Fabrication and Field Emission of Silicon Nano-Crystalline Film*

Wang Weiming[1], Yu Ke[1,2], Ding Yanfang[1], Li Qiong[1] and Zhu Ziqiang[1]

(1 *Department of Electronic Engineering, East China Normal University, Shanghai* 200062, *China*)
(2 *School of Physics and Microelectronics, Shandong University, Jinan* 250100, *China*)

Abstract: The silicon nano-crystalline (nc-Si) film is fabricated on 〈100〉 orientation, 0.01Ω·cm resistivity, and p-type boron-doped silicon wafer by the anodic etching. The microstructure and the orientation of nc-Si are examined by the scanning electron microscopy, transmission electron microscopy, and X-ray diffraction spectroscopy, respectively. The average size of particle is estimated by Raman spectroscopy. The results show that the particle size of nc-Si film is scattered from 10nm to 20nm, the alignment is compact, the orientation is uniform, the expansion of lattice constant is negligible, and mechanical robustness and stability are good. The correlations between film structure and the experiment parameters such as etching time, HF concentration, and etching current density are discussed. As a potential application, efficient field emission is observed from the nc-Si film, and the turn-on field is about 3V/μm at 0.1μA/cm^2 of current density, which is close to carbon nanotube film's.

Key words: nc-Si; anodic etching; uniform orientation; field emission
PACC: 8160C; 8280F
CLC number: TN304 **Document code:** A **Article ID:** 0253-4177(2004)06-0639-06

1 Introduction

Although crystal silicon is an indirect band gap material, the efficient room-temperature photoluminescence (PL) from nano-structure silicon has been observed[1], which has motivated a great number of studies on this material. In particular, the strong PL from porous silicon has caused much research interest. However, poor mechanical robustness and stability of porous silicon shade its application potentially[2]. On the other hand, there are many different methods to form nano-structure silicon with mechanical robustness and stability, such as magnetron sputtering[3], laser-induced chemical vapour deposition[4], Si^+ ion implantation in thermally silica[5,6], and plasma enhanced chemical vapour deposition[7,8]. These methods present a poor control on the orientation of nono-structure silicon.

In this paper, we report a process based on anodic etching for the fabrication of silicon nano-crystalline film with 10~20nm sized particles, compact alignment, uniform orientation, mechanical robustness and stability, negligible lattice constant expansion. This film exhibits efficient property of field emission.

2 Experiment

In the first experiment, the silicon samples used in our experiments were 〈100〉 orientation, 0.01Ω·cm resistivity, 500μm thickness, p-type boron-doped silicon

* Project supported by National Natural Science Foundation of China (Nos. 10374027, 69925409)
Wang Weiming male, was born in 1979, MS candidate. His current interests are semiconductor materials and devices.
Zhu Ziqiang male, was born in 1960, professor, advisor of PhD candidates. His research interests include semiconductor materials and devices.
Received 26 August 2003, revised manuscript received 31 October 2003

wafers. The anodizing solution consists of mixtures of hydrofluoric acid (40wt%), alcohol (99.7wt%), and the deionized water with 1: 2: 1 of volume ratio. The HF concentration is about 10wt%. The silicon sample was anodized in the solution for 60min at a constant current density of 1mA/cm^2. Then, the etched wafer was dipped into hydrogen peroxide (3wt%) for 10min. The morphology and microstructure of the as-prepared sample were examined by scanning electron microscopy (SEM, JEOL-JSM-6700F) and transmission electron microscopy (TEM, JEM200CX). The crystal structure of nc-Si film was characterized by X-ray diffraction (Philips X' PERT-MRD four-crystal XRD). The average size of nc-Si particle was estimated by Raman spectroscopy (Jobin Yvon INFINITY micro). In order to understand the correlations between the experiment parameters and the film characteristics, three groups of experiments were performed with scanning etching time, current density, and HF concentration systemically. The results are shown in Figs. 5, 6, and 7, respectively.

The nc-Si film with 1cm × 1cm in size as a cathode is separated by two Teflon spacers with 200μm from a phosphors/ITO/glass anode. The field light points on fluorescent anode can be recorded, and *I-V* curves are measured, and shown in Fig. 8.

