Ta nanotubes grown by glancing angle deposition

S. V. Kesapragada, P. R. Sotherland, and D. Gall

Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180

(Received 21 August 2007; accepted 14 January 2008; published 1 April 2008)

Regular arrays of vertical 200-nm-diameter hollow Ta tubes were grown by glancing angle deposition (GLAD) onto Cr nanoring patterns that were fabricated by positive-resist e-beam lithography followed by nondirectional Cr deposition and a lift-off process. During GLAD, nanorods nucleate around the edges of the patterned rings, broaden, and merge to form tubes with 50-nm-thick walls. The nanotubes remain open during continued growth, with a slight (13%) decrease in the effective inner diameter for an increasing tube height from 200 to 600 nm. These results demonstrate that complex patterned two-dimensional shapes can be extended into the third dimension using the GLAD process.

INTRODUCTION

Glancing angle deposition (GLAD) is a thin-film deposition technique where the deposition flux, consisting of atoms and molecules in the gas phase, impinges on the substrate from oblique angles ($\alpha$), resulting in highly under-dense and columnar microstructures. GLAD exploits atomic shadowing effects during line-of-sight physical vapor deposition by controlling polar $\alpha$ and azimuthal $\varphi$ deposition angles to nanoengineer columns into various shapes such as zigzags, pillars, chevrons, spirals, slanted posts, multi-stack columns, flowers, and Y-shapes, with potential applications as optically active layers, magnetic storage media, humidity and pressure sensors, emitters, actuators, and fuel-cell electrodes. Periodic arrays of nanostructures have been achieved by patterning the substrate with regular nanodot arrays prior to GLAD.

In this Brief Report, we show that more complex initial substrate patterns can be utilized to nucleate correspondingly complex three-dimensional GLAD nanostructures. In particular, we pattern the substrate with regular arrays of ~30-nm-wide and 200 ± 25-nm-diameter Cr nanorings using an e-beam lithography and lift-off process. The subsequent growth of Ta by GLAD using continuous polar substrate rotation yields vertical 200–600-nm-tall nanotubes that form by the merging of nanorods that nucleate on the edges of the rings. This demonstrates that the cross-sectional shape of GLAD nanostructures can be controlled by the initial substrate patterning, which, in combination with the extreme flexibility in materials combinations and vertical shapes accessible with GLAD, provides a unique method for nanostructure manufacturing.

EXPERIMENTAL APPROACH

The schematic in Fig. 1 illustrates the steps involved in the growth of nanotubes by GLAD. Nanoring patterns are generated on Si substrates by positive-resist e-beam lithography followed by Cr sputtering and a lift-off process. The subsequent Ta growth by GLAD leads to the formation of nanotubes on the nanoring pattern, as described in the following: In the first step, a 200-nm-thick layer of polymethyl methacrylate (PMMA–Microchem) is spin coated on an RCA-cleaned Si substrate at 500 rpm for 5 s followed by 4000 rpm for 20 s. The resist is then hardened at 160 °C for 60 min. A square array of dots with a period of 500 nm was written into the PMMA layer using a focused 30 keV electron beam with a current of 32 pA, obtained using a 10 μm aperture where each lattice point was exposed to an area dosage of 200 μC/cm². Patterns were created using DesignCAD and the writing was done in a ZEISS SUPRA 55 scanning electron microscope (SEM) equipped with a nanometer pattern generation system (NPGS–J C Nabity Lithography System). The layer was developed in a 3:1 ratio bath of isopropyl alcohol (IPA): methyl-isobutyl ketone for 70 s followed by a 20 s rinse in IPA, resulting in a regular array of 250-nm-diameter holes, illustrated in Fig. 1(a). The subsequent deposition of a nominally 150-nm-thick Cr layer onto the pattern using nondirectional large-angle sputtering causes deposition primarily on the PMMA top surface and the hole sidewalls, while the deposited layer on the bottom (Si) surfaces of the holes is considerably thinner as shown in Fig. 1(b). Such anisotropic hole filling is due to the large angular distribution of depositing species which is typical for conventional non-ionized sputter deposition into vias, as previously observed by both experiment and computer simulation. The subsequent lift-off process consists of an acetone wash for 5 min, which dissolves the PMMA and removes it from the substrate, leading also to the removal of

---

*Author to whom correspondence should be addressed. Electronic mail: gall@rpi.edu*
the Cr layer that is deposited on top of the PMMA layer. The remaining Cr at sidewalls of the holes forms an array of hollow 200-nm-diameter nanorings as illustrated in Fig. 1.

