Title	Application of Porous Silicon to Electron Devices
Author(s)	Harada, Hiroshi; Hosono, Akihiko; Okuda, Soichiro et al.
Citation	電気材料技術雑誌. 1998, 7, p. 35-40
Version Type	VoR
URL	https://hdl.handle.net/11094/81571
rights	
Note	

Application of Porous Silicon to Electron Devices

Hiroshi HARADA[1], Akihiko HOSONO[2], Soichiro OKUDA[2],
Kazuya TADA[3], Tooru SONODA[3] and Katsumi YOSHINO[3]

[1]Faculty of Science and Engineering, Shimane University
1060 Nishi-Kawatsu, Matsue, Shimane 690-8504

[2]Advanced Technology R & D Center, Mitsubishi Electric Corporation
8-1-1 Tsukaguchi-honmachi, Amagasaki, Hyogo 661-8661

[3]Department of Electronic Engineering, Graduate School of Engineering,
Osaka University
2-1 Yamada-oka, Suita, Osaka 565-0871

This paper describes novel approaches to fabricate electron devices using porous silicon. It is proved that pyramidal structured porous silicon exhibits the light emitting property, and also the field emitter of an anodized silicon tip shows the superior electron emitting characteristic. New process for both light and electron emitting devices is also proposed.

KEYWORDS : porous silicon, light emitting diode, EL, field emission, cold cathode, field emitter

多孔質シリコンの電子デバイスへの応用

原田曠嗣[1]、細野彰彦[2]、奥田荘一郎[2]、多田和也[3]、園田　通[3]、吉野勝美[3]

[1]島根大学総合理工学部
〒690-8504 島根県松江市西川津町1060

[2]三菱電機㈱先端技術総合研究所
〒661-8661 兵庫県尼崎市塚口本町８－１－１

[3]大阪大学大学院工学研究科電子工学専攻
〒565-0871 大阪府吹田市山田丘２－１

多孔質シリコンを用いた新規な構造の電子デバイスについて述べる。ピラミッド構造の多孔質シリコンと導電性高分子を用いたヘテロ接合が発光ダイオード特性を示すことを見出した。またシリコンを用いたフィールドエミッタの先端を陽極化成し多孔質化することにより、エミッション特性が向上することを示す。さらに、発光及び電子放出素子の両者に適した新しい製造プロセスを提案する。

1. Introduction

Since the first report of visible photoluminescence (PL) from anodized porous silicon[1)], many studies have been done extensively. But the PL is unstable and the physical mechanism of the PL is still controversial. It seems that the reason stems from poor control of surface states in porous silicon. Because all of those studies have been carried out by using sponge-like porous silicon with nanometer-size pores which spread over porous silicon, it is very difficult to control whole surface states of all pores. For the application of porous silicon to the light emitting device, it is desirable that the structure of porous silicon is susceptible of accurate surface state control. From such point of view, it is considered that the silicon surface with simple morphology is more suitable than that with the pore. We modified conventional porous silicon to the pyramidal structure, and expected that the apexes and edges among edges of the pyramids acted as quantum dots and wires, respectively. As described in chapter 2, our expectation was confirmed by the observation of the electroluminescence (EL) originated from pyramidal structured porous silicon incorporated to the heterojunction.

On the other hand, it is supposed that requirement for control of surface states in porous silicon is not so severe if its device is operated in vacuum condition, because contamination from atmosphere is very little. The field emitter using silicon is widely examined as the electron emitting device, and the major concerns are increase of emission current and stable operation. According to Fowler-Nordheim theory[2] for field emission, increase of the emission site, decrease of radius at the emission site and reduction of the work function are substantial to increase the emission current. The conventional silicon field emitter is usually fabricated by using the microfabrication technology. We expected that pores produced by an anodization on the conventioal silicon tip of the field emitter result in formation of subsidiary tips on the initial tip, which may contribute to both increase of the emission site and decrease of radius at the emission site. As shown in chapter 3, test devices were fabricated and the expectation was confirmed by the observation of increase of the emission current.

In chapter 4, we propose that pyramidal porous silicon followed by an additional anodization to form pores on it may be used for both light and electron emitting devices. The shape of the proposed structure is obtained without the expensive microfabrication technology.

2. Light emitting device[1]

The porous silicon/conducting polymer heterojunction was fabricated as follows. An n-type (100) silicon (3-6Ω・cm) back-metallized with gold was anodized in a 1:3:4 mixture of HF, H_2O and C_2H_5OH at a current density of 75 mA/cm² for 3 min under light irradiation. The cross-sectional view of the resulted porous silicon layer is shown in Fig.1, in which many pores exist. In case of a conventional EL, a thin metal film is successively evaporated on it. In this study, the porous layer was etched with a 1:7:17 mixture of HF, HNO_3 and CH_3COOH for 3 min. Then the silicon surface became the pyramidal structure as seen in Fig.2. This structure is due to the interface structure between the original porous silicon layer and substrate silicon. Apexes of pyramids and edges among apexes were expected to act as quantum dots and quantum wires, respectively. A chloroform solution of poly (2-methoxy-5-dodecyloxy-1, 4-phenylene vinylene) (MDDO-PPV) was spin coated onto the pyramidal porous silicon.

