanosphere lithography processing steps required for the two presented patterning techniques. Both start from a monolayer of SiO\textsubscript{2} nanospheres, with typical diameters ranging from 100 to 1000 nm, that are prepared by self-assembly from colloidal aqueous suspensions (Bangs Laboratories, Inc., 10 wt.%), forming hexagonal close-packed arrays on tilted hydrophilic Si(001) substrate surfaces during drying in a temperature and humidity controlled environment, as described in detail in Ref. [35].

Subsequently, the nanosphere monolayer is used as a mask for Cr deposition, using two distinct experimental setups: A) e-beam evaporation and B) magnetron sputter deposition. In step A\textsubscript{1}, a 100-nm-thick Cr layer was deposited by electron beam evaporation at a base pressure of $2 \times 10^{-7}$ Torr, and a growth rate of 5 Å/s, as measured using a quartz crystal thickness monitor. In step B\textsubscript{1}, sputtering from a 7.5-cm-diameter Cr target (99.95% pure) in a 3 mTorr (0.39 Pa) 99.999% pure Ar atmosphere with a target-to-substrate distance of 13 cm and a constant dc power of 500 W yields a deposition rate of 8 Å/s. The Cr deposition flux either passes through the quasi-triangular spaces between neighboring spheres to form patterns on the substrate or it impinges on the sphere surface where it develops into a growing layer which ultimately closes the holes between the spheres and limits the growth of surface patterns on the substrates. The angular distribution of the incoming deposition flux is considerably broader for sputtering than evaporation as illustrated in Fig. 1a. Therefore, the closing of the holes is more pronounced during...
sputtering than evaporation, and causes the pattern to be broader but considerably (~3 times) less tall.

In steps A2 and B2, the silica nanospheres are chemically etched and detached from the Si substrate in a room-temperature 0.5% hydrofluoric acid (HF) solution. This also removes the Cr-layer on top of the spheres, but leaves the Cr that is deposited directly on the Si(001) surface. For the case of normal deposition by evaporation (A1), the Cr on the surface forms a honeycomb nanodot pattern array (A2), which is subsequently used for GLAD growth. In contrast, the large angular distribution in the deposition flux during sputtering (B1) causes the Cr layer to form a relatively thin interconnected two dimensional mesh. This Cr mesh network is used as a second mask for anisotropic etching of Si(001), using a 25% sodium hydroxide (NaOH) solution at 70 °C for 30 s. The resultant substrate (B2) exhibits a hexagonal inverted pyramid hole array. For the following GLAD growth, the Cr layer was subsequently removed by a Cr etchant (ceric ammonium nitrate solution, Type 1020, Transene Co, Inc.) and the Cr layer was subsequently removed by a Cr etchant (ceric ammonium nitrate solution, Type 1020, Transene Co, Inc.) and the Cr was further purified through a Micro Torr purifier. Sputtering was carried out at a constant power of 500 W. The substrates were continuously rotated about the polar axis with 0.5% hydrofluoric acid (HF) solution. This also removes the Cr-etching and detached from the Si substrate in a room-temperature 0.5% hydrofluoric acid (HF) solution. This also removes the Cr-network layer which acts as a mask on the Si substrate surface to protect from hydroxide etching. The etching causes the formation of inverted pyramid-shaped holes, which are terminated by facets that are tilted along four orthogonal <110> directions by a measured angle of 55.3° between the pyramid sides and the (001) substrate surface. This angle is in good agreement with 54.7°, the angle between the (011) and {111} surfaces in a cubic system, indicating that the terminating facets of the inverted pyramids are four intersecting {111} crystal planes. We attribute the formation of {111} facets to the anisotropic etch rate, which is ~100 times faster along <001> than along <111> directions [37]. The hole array exhibits the same hexagonal arrangement as the initial nanospheres, with a center-to-center distance between holes of 440 nm, close to the nominal nanosphere diameter of D=450 nm. This indicates that each nanosphere in the initial self-assembled array leads to the formation of one hole, which is square-shaped despite the quasi-circular shape of the Cr masking holes. The average edge length and depth of these holes with D=450 nm are 283 nm and 460±62 nm, respectively.

Fig. 2 shows a 30° tilted SEM micrograph from a Ta nanopillar array grown by GLAD onto a honeycomb Cr nanodot pattern obtained by NSL using D=700 nm. The pillars replicate the honeycomb arrangement of the substrate pattern and exhibit an average pillar width and height of 286±97 nm and 460±62 nm, respectively. They show a relatively broad size distribution that is attributed to a growth competition during GLAD, which favors the growth of larger pillars at the expense of smaller neighbors [4,23]. The larger magnification plan-view micrograph in the inset shows that the pillars have rough surfaces and exhibit comparable honeycomb structures (not shown), which exhibit lateral widths of 85 nm and 250 nm and heights of ~15 nm and ~50 nm, respectively. That is, nanodot width, height, and spacing all scale approximately linearly with the D-value.

