PHYSICAL SELF-ASSEMBLY AND NANO-PATTERNING*

T.-M. Lu, D.-X. Ye, T. Karabacak, and G.-C. Wang,
Department of Physics, Applied Physics and Astronomy,
Rensselaer Polytechnic Institute, Troy, NY 12180-3590

Abstract

It is known that oblique angle deposition (or glancing angle deposition) can create 3D architectures that are otherwise difficult to produce using the conventional lithographic techniques. The technique relies on a self-assembly mechanism originated from a physical shadowing effect during deposition. In this paper we show examples of 3D nanostructures obtained by this oblique angle deposition on a templated substrate with regularly spaced pillar seeds. We show that common to this technique is the phenomenon of side-way growth on the seeds. The side-way growth leads to a fan-like structure at the initial stages of growth if the incident oblique angle is fixed during growth. Simulations based on a steering effect due to the attractive force between the incoming atom and the existing atoms on the surface produce a fan-like structure similar to that observed experimentally. We show that a two-phase substrate rotation scheme during deposition can dramatically reduce this fan-out effect and can lead to uniform and isolated columns.

Introduction

The morphology of thin film growth fronts formed by a physical vapor deposition technique is controlled by many factors including: surface diffusion, sticking coefficient, and shadowing. Instabilities of growth can occur if the shadowing is more dominant compared to other surface effects and can lead to many diverse physically self-assembled 3D nanostructures. One way to create a dominant shadowing effect is by oblique angle deposition [1-7]. In this technique, incident deposition flux arrives at the substrate at an angle θ with respect to the surface normal. A variety of evaporation sources such as thermal evaporation and sputter deposition can be employed in

Fig. 1. *Left:* A schematic of the oblique angle deposition setup. *Right:* examples of Si structures (amorphous) that we recently fabricated in our lab on templated Si wafer (vertical rods (a), tilted beams (b), top view of helical springs (c), and side view of helical springs (d)) using oblique angle deposition. The scale bars are one micron.

the oblique angle deposition configuration. The technique has been known for more than a century [8,9]. Only recently research activities using the oblique angle deposition has increased. This is perhaps due to the recognition that this technique allows one to produce diverse morphologies and microstructures that possess a wide range of interesting optical, electrical, and magnetic properties.

Figure 1 (left) shows the deposition configuration during an oblique angle deposition. The flux strikes the substrate with an angle θ normal to the substrate surface. The substrate can be rotated around the substrate normal with an angular speed ω . If the substrate is templated with a seed pattern having periodic arrays of pillars, then a number of ordered 3D structures can be formed depending on the deposition rate and how and what speed one rotates the substrate. Figure 1 (right) show some examples of such structures. The seeds can be obtained either by the lithographic techniques including deep UV lithography and e-beam lithography, or more recently available nano-imprint or dip pen techniques. Although the seed layer can be obtained by lithographic techniques, most of the 3D structures themselves shown in Fig. 1 (right) cannot be obtained by any lithographic techniques. If the substrate is flat with no seeds, similar isolated 3D nanostructures can also be formed. This is due to the fact that initially islands are nucleated and because of shadowing, only taller islands survive in the later stages of growth. However, in this case the correlation between the nanostructures grown on the taller islands would not be perfectly periodic and only a quasi-periodic relation exists [10].

The oblique angle deposition is a physical self-assembly growth technique that can produce 3D nanostructures with a very large aspect ratio and controllable porosity, shape and symmetry. The technique is very robust in that practically any material (e.g., Si, C, W, Co, SiO₂, MgF₂, etc.) or combination of materials can be used for fabrication. The nanostructures can be integrated onto a substrate platform with controllable length, diameter, aspect ratio, and density, which make them very convenient to pattern devices for realistic applications. However, basic quantitative understanding on the formation of nanostructures is still far from complete. Here we shall focus on one aspect of it, namely the side-way growth phenomenon that often occurs during the oblique angle deposition.

Shadowing and side-way growth

Figure 2 defines a typical deposition configuration in an oblique angle deposition technique. The flux $\vec{F}$ is incident from the left with an angle θ with respect to the surface normal onto the array of pillars (seeds). The h is the height of the pillars and D is the separation of the pillars. The shadowing length is defined as $S = h \tan \theta$. We consider the case where $S > D$, so that only the top portion of the nearest-neighbor pillars with a dimension of $D / \tan \theta$ can receive the incident flux. No flux can arrive in between the pillars. The top view of a realistic template with a square pattern is shown in Fig. 3 (left). The pattern contains W pillars with a width of 150 nm and pillar to pillar distance of 1,000 nm. The height of the pillars is 360 nm.

Fig. 2. A typical oblique angle deposition configuration. The flux $\vec{F}$ is incident from the left onto the array of pillars (seeds). The h is the height of the pillars and D is the separation of the pillars. The shadowing length is defined as $S = h \tan \theta$.

