Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 776-778

S-VI-3

Preferential Nucleation of Nanocrystalline Silicon along Microsteps

Masanori Otobe, Jun Kawahara and Shunri Oda*

Research Center for Quantum Effect Electronics, Tokyo Institute of Technology
2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan
**Also with PRESTO, JRDC*

We propose digital plasma processing for the fabrication of silicon quantum dots on SiO_2 substrates patterned with micro trenches. It has been found that nucleation of nanocrystalline Si (nc-Si) takes place preferentially along the trench structure with post hydrogen plasma treatment of hydrogenated amorphous Si (a-Si:H) layer. The preferential nucleation of nc-Si can be explained in terms of "hydrogen diffusion model", in which hydrogen radicals diffused through the a-Si:H layer to the interface of a-Si:H and SiO_2, trigger the crystallization.

1. INTRODUCTION

Recently, nanocrystalline silicon (nc-Si) with a grain size of less than 10nm attracts considerable attention because of an expectation to manifest a quantum dot structure, which has potential application to silicon-based optoelectronics and the next generation ultra large scale integrated circuits.[1] We have proposed[2] digital plasma processing for the fabrication of nc-Si. Using the pulsed gas supply of SiH_4 and H_2 in the very-high-frequency (VHF) plasma, we have clarified[3] the role of atomic hydrogen in the growth of nc-Si in solid phase of a-Si:H. The growth of nc-Si in a-Si:H can be explained by a "hydrogen diffusion model" in which hydrogen radicals diffuse through the a-Si:H layer and trigger the crystallization. However, the position of nc-Si on a substrate can not be controlled only by the pulsed plasma processing.

Moniwa et. al.[4] prepared polycrystalline Si with the grain size of several μm preferentially at the steps 100nm height on SiO_2 substrate by thermal annealing of a-Si at 600℃. We apply this technique to the position control of nc-Si. We have used the substrate on which micro trenches with the dimension of several tens of nm are fabricated. In this paper, we describe the results of experiments on preferential growth of nc-Si along micro step. The mechanism of preferential nucleation is also discussed. Prepared samples were characterized by a transmission electron microscopy (TEM) with an accelerating voltage of 200kV.

2. EXPERIMENTAL

Trench structure with 16nm in height and 40nm in width, separated by 500nm were fabricated on SiO_2 which was prepared by thermal oxidation of Si(100) substrate. Line patterns were drawn by an electron beam lithography machine of JEOL JBX-5FE with the resist of ZEP520. In order to fabricate the trench structure, electron cyclotron resonance reactive ion etching with CHF_3 gas was used.

A 2.5nm-thick device-grade a-Si:H was deposited on the trench substrates by a capacitively coupled plasma enhanced chemical vapor deposition (PECVD) with a gaseous mixture of SiH_4 and H_2. Electric power of 144MHz in the very-high-frequency (VHF) band was used for PECVD. The features of VHF plasma are higher efficiency of radical formation[5] and absence of ion-bombardment damage to the film thanks to lower self-bias of plasma[6] compared to a 13.56MHz plasma.

Next, deposited a-Si:H films were annealed by a VHF hydrogen plasma for various periods t_a. Finally, a layer of a-Si:H was deposited with the thickness of 40nm in order to protect the sample during the preparation process of plan view TEM.

3. RESULTS

Figure 1 shows a cross-section TEM image of the micro trench topped with an a-Si:H layer. In this sample, a 40nm-thick protection layer of a-Si:H is not deposited. The trench structure is well defined with sharp and steep wall angle and conformal deposition of a-Si:H.

Figure 2 shows plan view TEM images of the samples

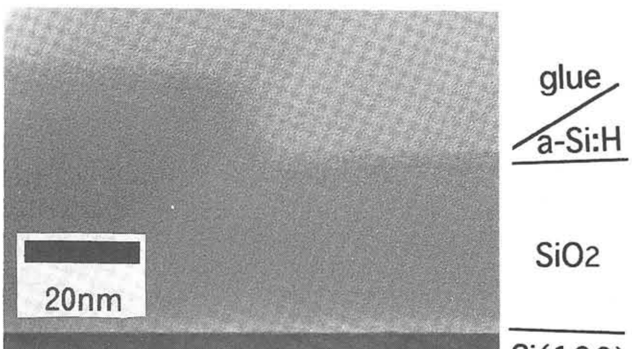

Fig. 1 Cross-section TEM image of the micro trench and a-Si:H layer.