**3. Result and discussion**

Fig. 1b–d show plan and cross-sectional scanning electron micrographs of surface patterns on Si(001) prepared by the two NSL processing routes illustrated in Fig. 1a and described in detail in the previous section. The plan-view image in Fig. 1b is from a honeycomb array of Cr nanodots corresponding to the result at step A2. It was prepared using a monolayer of 450-nm-diameter silica spheres as a template. The Cr dots appear as bright triangles with a lateral width of 130±20 nm, separated by dark circles from the bare Si substrate. The spacing s between neighboring dots in this honeycomb array is 250 nm, in good agreement with the expected value s=D/√3=260 nm, where D=450 nm is the initial sphere diameter. The nanodot height of 30 nm, as estimated by SEM tilting analyses, is considerably smaller than the thickness (100 nm) of the complete Cr layer, indicating that only a fraction of the deposited Cr reaches the substrate before the quasi-triangular holes close up. Some of the dots are connected with their neighbors to form a dumbbell structure. This is attributed to the non-uniform size distribution of the silica spheres causing gaps and, in turn, Cr deposition between smaller-than-average spheres. Starting the patterning process using silica spheres with D=260 and 700 nm yields

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**Fig. 2. 30° tilted SEM micrograph from a honeycomb Ta nanopillar array, with a corresponding higher magnification plan-view micrograph in the inset.**
internal porosity. This indicates that the room-temperature Ta surface diffusion is insufficient to smoothen surface irregularities or to cause a densification of pores that form due to intra-pillar atomic shadowing. The deposition between initial nanodots and the growing nanopillars is suppressed, leading to 450-nm-wide pores which are each encircled by six pillars. The presence of these pores leads to a measured layer porosity of 70%, as determined from large-area analyses of plan-view micrographs. This value does not include the internal porosity of pillars which, if accounted for, would lead to a larger porosity value.

Similar Ta nanopillar arrays with, however, smaller average pillar widths of 109 and 163 nm were grown previously [4] on honeycomb nanodot patterns prepared using $D=260$ nm and 450 nm, respectively. They exhibited porosities ranging from 70 to 75%, comparable to the here reported 70% porosity. Consequently, the porosity $\sim 70\%$ is nearly independent of the lateral length-scale of the initial pattern, indicating a linear scaling during GLAD. That is, the nanopillar width increases proportionally with $D$ [4], leading to the same ratio of occupied space over total layer volume for different pattern sizes. In addition, the observed porosity $\sim 70\%$ is just slightly larger than 65%, the measured porosity for layers grown on flat substrates using the same deposition conditions (not shown), indicating that the packing density is independent on the presence or absence of surface patterns. These results are in agreement with reported previous studies suggesting that the overall density of GLAD layers is a primary function of the deposition angle [19,22] but is independent of the nanodot diameter which can change with layer thickness [2,38]. One potential advantage of smaller pattern sizes is the higher surface area per volume, which would be preferred for sensing and catalytic applications. The honeycomb arrangement is particularly well suited to create layers with wide pores, due to the “holes” in its lattice. A simple geometrical calculation, using the same nearest neighbor distance and pillar diameter as in our honeycomb arrays, predicts diameters of 60 nm and 110 nm for hexagonal close-packed and square lattices, which is nearly seven and four times smaller than our measured honeycomb pore diameter of 450 nm, respectively.

Fig. 3 is a $30^\circ$ tilted SEM micrograph from a porous Ta layer grown on a Si(001) substrate that is patterned with a hexagonal array of inverted pyramid holes. Ta nanorods, 60–130 nm wide, grow vertically on the edges between the square shaped holes. Deposition in the holes is suppressed by atomic shadowing, leading to the development of 280-nm-wide square-shaped nanochannels that elongate along the growth direction perpendicular to the substrate surface. The channels are terminated by a nanopillar arrangement is particularly well suited to create layers with wide pores, due to the “holes” in its lattice. A simple geometrical calculation, using the same nearest neighbor distance and pillar diameter as in our honeycomb arrays, predicts diameters of 60 nm and 110 nm for hexagonal close-packed and square lattices, which is nearly seven and four times smaller than our measured honeycomb pore diameter of 450 nm, respectively.

competition due to the open channels results in a broader and faster rod growth on hole-patterned substrates. The overall porosity of this layer is 76%, which can be divided into the porosity due to the square-shaped pores (50%) caused by the initial hole pattern, and the porosity of the Ta nanorod rows on the edge (26%), due to the small pores between Ta nanorods. The latter value is considerably smaller than the porosity for Ta rods grown on flat substrates (65%). This is attributed to the reduced growth competition associated with the channels on the patterned substrates, which leads to a denser rod packing on the edges in comparison to rods on flat substrates.

4. Conclusions

Nanosphere lithography is exploited to create honeycomb nanodot and pyramidal hole array surface patterns, which are, in turn, used to control the arrangement of pores in subsequently grown Ta GLAD layers. Layers grown on both types of patterns exhibit a regular array of pores, 450-nm-wide circular pores that are surrounded by six nanopillars in the case of honeycomb arrays, and 280-nm-wide square pores that are terminated by nanorod walls for growth on pyramidal hole arrays. These layers exhibit a two-level porosity consisting of wide pores with controlled size and arrangement that are interconnected by narrower pores which are $\sim 60$- and $\sim 10$-nm-wide for honeycomb and hole patterns, respectively. In comparison to GLAD layers on flat substrates, these novel layers exhibit a comparable overall porosity. However, their pore-size distribution is much narrower and their pores are equally spaced. That is, substrate patterning by nanosphere lithography is a powerful tool to control pore size and arrangement during GLAD.

Acknowledgements

This research was supported by the National Science Foundation, Division of Manufacturing and Industrial Innovation, under grant No. DMII-0423358. We also acknowledge
funding from the Donors of the American Chemical Society Petroleum Research Fund under grant no. 44226-G10.

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