Fig. 3. *Left*: a template with W pillars arranged in a square lattice. *Right*: the top view of a sample at an initial stage of Si deposition at an oblique angle of $\theta = 85^\circ$ by thermal evaporation.

A fundamental aspect of the oblique angle deposition is the development of a “fan-out” structure as a result of a side-way growth phenomenon. Figure 3 (right) shows the top view of a sample obtained at an initial stage of Si deposition at an oblique angle of $\theta = 85^\circ$. The incident flux was from the left. The deposition rate was 30 nm/min. The distance between the source and the substrate is 30 cm. A fan-out structure was developed during deposition. The fan-out structure eventually merged with adjacent columns into a slanted wall-like structure shown in Fig. 4a (side view) and Fig. 4b (top view). It is therefore not possible to produce isolated structures on the template by fixing an incident oblique angle.

Fig. 4. (a) and (b) are side view and top view of columnar growth with $\theta = 85^\circ$ on the square lattice template shown in Fig. 3. The side-way growth (fan-out) eventually leads to connected rectangular columns and forms a wall-like structure.

Monte Carlo simulations of side-way growth

In order to understand the side-way growth phenomenon on the templated substrate, we use a three-dimensional Monte Carlo (3D MC) method to simulate the growth of the columns produced by the oblique angle deposition. A 3D lattice, which allows overhangs, is formed by cubic lattice points and each incident atom has the dimension of one lattice point. The simulations include a substrate with seeds, an obliquely incident flux, and surface diffusion. We assume a uniform flux of atoms approaching the surface with an angle $\theta = 85^\circ$. At each simulation step an atom is sent towards a randomly chosen lattice point on the surface of size $L \times L$. After the incident atom is deposited onto the surface, an atom that is chosen randomly within a box around the impact point is set to diffuse to another nearest neighbor random location. The diffusion step is repeated until Q number of jumps is made. Then another atom is introduced, and the deposition and diffusion steps are repeated in a similar way. This strategy mimics the surface diffusion at the first impact point during the growth by evaporation deposition.

Our simulations involved a system size of $L \times L \times N = 512 \times 512 \times 512$, with a periodic boundary condition. Here L and N are the lateral and vertical dimensions of the 3D lattice. The simulations were conducted at a diffusion rate of $Q = 300$. Diffusion improves the columnar structure by making columns denser and column edges smoother [11]. Seed pillars are placed on

a planer substrate with a square-lattice geometry separated by 84 lattice units (center-center distance). The individual pillar has dimensions of 16, 16, 24 lattice units in height, top diameter, and bottom diameter, respectively.

In our simulations, we compared two types of sticking rules. As illustrated in Fig. 5, the first one is the head-on collision (HC) mode where the incident particle sticks to the first surface site that stands along its trajectory. The second sticking rule we tested is the nearest neighbor attraction which is also called the NN ballistic deposition technique [12]. In the NN rule, the incident particle can be deposited to a surface site within the vicinity of its trajectory (Fig. 5). The growth rate can be faster in the lateral direction during the NN sticking rule compared to that of the HC rule. A possible growth mechanism that can lead to the NN rule is the “steering effect” [13,14] that originates from van der Waals interactions between the obliquely incident particles of low energies (e.g. < 1 eV) and the nearby surface atoms.

Fig. 5. A schematic showing our 3D Monte Carlo simulations including surface diffusion and overhangs. Two different sticking rules were tested: nearest neighbor (NN) and head-on collision (HC).

Fig. 6. Top-view images of simulated nanocolumns grown on templated substrates by (a) the head-on collision (HC) and (b) the nearest neighbor (NN) sticking rule.

Figures 6(a) and 6(b) show the top view images of simulated columns deposited on the templated substrate with the HC and NN sticking rules, respectively. In the HC rule, the columns grow uniformly towards the incident flux with no significant change in their width. On the other hand, the columns that grow according to the NN sticking rule show a fan-out geometry that is similar to our experimentally observed results shown in Fig. 3. The nanocolumns grown by thermal evaporation involves obliquely incident atoms having low energies (typically < 1 eV). Therefore, NN sticking in our simulations can mimic the steering effect that is believed to lead to the fan-out shaped nanostructures.

Fig 7. A schematic showing the top views of the substrate rotation and the coated pillar seed using the two-phase rotation scheme. The substrate is rotated around the surface normal and the rotation is divided into two regions, I and II, with the angles of rotation ϕ and $2\pi-\phi$, respectively. The rotation speeds are ω_I and ω_{II} for region I and region II, respectively.