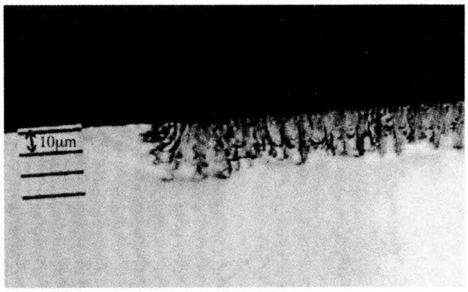


Fig.1　Micrograph of porous silicon after anodization.

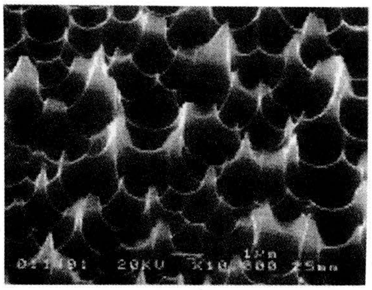


Fig.2　Micrograph of pyramidal porous silicon obtained by etching anodized porous silicon.

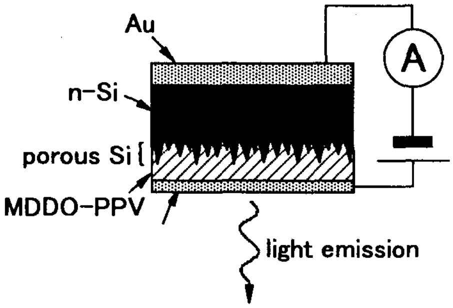


Fig.3 Schematic structure of the heterojunction of Au/pyramidal porous silicon/MDDO-PPV/Au.

MDDO-PPV works as both a conducting layer and a planarizing material for the pyramidal surface. Then the half-transparent gold film was evaporated. The schematic structure of the resulted heterojunction is shown in Fig.3. Size of the active area was 3x3 ㎜^{2}.

Electrical and optical characteristics of this device were measured in vacuum at room temperature. Definition of forward bias is that MDDO-PPV is positively biased as shown in Fig.4. As shown in Fig.4 of the current-voltage characteristic, the device showed a diode characteristic with a rectification ratio of more than 10^2, as seen in the inset.

Above +6V, a red emission was observed easily with the naked eye. Emission intensity versus applied voltage is also shown in Fig.4. A light emission spectrum of the device is shown in Fig.5 with a solid line. In this spectrum, a broad peak was observed at around 660 nm. The observed spectrum is similar to that of EL devices with conventional porous silicon. In Fig.5, the light emission spectrum of the Mg-In/MDDO-PPV/ITO is also shown with a dotted line for reference to clarify that EL of our device originates from pyramidal porous silicon and not from MDDO-PPV.

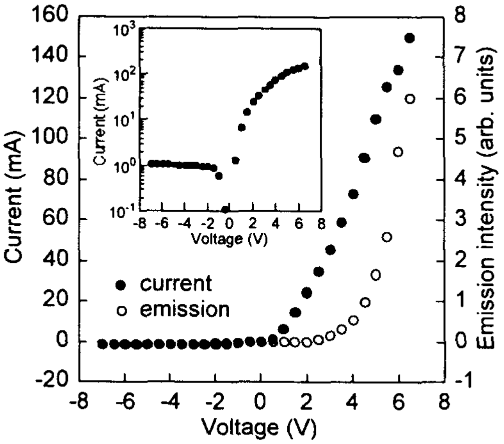


Fig.4 Current-voltage and light emission intensity-voltage characteristics of a Au/pyramidal porous silicon/MDDO-PPV/Au structure. Inset shows the semi-logarithmic plot of the current-voltage characteristic.

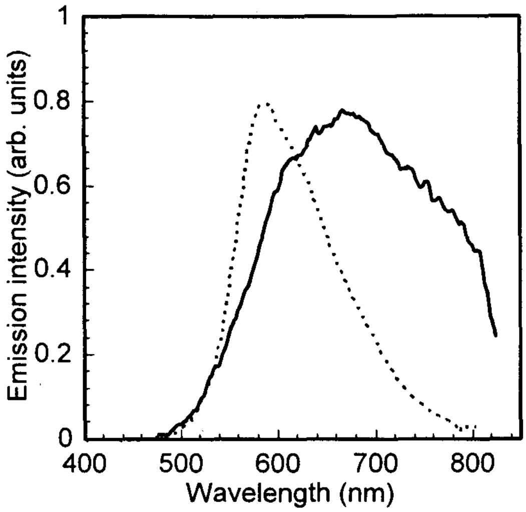


Fig.5 Light emission spectra of Au/pyramidal porous silicon/MDDO-PPV/Au (solid line) and Mg-In/MDDO-PPV/ITO (dotted line) structures.

