

Available online at www.sciencedirect.com



Acta Materialia 52 (2004) 5633-5637



www.actamat-journals.com

Formation of Si-based nano-island array on porous anodic alumina

Y.F. Mei ^{a,*,1}, G.S. Huang ^{b,1}, Z.M. Li ^c, G.G. Siu ^a, Ricky K.Y. Fu ^a, Y.M. Yang ^b, X.L. Wu ^b, Z.K. Tang ^c, Paul K. Chu ^a

^a Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

^b National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, PR China

^c Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

Received 23 July 2004; received in revised form 19 August 2004; accepted 21 August 2004 Available online 15 September 2004

Abstract

Si-based nano-island arrays were fabricated on porous anodic alumina by two methods. In the first method, a thick silicon film was first deposited onto the surface with highly ordered bowl array prepared by anodizing an Al foil, followed by the formation of a polycrystalline silicon nano-island array on the surface close to the bowl array after dissolving aluminum. In the second method, porous anodization was performed on an Al thin film on Si and a SiO₂ nano-island array was subsequently formed electrochemically. Time-resolved atomic force microscopy and photoluminescence were used to investigate the growth process as well as the mechanism of the growth process. Our proposed mechanism as well as assumptions made to formulate the model were found to be in agreement with the experimental results.

© 2004 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Nanostructures; Chemical synthesis; Semiconductor

1. Introduction

Porous anodic alumina (PAA) with highly ordered pore arrangement, controllable pore diameter, channel length, and fine insulating property [1–3] is widely used as a template to grow nanowires or nanotubes [4,5] since the pioneering work of Martin's groups [6]. On the other hand, the self-organization mechanism to achieve an ordered nanopore arrangement is still a problem [7] and a better understanding is vital to applications such as selfassembled nano-electronic quantum computers [8]. Sibased quantum computation has attracted much interest because of its compatibility with conventional microelectronics [9]. Hence, the fabrication of self-assembled nanostructures based on silicon is becoming more important for further potential applications in self-assembled nano-electronics.

In this work, two methods were adopted to produce Si-based nano-island arrays on PAA templates. In the first method, a thick silicon film was sputter deposited onto a surface with highly ordered bowl array that was produced by anodizing an Al foil. Afterwards, a silicon nano-island array was formed on the surface close to the bowl array after dissolving aluminum substrate. In the second method, porous anodization was conducted on a Al thin film on Si substrate and the SiO_2 nano-island array was subsequently formed electrochemically with careful manipulation. The sample synthesized by the first method showed nano-island array with a highly ordered arrangement, but the fabrication of the nano-island array with a large area was easier by the second method. The growth process was analyzed by time-resolved atomic force microscopy (AFM) and

^{*} Corresponding author. Tel.: +852 21942824; fax: +852 27887830. *E-mail addresses:* yf.mei@plink.cityu.edu.hk, meiyongfeng@nju.org.cn (Y.F. Mei).

¹ Y.F. Mei and G.S. Huang contributed equally to this work.

^{1359-6454/\$30.00} @ 2004 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved. doi:10.1016/j.actamat.2004.08.024

photoluminescence (PL) measurements and the formation details were studied by transmission electron microscopy (TEM).

2. Experiments

Fig. 1(a) illustrates the schematic diagram of method 1. The PAA template on bulk aluminum was obtained by a conventional two-step method [10]. High-purity aluminum foils (99.99%) were used in our anodization experiments to fabricate the PAA template. Before anodization, the aluminum foil was degreased with acetone and then annealed at 400 °C in N₂ for 3 h. Then, the Al foil was electropolished in a solution of perchloric acid and ethanol (1:5 in volume) under a constant voltage of 18 V for 3 min. Anodization in oxalic acid (0.5 M) was conducted under a constant DC voltage of 40 V at \sim 0 °C for 8–10 h to form the surface PAA film. After chemically removing the surface film in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%), anodization was performed again under the same conditions for several hours to produce the PAA with nanopores of about 50 nm and interpore distance of about 88 nm. The PAA template was again dissolved in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) and a highly-ordered nano-scale bowl array was obtained on the surface of bulk aluminum. Polycrystalline silicon was subsequently deposited into the bowl by radio-frequency (RF) magnetron sputtering and after dissolution of aluminum substrate, polycrystalline Si nano-island array was produced.