3 Results and discussion

SEM images of the surface and the cross-section of the nc-Si film are show in Figs. 1(a) and (b), respectively. In the low-magnification SEM image of Fig. 1(a), the film presents a homogeneous surface structure; moreover, after the film was dried by rotating and baking, no cracks appear, which indicate that the mechanical robustness and stability of the nc-Si film are good. In the high-magnification SEM images of Fig. 1(a), the nc-Si film is composed of particles with 10~20nm in size and highly compact alignment. In the low-magnification SEM image of Fig. 1 (b), it is found the thickness of the nc-Si film on silicon substrate is about 1.8μm. And the high-magnification image of Fig. 1(b) confirms the ball shape of nc-Si.

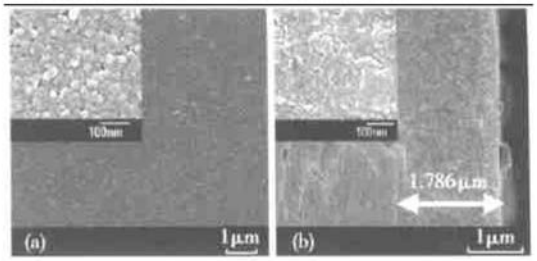

Fig. 1 SEM images of nc-Si film on p type, 0.01 Ω·cm resisitivity, ⟨001⟩ orientation wafer (a) Surface image; (b) Cross-section image

The crystallinity of Si nanoparticles, which were stripped off from the nc-Si film, was evidenced by TEM as shown in Fig. 2. It presents that a Si nanocrystallite has about a 10nm crystalline core and a 2nm oxide outer-layer.

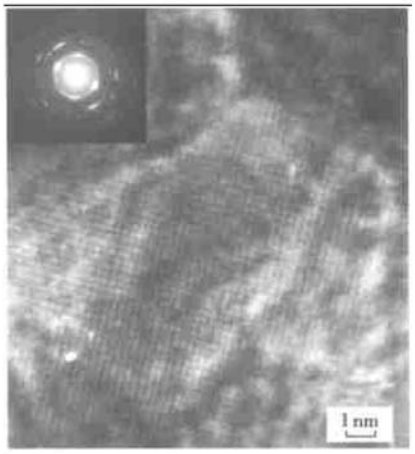

Fig. 2 High-magnification TEM image and the SAED pattern of a nc-Si particle from Fig. 1

Figure 3(a) shows XRD spectroscopy of the porous silicon film about 1.8μm of thickness on p type, 0.01Ω·cm resisitivity, ⟨001⟩ orientation wafer. The peak S comes from the substrate and the peak P from the lattice constant expansion of porous layer. A broad hump D with low intensity is due to the diffuse scattering from the small silicon crystallites[9]. In Fig. 3(b), the XRD of the nc-Si film also about 1.8μm is plotted. Peak S and hump D are the

same as in Fig. 3(a). However, the peak P cannot be observed, which indicates that the expansion of nc-Si's lattice constant is negligible[10]. Furthermore, it is reasonable that the orientation of the nc-Si film is uniform since every particle of the film is etched from the single-crystalline silicon substrate.

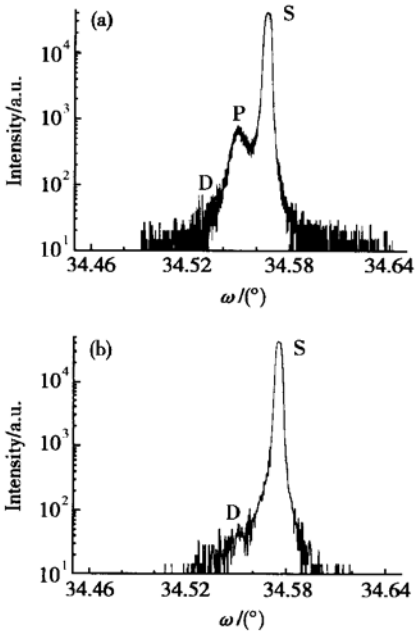

Fig. 3 (a) XRD pattern of the porous silicon film on p type, 0.01Ω·cm resisitivity, 〈001〉 orientation wafer with etching current 4mA/cm^2 for 60min; (b) XRD pattern of the nc-Si film

The Raman spectroscopies of Si substrate and nc-Si film are illustrated in Figs. 4(a) and (b), respectively. The Raman shift indicates that Si nanocrystalline regions cause phonon confinement effects. We estimated the average size of phonon confinement regions based on the theory presented by Campbell and Fauchet[11]. As a result, the average size of particle is about 13nm.