Based on the above mentioned data, it is concluded that pyramidal porous silicon is a promising candidate for the light emitting device.

3. Electron emitting device4)

The structure of the conventional field emitter using silicon is shown in Fig.6. Fig.6 (a) is a micrograph of a scanning electron microscope (SEM) and Fig.6 (b) is its schema. The sharp silicon tip was fabricated by using the microfabrication technology, which was widely applied to the integrated circuit. Then we modified the surface of the silicon tip by an anodization and or tungsten deposition, and fabricated several test devices. These schematic structures based

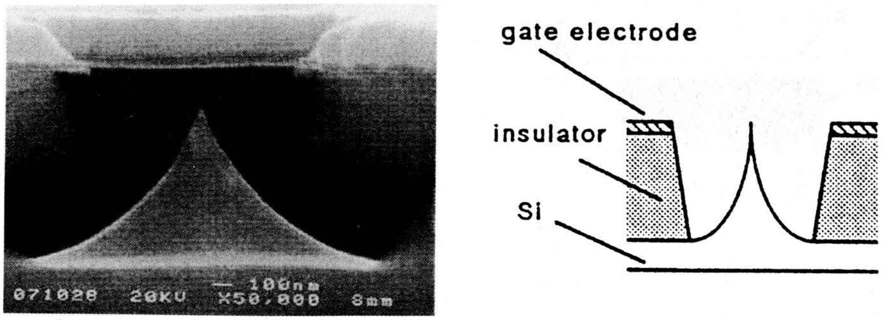


Fig.6　Cross-sectional view of conventional field emitter using silicon fabricated by the microfabrication technology.

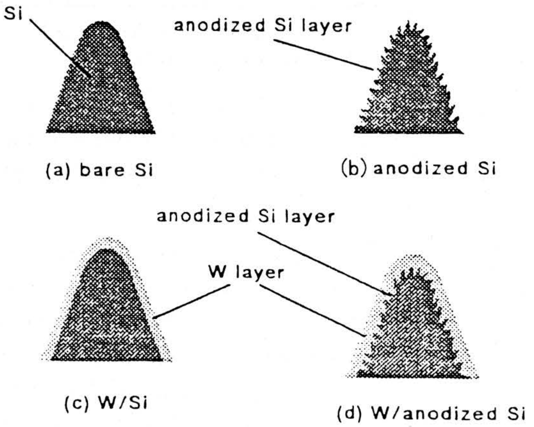


Fig.7　Schematic tip structures of various field emitter.

on SEM micrographs are shown in Fig.7. Fig.7 (a) is a conventional tip, hereafter called device (a). In case of Fig.7 (b) (device (b)), the surface of a tip was anodized to form porous silicon for the purpose of both increase of the emission site and decrease of radius at the emission site. Thickness of the porous layer measured at separate plain position was 80 nm. In case of Fig.7 (c) (device (c)), the surface of a tip was covered by tungsten for the purpose of reduction of the work function. Reported values[5] of the work functions of bulk silicon and tungsten are 4.80 and 4.55 eV, respectively. Tungsten was deposited by sputtering and its thickness was 6 nm. In case of Fig.7 (d) (device (d)), an anodization of a tip was followed by tungsten sputtering for the purpose of synergetic effect. Thicknesses of the porous layer and tungsten were the same as ones mentioned above.

Emission currents of these devices were measured in vacuum of $1.3\mathrm{x}10^{-6}$ Pa. Circuitry arrangement for the measurement is shown in Fig.8. The emission current from a silicon tip flowed into both the anode plate and the gate electrode. Because the gate current Ig was

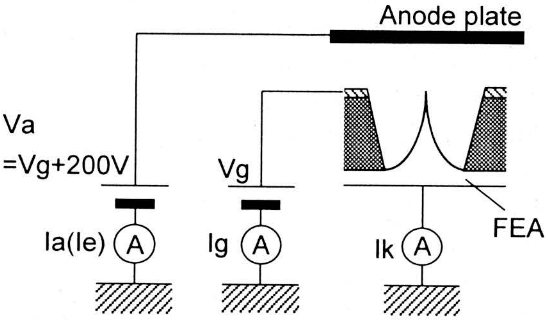


Fig.8　Circuitry arrangement for the emission current measurement.