The schematic diagram of method 2 is shown in Fig. 1(b). A 440 nm thick aluminum film (99.99%) was deposited on p-type, 0.5Ω cm, $\langle 100 \rangle$ silicon using electron beam evaporation in which the vacuum chamber pressure was 2.5×10^{-6} Pa. The electron beam voltage was ~ 10 kV and electron current was 0.5 A. The Al/Si structure was used directly as an anode with a platinum plate as a cathode. Several Al/Si samples were anodized in sulfuric acid (15 wt%) under a constant DC voltage of 20 V at room temperature. The growth could be monitored by the current density versus time (*j*-*t*) curves

[11,12]. The SiO_2 nano-island array was formed as shown in step iii in Fig. 1(b).

Atomic force microscopy measurements were carried out using nanoscope IIIa Digital Instruments. TEM was conducted employing the Philips CM20. PL was conducted on a FluoroMax-2 photo-spectrometer at room temperature.

3. Results and discussion

3.1. Method 1

Fig. 2(a) reveals the AFM image of the nano-scale Al bowl array with a highly ordered arrangement on aluminum substrate. The distance between two bowls was about 88 nm and in agreement with the interpore distance. After deposition of Si by RF magnetron sputtering, a Si-based nano-island array (Fig. 2(b)) was produced mimicking the arrangement of nano-scale Al bowl array. Raman scattering results show that the component of our nano-scale islands was polycrystalline silicon that possesses a large enough size such that quantum confinement effects do not play a significant role.

3.2. Method 2

Anodization of Al/Si can be monitored using the j-t curve (Fig. 3(a)). In order to investigate the growth process at the interface of Al/Si, six growth points (A–F) were selected along the j-t curve corresponding to various anodizing times similar to our previous work [11] and these samples were divided into two groups.

The first group of samples was immersed into a 5 wt% phosphoric acid solution at 27 °C for a long time until no alumina existed on the surface. The samples were then studied by AFM for possible silicon oxide and the results are shown in Fig. 3(b)–(e) for samples A, C, D and F, respectively. In sample A, there were only very few SiO₂ islands formed on the Si substrate and most of the surface was smooth as shown in Fig. 3(b). Fig. 3(c) reveals the formation of a few silicon oxide



Fig. 1. Schematic diagrams illustrating: (a) method 1; (b) method 2.





Fig. 2. AFM images of: (a) nanoscale Al bowl array with highly ordered arrangement on aluminum substrate; (b) polycrystalline silicon nano-island array mimicking the arrangement of (a).



Fig. 3. (a) *j*-*t* curve for anodization of Si-based PAA film in 15 wt% sulfuric acid. Also shown are the AFM images of samples, (b) A, (c) C, (d) D, and (e) F according to the selected point in (a).



Fig. 4. (a) PL spectra of samples A–F. (b) PLE spectra of sample A at three PL peak positions.

islands on sample C. More silicon oxide islands, 15-20 nm in diameter and 5-10 nm in height, appeared in sample D (Fig. 3(d)). A SiO₂ nano-island array with a uniform arrangement was observed on sample F in Fig. 3(e). This feature is useful in silicon-based self-assembled nano-electronics. Our Fourier-transform infrared (FTIR) absorption spectra also identified the presence of silicon oxide with silicon dioxide (SiO₂).

PL spectra acquired from samples in the second group are compared as shown in Fig. 4(a) using excitation by the 240 nm line of a Xe lamp. The PL spectra are also shown in Fig. 4(b). Since PL behavior of PAA is generally due to color defects [11-13] such as F^+ , F, or even both, the three PL peaks in our results should originate from the same defect because of the same positions of the PLE peaks monitoring at different PL peaks. There is another piece of information [12] showing PL with high intensity because of the contrast of E-fields across the barrier layer. The transition from the F^+ to F center has been considered for PAA film on Si substrate anodized in oxalic acid [11]. However, there was no obvious change in the PL shapes in our present system which was anodized in sulfuric acid under high contrast of *E*-field across barrier layer [12]. Hence, we consider that the PL behavior would involve only one defect $(F^+ \text{ or } F)$ based on our present PL results together with previous works [13]. Regardless of the F or F^+ defect in our PAA film which is under further investigation, there is an interesting phenomenon concerning the shifts of the PL peaks in samples A-F, which may be used as a sensor. When the anodizing time was increased at the Al/ Si interface, a serious of red shifts appeared in the PL spectra. Because of the SiO_2 formed at the interface, the expansion of SiO₂ relative to Si induced a tensile stress on the alumina. Increasing the stress causes a red shift due to the increase in the wave function overlapping, i.e., decrease in the spacings of the energy levels of the defect centers. When aluminum is oxidized to alumina, the volume expands by roughly a factor of 2 because the atomic density of aluminum in alumina is a factor of 2 lower than that of metallic aluminum [14]. The volume expansion that leads to compressive stress in the film is proportional to the volume expansion of SiO_2 i.e., anodization time. Hence, red shifts were observed in samples A–F. Since the PL behavior changes according to the formation process of the SiO₂ nano-island array, it can be employed to monitor and control the growth of the SiO₂ nano-island array.

