ELECTROCHEMICAL FORMATION OF POROUS SILICON

Qian Bidong Cai Shengmin *

(Department of Chemistry, Peking University, Beijing 100871, China)

He Yongtian He Guoshan Zhang Shulin

(Department of Physics, Peking University, Beijing 100871, China)

Keywords: Porous silicon, Electrochemistry, Photoluminescence spectrum, Raman spectrum

1 Introduction

Porous silicon is the material obtained by anodic oxidation of monocrystalline silicon in concentrated hydrofluoric acid which was first reported by Uhlir^[1] and Turner^[2]. Over the past three decades, a great deal of studies have been devoted to its characterisation and measurements of various properties^[3-8] mostly because of its promising application in the silicon-on-insulator(SOI) technologies. Quite recently, photoluminescence(PL) in the near-infrared^[9,10] and Electroluminescence(EL) in the visible region^[11] have been reported and attributed to quantum confinement effects in the free standing silicon quantum wires formed in the porous silicon. The measurements of the transmission for monochromatic light^[12] and other optical properties^[13] of porous silicon supported the existence of the quantum size effect in it. This discovery makes it possible to fabricate efficient light emitting devices. In this short communication we report for the first time a Raman spectrum of porous silicon layer grown on *p*-type non-degenerated silicon substrate, lending an additional evidence for the quantum confinement effect in the porous silicon.

2 Experimental

Silicon wafers used in this experiment were (100) *p*-type single crystals(10—15 cm in resistivity) with a mirror like surface. Prior to anodisation, the wafers were cleaned and a thin Al film was deposited on the back side in order to form an ohmic contact. Nonanodized parts of the wafers were then covered with wax. Anodisation

Received 1992-02-19, Revised 1992-03-30. Supported by the National Natural Science Foundation of China; *To whom correspondence should be addressed

was carried out in certain mass fraction HF solution containing some ethanol under constant current density supplied by a current power (DH 1719 DC Power Supply, China). The employed hydrofluoric acid and ethanol are analytically pure reagents, and water is deionized. Anodisation was performed at room temperature.

Photoluminescence and Raman spectra were measured by a Spex-1403 double monochromator with a cooled PMT and a conventional photocounting electronics in a near backscattering configuration at room temperature. No analyser was used. The spectral resolution of the instrument is 2.5 cm^{-1} and the scan step is 1 cm^{-1} .

Fig.1 Photoluminescence spectrum of porous silicon grown on *p*-type non-degenerated silicon substrate upon electrochemical anodic dissolution in 0.24 HF solution at $20\text{ mA}\cdot\text{cm}^{-2}$ for 8 min. Excitation source is 488 nm in wave length

Fig.2 Raman spectrum of porous silicon grown on *p*-type non-degenerated silicon substrate upon electrochemical anodic dissolution in 0.24 HF solution at $20\text{ mA}\cdot\text{cm}^{-2}$ for 8 min. Argon-ion laser operated at 457.9 nm

3 Results

3.1 Photoluminescence spectrum of typical porous silicon is shown in Fig.1. Since the band-gap of silicon is 1.09 eV ^[14], an intense photoluminescence peak appears near 1.86 eV , it means that the porous silicon has been formed and is attributed to the quantum confinement effect existing in the porous silicon structure^[9-13].

3.2 As-prepared porous silicon layers show different colors, changing from poor blue to orange-red under the treatment in HF acid from 0.21 to 0.40 at $50\text{ mA}\cdot\text{cm}^{-2}$ for 8 min. The porous silicon layer formed at low HF concentration is easily crazed and seems of low mechanical stability in the ambient air.

3.3 As-formed porous silicon layer exhibits more chemical activity than that of Si substrate. When the porous silicon was kept in water, hydrogen gas evolved on it in accompanying with the gradual subtraction of the porous silicon layer.

3.4 Raman spectrum of typical porous silicon is shown in Fig.2. By comparing with the Raman spectrum of the silicon substrate, we have assigned the sharp peak

occurring at 520 cm^{-1} to silicon substrate, but the weak peak at 509 cm^{-1} with a broad tail extending to the frequency lower than 509 cm^{-1} to the quantum wire effects of the porous silicon layer instead of amorphous Si component. All these findings are quite different from the previous results^[15].

A detailed theoretical analysis is in progress and will be published elsewhere.

REFERENCES

- 1 Uhler A. *Bell System Tech. J.*, 1956, 35:333
- 2 Turner D R. *J. Electrochem. Soc.*, 1958, 105:402
- 3 Herino R, Bomchil G, Barla K, Bertrand C. *J. Electrochem. Soc.*, 1987, 134:1994
- 4 Beale M I J, Uren J J, Chew N G, *et al. J. Cryst. Growth*, 1985, 73:362
- 5 Bomchil G, Halimaoui A, Herino R. *Microelectron. Eng.*, 1988, 8:293
- 6 Toshimichi Ito, Yoshihisa Kato. *Oyo Butsuri*, 1988, 37(11):1710
- 7 Sylvia S Tzao. *Mater. Res. Soc. Symp. Proc.*, 1988, 107:426
- 8 Bomchil G, Halimaoui A, Herino R. *Appl. Surf. Sci.*, 1989, 41/42:602
- 9 Canham L T. *Appl. Phys. Lett.*, 1990, 57(10):1046
- 10 Biesy A, Vial J C, Gaspard F, *et al. Surf. Sci.*, 1991, 254:195
- 11 Halimaoui A, Oules C, Bomchil G. *Appl. Phys. Lett.*, 1991, 58(3):304
- 12 Lehmann V, Gosele U. *Appl. Phys. Lett.*, 1991, 58(8):856
- 13 Gardelis S, Rimmer J S, Dawson P, Hamiton, *et al. Appl. Phys. Lett.*, 1991, 59(17):2118
- 14 Huang Kun, Han Ruqi, *Physics Fundament of Semiconductor*, Beijing: Science Press, 1979:50
- 15 Goodes S R, Jenkins T E, Beale M I J, *et al. Semicond. Sci. Technol.*, 1988, 3:438

多孔硅的电化学制备

钱必东 蔡生民*

侯永田 何国山 张树霖

(北京大学化学系, 北京 100871)

(北京大学物理系)

摘要 单晶硅在氢氟酸溶液中阳极氧化可制得多孔硅, 多孔硅是一种以新形态存在的硅, 与单晶硅相比, 它表现出独特的物理性质和化学活性。荧光光谱峰的蓝移表明, 在 p -型低掺杂衬底硅上形成的多孔硅中存在量子尺寸效应, 新近获得的 Raman 光谱也证实了这一点。

关键词: 多孔硅 电化学 荧光光谱 Raman光谱