Two-phase rotation scheme

There are ways to reduce the side-way growth. One strategy is called the two-phase rotation scheme [7]. In this scheme, the substrate is rotated around the surface normal and the rotation is divided into two regions as shown in Fig. 7. The rotation speed is ω_I in region I and the rotation speed changes to ω_{II} in region II. We set $\omega_{II} \gg \omega_I$ and during the deposition the rotation in region II is much faster. The reason that this scheme can reduce the side-way growth is that during the deposition, before the “fan” gets spread out further, the substrate is rotated to a position such that the corner of the fan (which is sharper) is facing the flux, not the center of the fan. This has quite a dramatic effect in the formation of the columns. Figures 8(a) and 8(b) show the side view and top view of the columns deposited with the two-phase rotation, respectively. In

this experiment we set $\omega_I = 0.015$ Hz, $\frac{\omega_{II}}{\omega_I} = 5$, and $\phi = 135^\circ$. It is seen that there is a dramatic

change in the structure when changing from the fixed angle to a two-phase rotation scheme. In the two-phase rotation scheme, isolated columns (slanted) are created without touching each others. The fan-out phenomenon still exists at the very initial stages of growth and the diameter of the columns grows as a function of time, but the growth quickly stops after the initial transient. Another scheme to reduce the side-way growth is a “sweeping” technique [15] where the incident angle alternatively changes between position ϕ_1 and position ϕ_2 . It was shown that the size (diameter) of the columns grown on a flat surface can be maintained.

Fig. 8. (a) and (b) are side view and top view of column growth on the square lattice template shown in Fig. 3 with the two-phase rotation technique at $\theta = 85^\circ$. No side-way growth (fan-out) is observed.

Scale bars = 1μ

Conclusion remarks

The side-way growth discussed above is a common phenomenon that occurs during most oblique angle deposition configurations. Take for example the growth of vertical rods on a templated substrate. If one rotates the substrate with a sufficiently large and constant speed, vertical columns would be formed on the seed pillars. Typically the diameter of the columns would initially grow as a power law in time and will stop growing after a certain height is reached [16]. The columns would not touch each other. Figure 9 shows a schematic diagram of such columnar growth on a templated substrate. There exists a gap between the columns which is a function of the pillar to pillar distance. If the pillar spacing is sufficiently small, then the initial growth of the diameter only occurs at a very short time and the columns appear to have a uniform diameter such as the ones shown in Fig. 1 (right).

Fig. 9. A schematic diagram showing the growth of vertical columns on a templated substrate. $2R$ = diameter of the column. $2R_{\text{sat}}$ = saturation diameter. S = saturation column to column distance.

Acknowledgements

*Work support by the NSF. The authors would like to thank Professors Y.-P. Zhao and C. Picu for valuable discussions. We also would like to acknowledge Dr. B.-K. Lim who provided us the templates.

References

- [1] K. Robbie, M.J. Brett, and A. Lakhtakia, *Nature* **384**, 616 (1996).
- [2] K. Robbie, J.C. Sit, and M.J. Brett, *J. Vac. Sci. Technol. B* **16**, 1115 (1998).
- [3] A. Lakhtakia and R. Messier, *Optics & Photonics News* **12**, 27 (2001).
- [4] R. Messier, V.C. Venugopal, and P.D. Sunal, *J. Vac. Sci. Technol. A* **18**, 1538 (2000).
- [5] M. Suzuki and Y. Taga, *J. Appl. Phys.* **90**, 5599 (2001).
- [6] Y.-P. Zhao, D.-X. Ye, G.-C. Wang, and T.-M. Lu, *Nano. Lett.* **2**, 351 (2002).
- [7] D.-X. Ye, T. Karabacak, B.K. Lim, G.-C. Wang, and T.-M. Lu, *Nanotechnology* **15**, 817 (2004).
- [8] A. Kundt, *Ann. Phys. Chem. Lpz.* **27**, 59 (1886).
- [9] N. O. Young and J. Kowal, *Nature* **183**, 104 (1959).
- [10] T. Karabacak, G.-C. Wang, and T.-M. Lu, *J. Appl. Phys.* **94**, 7723 (2003).
- [11] T. Karabacak, J. P. Singh, Y.-P. Zhao, G.-C. Wang, and T.-M. Lu, *Phys. Rev. B* **68**, 125408 (2003).
- [12] A.-L. Barabasi and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, England, 1995), p.20.
- [13] J. Seo, S.-M. Kwon, H.-Y. Kim, and J.-S. Kim, *Phys. Rev. B* **67**, 121402 (2003).
- [14] J. G. Amar, *Phys. Rev. B* **67**, 165425 (2003).
- [15] M.O. Jensen and M.J. Brett, *Appl. Phys. A* (2004), online.
- [16] E. Main, T. Karabacak, and T.-M. Lu, *J. Appl. Phys.* **95**, 4346 (2004).