4. Growth details of method 2

As aforementioned, SiO_2 can, for example, be produced at point C and the results are not consistent with our previous explanation of the growth process [11]. However, our further study on the growth mechanism suggests some clues to the self-organization mechanism. As shown in Fig. 5(a), the grains can be easily observed in the thin Al film and the surface morphology is not very smooth. The TEM image of the formed PAA template on Si is depicted in Fig. 5(b) and it can be seen that the nanochannels are not so straight especially near the surface.

As a result, a model (the inset of Fig. 5(b)) can be postulated to explain the growth mechanism. Because of the relatively rough surface and that no polishing has been performed, the growth of the nanochannel should adjust to its growth direction because of the guide of the *E*-field on the surface based on the field-assistant dissolution mechanism for PAA growth [15]. Hence, the surface to interface distances along the nanochannels are different although the differences are small, but it is enough to affect the growth of the SiO₂ nano-island at the Al/Si interface. We believe that a high-quality SiO₂ nano-island array can be fabricated if a Al film with a smooth surface is employed, and our two-step method will yield the desired results although care must be exercised during the experimental process [16].



Fig. 5. (a) AFM image of the surface of Al film on Si substrate. (b) Cross-sectional TEM image of sample F (the inset is a shematic diagram of the growth process in a crystal grain).

5. Conclusion

A Si-based nano-island array was obtained on the PAA template using two different methods. The procedures were designed for efficient nano-island growth. The two methods possess different unique advantages. The array produced by method 1 exhibits a highly ordered arrangement, while method 2 can be more easily controlled and has potential applications in large area processing. Details of method 2 are also discussed and the PL behavior is believed to stem from a single center (F^+ or F). The pilot of *E*-field and relative rough surface of the Al film is believed to induce non-uniform growth and distribution of the SiO₂ nano-islands.

Acknowledgements

Y.F. Mei, one of the authors, expresses his gratitude to Mr. M.K. Tang and Dr. Amy X.Y. Lu for their kind experimental assistance. This work was supported by Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) # CityU1137/ 03E and City University of Hong Kong Strategic Research Grant #7001642 as well as grants from the Natural Science Foundations of China and JiangSu province. Thanks to Mr. Y.J. Wang and Dr. O.K.C. Tsul for part of AFM measurements.

References

- [1] Masuda H, Fukuda KS. Science 1995;268:1466.
- [2] Thompson GE. Thin Solid Films 1997;297:192.
- [3] Li AP, Müller F, Birner A, Nielsch K, Gösele U. J Appl Phys 1998;84:6023.
- [4] Mei YF, Wu XL, Li XF, Bao XM, Wang XZ, Hu Z, et al. J Cryst Growth 2003;255:414.
- [5] Sha J, Niu JJ, Ma XY, Xu J, Zhang XB, Yang Q, et al. Adv Mater 2002;14:1219.
- [6] Martin CR. Science 1994;266:1961. and reference therein.
- [7] Nielsch K, Choi J, Schwirn K, Wehrspohn RB, Gosele U. Nano Lett 2002;2:677.
- [8] Bandyopadhyay S. Phys Rev B 2000;61:13813.
- [9] Kane BE. Nature 1998;393:133.
- [10] Masuda H, Fukuda KS. Science 1995;268:1466.
- [11] Mei YF, Siu GG, Huang GS, Wu XL. Appl Surf Sci 2004;230:393.
- [12] Mei YF, Siu GG, Zou JP, Wu XL. Phys Lett A 2004;324:479.
- [13] Wu JH, Wu XL, Tang N, Mei YF, Bao XM. Appl Phys A 2001;72:735.
- [14] Jessensky O, Müller F, Gösele U. Appl Phys Lett 1998;72:1183.
- [15] Thompson GE. Thin Solid Films 1997;297:192.
- [16] Mei YF, Siu GG, Yang Y, Fu RKY, Hung TF, Chu PK, et al. Acta Mater 2004 (in press).