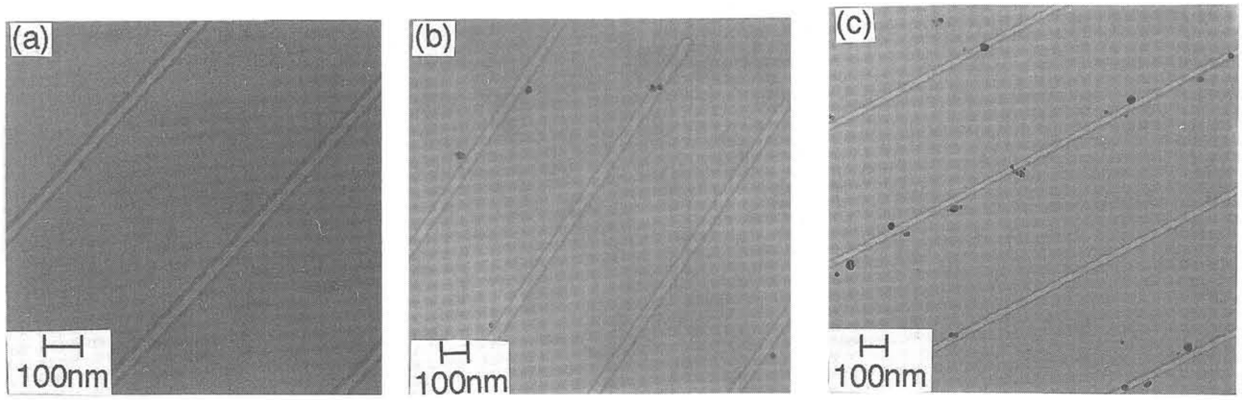

Fig. 2 Plan view TEM images of samples with various hydrogen redical annealing time t_a of (a) 0s, (b) 10s, (c) 20s.

with various t_a of (a) 0s, (b) 10s, (c) 20s. As shown in Fig. 2(a), we have confirmed that nc-Si is not formed without hydrogen plasma annealing. It has been found , as shown in Fig. 2(b), that nucleation of nc-Si takes place preferentially along the trench structure with t_a of 10s. Nanocrystalline Si is apparent as dark spots. The crystallinity of nc-Si was characterized by the transmission electron diffraction and dark-field observation. It should be noted that nucleation occurs only at the upper edge of trench structure. Hydrogen plasma annealing for 20s causes nucleation on the plane as well as at the edge of trench structure, as shown in Fig. 2(c).

4. DISCUSSION

Preferential nucleation at the upper edge of trench structure can be explained by "hydrogen diffusion model", in which hydrogen radicals diffused through the a-Si:H layer to the interface of a-Si:H and SiO_2, trigger the crystallization. Here, the concentration of hydrogen radicals diffused through a-Si:H at the upper corner of trench structure after post hydrogen plasma annealing is calculated.

The two dimensional diffusion equation can be expressed as,

$$\frac{\partial^2 N(x, y, t)}{\partial x^2} + \frac{\partial^2 N(x, y, t)}{\partial y^2} = \frac{1}{D}\frac{\partial N(x, y, t)}{\partial t} \tag{1}$$

where N is the concentration of hydrogen radicals, D is the diffusion coefficient, x and y are the position and t is the diffusion time. For the condition of constant surface concentration N_0 and the infinite rectangular solid (i.e., $0 \leq x$, $0 \leq y$), The solution of Eq. (1) is given as[7],

$$N(x, y, t) = N_0\left\{1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \mathrm{erf}\left(\frac{y}{2\sqrt{Dt}}\right)\right\} \tag{2}$$

In this equation, a rectangular corner (i.e., the upper edge of trench) is x=y=0.

Figure 3 shows the calculated concentration of hydrogen radicals in a-Si:H at the upper edge of trench structure after post hydrogen plasma annealing of 10s. The vertical wall angle is assumed. The concentration of hydrogen radicals is normalized at the surface. The diffusion coefficient of hydrogen radicals in amorphous silicon is reported[8-10] as 6×10^{-16} - 3×10^{-15} cm^2/s. at 250℃ In this calculation, we adopt the diffusion coefficient of 1×10^{-15} cm^2/s. In this figure, the dotted line represents the interface of a-Si:H and SiO_2. The point of x = 2.5nm and y = 2.5nm is the upper edge of SiO_2 trench structure. The concentration at x = y = 2.5 and x = 5, y = 2.5 are 0.15 and 0.078, respectively. This means the concentration of hydrogen radicals at the edge of SiO_2 trench surface is almost twice as much as that