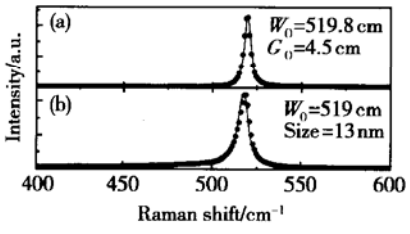

Fig. 4 Raman shifts pattern of Si substrate (a) and the nc-Si film (b)

The results above show that the nc-Si film with 10~20nm particle size, compact alignment, uniform orientation, mechanical robustness and stability, and negligible lattice constant expansion is manifestly different from those of porous silicon film though these films are both formed by anodic etching method.

The dependence of film thickness on etching time is plotted in Fig. 5. The parameters except etching time are the same as those of the first experiment. It is found there is linear relationship between the etching time and the film thickness in the period of first 60min. It can be estimated the etching rate is about 30nm/min.

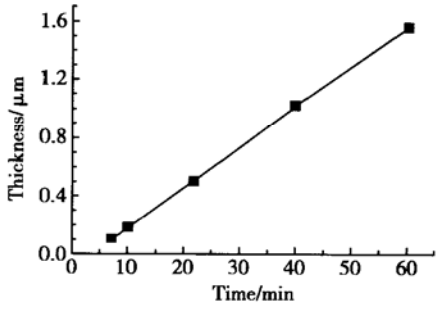

Fig. 5 nc-Si film thickness dependence on etching time

The dependence of film structure on HF concentration is shown in Fig. 6. The parameters except HF concentration are the same as those in the first experiment. The anodizing solution consists of mixtures of hydrofluoric acid (40wt%) and alcohol (99.7wt%). HF concentrations are 6.7wt%, 13.4wt%, and 26.8wt% in Figs. 6(a), (b), and (c), respectively. Figures 6(a) and (b) show a typical porous silicon layer. Figure 6(c) presents a polished surface[12]. All of them are apparently different from the nc-Si film in Fig. 1, which is formed in 10wt% HF concentration. It can be concluded that there is a small parameter window for nc-Si film-fabrication respect to HF concentration around 10wt%.

The dependence of film structure on etching current density is presented in Fig. 7. The parameters except current density are the same as those in the first experiment. The current density is 1, 2, and 8mA/cm^2 in Figs. 7(a), (b), and (c), respectively. Obviously, more and more

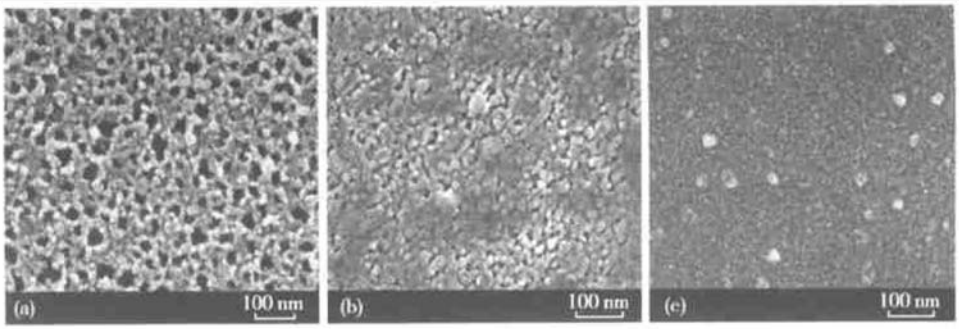

Fig. 6 SEM images of surface structure from p type, 0.01Ω·cm resisitivity, 〈001〉 orientation wafer with 1mA/cm^2 current density for 60min HF concentration: (a) 6.7wt%; (b) 13.4wt%; (c) 26.8wt%