Figure 2 shows SEM micrographs of Ta nanotubes grown by GLAD on arrays of 200-, 400-, and 600-nm-tall Ta nanotubes, and (d) 35° tilted image from 400-nm-tall tubes, including a higher magnification image in the inset.

RESULTS AND DISCUSSION

Figure 2 shows SEM micrographs of Ta nanotubes grown by GLAD on arrays of 200±25-nm-diameter nanoring patterns. The plan-view micrographs in Figs. 1(a)–1(c) and 2(a)–2(c) are from the same nine tubes during different
stages of growth, corresponding to nominal heights of 200, 400, and 600 nm, respectively. Imaging of the same sample area was achieved using e-beam tagging and indexing, which allows us to sequentially monitor the morphological evolution of specific nanostructure features. The micrographs indicate that the deposited Ta initially forms seven to nine nuclei on each Cr ring. The nuclei grow into 68 ± 15-nm-wide and 200-nm-tall vertical nanocolumns, as observed in Fig. 2(a). Continued deposition leads to the merging of neighboring columns, the reduction in their number density to three to five per ring [Fig. 2(b)], and the development of continuous 600-nm-tall tubes as observed in Fig. 2(c). The merging of Ta nanocolumns during GLAD has been reported previously and is attributed to column broadening during a competitive growth mode caused by non-negligible adatom mobility in combination with an irregular column size and space distribution. The irregular size distribution is also evident from Fig. 2(d), which is a “bird’s-eye view” 35° tilt SEM image of 400-nm-tall nanotubes. Such imaging conditions exaggerate the tube roughness and also shorten the apparent tube height. The tubes in Fig. 2(d) and the tube in the larger magnification micrograph in the inset exhibit an aspect ratio of 2, with diameters of 200 nm and heights of 400 nm. These micrographs also show that the tubes are built from individual columns, which themselves have rough surfaces and intracolumnar voids, comparable to previously reported morphologies of GLAD columns.34–38 The effective diameter ranges from 175 to 240 nm for 200-nm-tall tubes. These values are close to the nominal diameter of 200 nm of the initial Cr nanoring pattern, indicating that GLAD replicates the approximate dimensions of the substrate pattern. The diameters decrease to 140–225 nm for the 600-nm-tall tubes, corresponding to an average decrease of 13%. The linear fits through the nine data sets in Fig. 3 have an average slope of $4.2 \times 10^{-2}$, corresponding to a 4.2 nm reduction in tube diameter for every 100 nm of growth. Extrapolating this data, we expect that overgrowth will cause the nanotubes to close up at $h = 4.8 \mu m$. Correspondingly, 2-µm-tall tubes with a height-to-width aspect ratio of 10 would still be open structures with an inner diameter of 120 nm.

CONCLUSIONS

We have shown that GLAD on hollow ring patterns has the potential to create high aspect-ratio nanotube structures. Regular arrays of 200–600-nm-tall and 200-nm-diameter Ta nanotubes were grown on Cr hollow ring patterns. We attribute the nanotube formation during GLAD to multiple nanorod nucleation on the ring surface followed by the merging of those individual nuclei under conditions of extreme shadowing and non-negligible adatom mobility. The effective diameter of the tubes decreases by 13% when the tube height increases from 200 to 600 nm. These results demonstrate, in agreement with other reported work, that GLAD provides a unique approach to extend complex 2D surface patterns into 3D nanostructures.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grant Nos. CMMI-0423358 and CMMI-0727413. We also acknowledge funding from the Donors of the American Chemical Society Petroleum Research Fund under Grant No. 44226-G10.