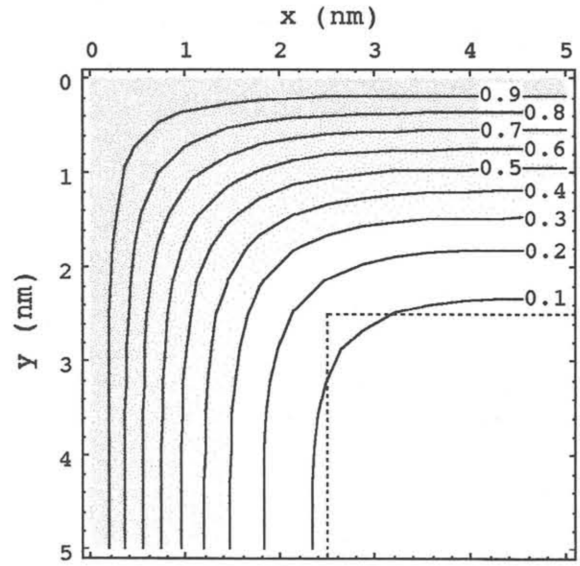

Fig. 3 Calculated concentration of hydrogen radicals in a-Si:H at the edge of trench structure after post hydrogen plasma annealing of 10s. The concentration of hydrogen radicals is normalized at the surface.

on the plane, resulted in the preferential nucleation of nc-Si at the upper edge of trench structure. The threshold of hydrogen radical concentration occurring crystallization N_{th} can be considered between 0.078 and 0.15. Even if the diffusion coefficient of 6×10^{-16} - 3×10^{-15} cm^2/s is applied, the result is same.

Figure 4 represent the hydrogen radical concentration at the edge and plane of trench structure of SiO_2, as a function of t_a. The concentration of hydrogen radicals is normalized. When t_a is 20s, the concentration of hydrogen radicals on the plane exceeds N_{th}, which causes growth of nc-Si even on the plane.

5. CONCLUSIONS

It has been found, for the first time, that nucleation of nc-Si takes place preferentially along the trench structure with post hydrogen plasma treatment of a-Si:H layer. The preferential nucleation of nc-Si can be explained by "hydrogen diffusion model", in which hydrogen radicals diffused through the a-Si:H layer to the interface of a-Si:H and SiO_2, trigger the crystallization. Other effect for preferential nucleation, *e.g.*, stress of the a-Si:H at the edge of trench structure, will be discussed elsewhere for more detailed discussion.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Professor K. Yagi and Professor N. Yamamoto for use of the TEM apparatus and their useful suggestions. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, by the Asahi Glass Foundation and by the Kurata Foundation. One of the authors (M. O.) was supported by the Research Fellow Program of the Japan Society for the Promotion of Science. Ultra-high-purity SiH_4 was donated by Mitsui Toatsu Chemicals, Inc.

REFERENCES

1) S. Oda and M. Otobe: Mater. Res. Soc. Symp. Proc. **358** (1995) 721. Also refer to the other papers in this volume.

2) M. Otobe and S. Oda: Jpn. J. Appl. Phys. **31** (1992) 1948.

3) M. Otobe and S. Oda: J. Non-Cryst. Solids **164-166** (1993) 993.

4) M. Moniwa, M. Miyao, R. Tsuchiyama, A. Ishizaka, M. Ichikawa, H. Sunami and T. Tokuyama: Appl. Phys. Lett. **47** (1985) 113.

5) S. Oda, J. Noda and M. Matsumura: Mater. Res. Soc. Symp. Proc. **118** (1988) 117.

6) S. Oda: Plasma Sources Sci. Technol. **2** (1993) 26.

7) H. S. Carslaw and J. C. Jaeger: *Conduction of Heat in Solids*, (Oxford Univ. Press, Oxford, 1959) 2nd ed., p.171.

8) A. E. Widmer, R. Fehlmann and C. W. Magee: J. Non-Cryst. Solids **54** (1983) 199.

9) P. V. Santos and W. B. Jackson: Phys. Rev. **B46** (1992) 4595.

10) T. Shiraiwa, O. Sugiura, H. Kanoh. N. Asai, K. Usami, T. Hattori and M. Matsumura: Jpn. J. Appl. Phys. **32** (1993) L20.

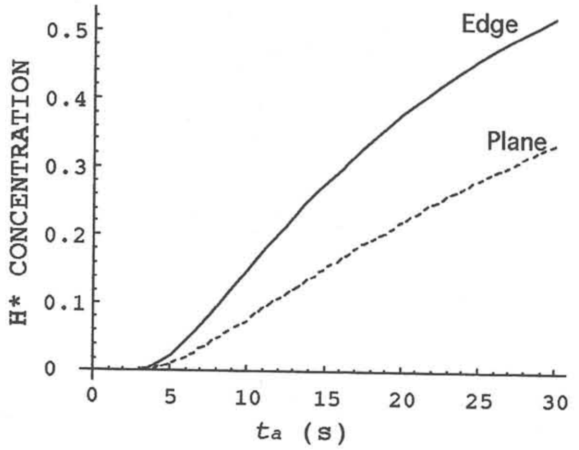

Fig. 4 Calculated hydrogen radical concentration at the edge and plane of trench structure, as a function of t_a. The concentration of hydrogen radicals is normalized at the surface.