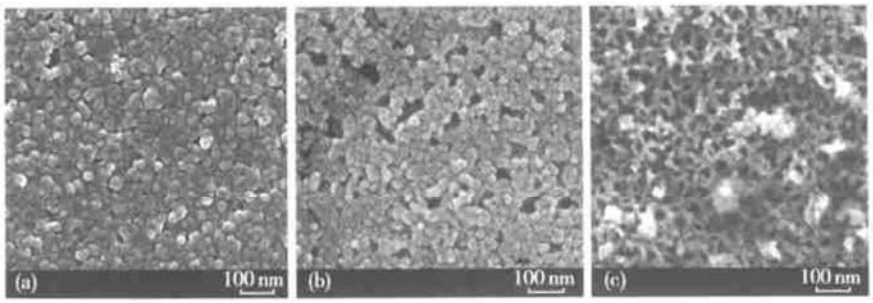

Fig. 7 SEM images of surface structure from p type, 0.01Ω·cm resisitivity, 〈001〉 orientation wafer with 10wt% HF concentration for 60min Current density: (a) 1mA/cm^2; (b) 2mA/cm^2; (c) 8mA/cm^2

pores are formed with increase of current density. The film structure is very sensitive to the etching current density. In this group experiments, 1mA/cm^2 is a typical current value. Results show that it is difficult to form the compact alignment nc-Si film by a large current density.

The curve of electron emission current density versus electric field from nc-Si film is shown in Fig. 8. The inset shows the corresponding Fowler-Nordheim plots. First electrons are injected from the silicon substrate into nc-Si film without scattering due to the small size of the dots. The electric field is applied mainly within SiO_2 regions covering the nc-Si. Thus the electrons from nc-Si are accelerated into the vacuum by the electric field, allowing ballistic transport through subsequent nc-Si layers. When the grain size decreases, the turn-on field of the samples decreases. However, the threshold field of the samples increases with decreasing of the grain size, presumably due to the field screening effect caused by high density of the

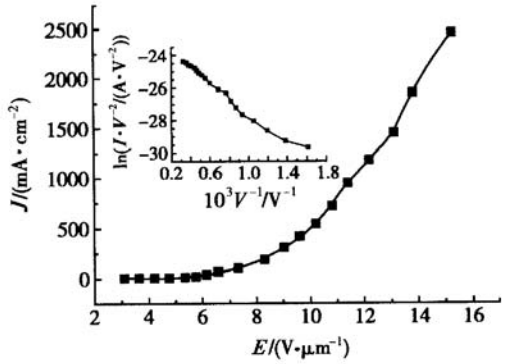

Fig. 8 Emission current density versus electric field curves of the nc-Si film from Fig. 1 The inset shows Fowler-Nordheim plots correspondingly.

grain[13]. The impact of boron dope concentration on the turn-on field has been studied systematically. It is obvious that the FN plots for the samples follow the linear behavior. These measurements suggest that a field-induced tunnel process occurs during the electron emission. It can be found that the turn-on field is about 3V/μm at 0.1μA/

cm^2 of current density and $1mA/cm^2$ of current density, which is required for application to flat panel display.

4 Conclusions

In summary, a nc-Si film having 10~ 20nm of particle size, compact alignment, uniform orientation, negligible lattice constant expansion, and mechanical robustness is fabricated by anodic etching in HF and ethanol mixture solution with a small current density. The nc-Si film thickness is linear to etching time with a 30nm/min forming rate in first 60min. There is a small parameter window of HF concentration around 10wt% in fabrication of the nc-Si film. The film structure is very sensitive to current density. $1mA/cm^2$ is a typical value adopted in our experiments. It is a simple method to form the compact alignment and uniform orientation silicon nano-crystalline film, which can be used for nano-sized efficient field emission devices.

Acknowledgments The authors are grateful to Professor Tang Xiongxin in Shanghai Institute of Microsystem and Information Technology, The Chinese Academy of Sciences for offer of the XRD measurements.

References

[1] Koshida N, Koyama H. Visible electroluminesecence from porous silicon. Appl Phys Lett, 1992, 60(3): 347

[2] Bisi O, Ossicini S, Pavesi L. Porous silicon: a quantum sponge structure for silicon based optoelectronics. Surface Science Reports, 2000, 38: 1

[3] Charvet S, Madelon R, Gourbilleau F, et al. Spectroscopic ellipsometry analyses of sputtered Si/SiO_2 nanostructures. J Appl Phys, 1999, 85: 4032

[4] Chiussi S, Serra1 C, Serra1 J, et al. Laser crystallisation of poly-SiGe for microbolometers. Appl Surf Sci, 2002, 186: 166

[5] Rebohle L, Von Borany J, Yankov R A, et al. Room-temperature, short-wavelength (400~ 500nm) photoluminescence from silicon-implanted silicon dioxide films. Appl Phys Lett, 1996, 68: 2410

[6] Liao L S, Bao X M, Zheng X Q, et al. Blue luminescence from Si^+-implanted SiO_2 films thermally grown on crystalline silicon. Appl Phys Lett, 1996, 68: 850

[7] Kansagawa Y, Kageyama T, Takeoka S, et al. Size-dependent near-infrared otoluminescence spectra of Si nanocrystals embedded in SiO_2 matrices. Solid State Commun, 1997, 102: 533

[8] Peng Yingcai, Liu Ming, He Yuliang, et al. Conductive properties on doping nanometer silicon thin films. Chinese Journal of Semiconductors, 2000, 21(3): 308(in Chinese) [彭英才, 刘明, 何宇亮, 等. 掺杂 nc-Si: H 膜的电导特性. 半导体学报, 2000, 21(3): 308]

[9] Bellet D, Doline G, Ligeon M, et al. Studies of coherent and diffuse X-ray scattering by porous silicon. J Appl Phys, 1992, 71: 145

[10] Bellet D, Doline G. X-ray diffraction studies of porous silicon. Thin Solid Film, 1996, 276: 1

[11] Makino T, Yamada Y, Suzuki N, et al. Anealing effects on structures and optical properties fo silicon nanostructured films prepared by pulsed-laser ablation in inert backgroud gas. J Appl Phys, 2001, 90(10): 5075

[12] Föll H, Christophersen M, Carstensen J, et al. Formation and application of porous silicon. Mater Sci Eng R, 2002, 39: 93

[13] Koshida N, Sheng X, Komoda T. Quasiballistic electron emission from porous silicon diodes. Appl Surf Sci, 1999, 146: 371

单晶纳米硅薄膜的制备及其场发射特性*

王伟明[1] 郁 可[1,2] 丁艳芳[1] 李 琼[1] 朱自强[1]

(1 华东师范大学信息学院 电子系, 上海 200062)

(2 山东大学物理与微电子学院, 济南 250100)

摘要: 用小电流、特殊配比溶液的电化学阳极腐蚀法在 p 型、〈100〉晶向、0.01Ω·cm 电阻率的硅片制备了大面积纳米硅薄膜. 通过 SEM, TEM, XRD 和 Raman 光谱技术分析薄膜颗粒的微细结构. 实验结果表明该纳米硅薄膜由直径为 10~ 20nm, 晶向一致的颗粒紧密排列而成, 具有很好的物理化学稳定性. 系统研究了薄膜结构特征和溶液配比、腐蚀时间、腐蚀电流密度的关系. 成功观察到该薄膜具有很好的场发射特性, 在 0.1μA/cm^2 电流密度下, 其开启电场为 3V/μm, 接近碳纳米管的 1.1V/μm.

关键词: 单晶纳米硅; 阳极腐蚀; 晶向一致; 场发射

PACC: 8160C; 8280F

中图分类号: TN304 **文献标识码**: A **文章编号**: 0253-4177(2004)06-0639-06

* 国家自然科学基金资助项目(批准号: 10374027, 69925409)

王伟明 男, 1979 年出生, 硕士研究生, 主要研究方向为硅基半导体材料和器件.

朱自强 男, 1960 年出生, 教授, 博士生导师, 从事半导体材料和器件研究.

2003-08-26 收到, 2003-10-31 定稿