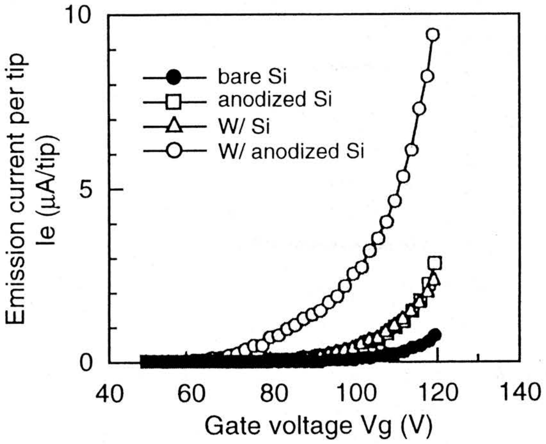


Fig.9　Emission characteristics of field emitters with various tip structures.

negligible in this study, the emission current Ie was to be equal to the anode current Ia.

Observed emission currents versus gate voltage Vg are shown in Fig.9. At Vg=120 V, Ies of devices (a), (b), (c) and (d) were 0.7, 2.8, 2.4 and 9.5 μA, respectively. Ie of device (b), device (c) and device (d) were about 4 times, 3.4 times and 14 times larger than that of device (a), respectively. The value of 14 is nearly equal to 13.6 (=4x3.4), which suggests that synergetic effect of devices (b) and (c) occurred at the device (d).

It is confirmed that that the modification of the surface of the field emitter tip is effective to increase the emission current.

4. Proposal of novel process

The shape of pyramidal porous silicon is very similar to that of the field emitter fabricated by the microfabrication technology, as seen in Fig.2 and Fig.6. Therefore pyramidal porous silicon may be used for the electron emitting device as well as the light emitting device. An additional anodic process after the process for pyramidal porous silicon may result in the structure similar to the device (b) in chapter 3.

The process is very simple and does not require the expensive microfabrication technology.

5. Conclusion

Applications of porous silicon to both the light and the electron emitting devices are described. The new anodic process, which is useful to both the light and the electron emitting devices, is also proposed.

References

1) L.T.Canham : Appl. Phys. Lett., Vol.57, No.10, pp.1046- 1048 (1990).

2) I.Brodie and P.R.Schwoebel : Proc. IEEE, Vol.82, No.7, pp. 1006-1034 (1994).

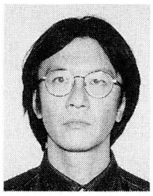
3) K.Tada, M.Hamaguchi, A.Hosono, S.Yura, H.Harada and K. Yoshino : Jpn. J. Appl. Phys., Vol.36, No.4A, pp.L418-L420 (1997).

4) A.Hosono, S.Yura, K.Morikawa, S.Kawabuchi, T.Okumura, S.Horibata, S.Okuda, H.Harada and M.Takai : The Third International Display Workshops, Proceedings of The Third International Display Workshops, Vol.2, pp.531-532 (1996).

5) A.Koma, K.Yagi, M.Tsukada and M.Aono : Surface Physics Engineering Handbook, Tokyo, Maruzen, p.536 (1987) (in Japanese).

（　　年　月　日受理）

Hiroshi Harada was born in Okayama on June 4, 1941. He received BE, ME and PhD degrees in Electrical Engineering from Osaka University in 1964, 1966 and 1972, respectively. In 1969, he joined Mitsubishi Electric Corp. and engaged in research, development and production of LSI and CRT. From 1974 to 1975, he was a visiting scholar at Purdue University on leave from Mitsubishi. In 1998, he has moved to Shimane University and is engaged in research of semiconductor engineering. He is a member of the Institute of Electronics, Information and Communication Engineers of Japan and the Japan Society of Applied Physics.



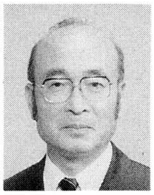
Akihiko Hosono was born in Kumamoto Prefecture, Japan, on Feb. 12, 1962. He received the B.E., the M.E. and the Ph. D. degrees in Engineering from Tohoku University, Japan, in 1985, in 1987, and in 1990, respectively. Since 1991 he has been working in the R & D Center, Mitsubishi Electric Corporation, where he has been studying display devices.

Soichiro Okuda was born in Ooita Prefecture, Japan, on April 11, 1949. He received the B.E. and the M.E. degrees in applied mathematics from the University of Tokyo, Japan, in 1973 and in 1975, respectively. He received the Ph.D. degree in Electrical Engineering from the University of Tokyo in 1990. Since 1975 he has been working in the R & D Center, Mitsubishi Electric Corporation, where he studied plasma physics, electomagnetic field analysis, particle accelerators, cathode ray tubes, and display devices. He is now the Deputy Manager, Display Technology Department, Advanced Technology R & D Center, Mitsubishi Electric Corporation. He is a member of the Institute of

Electrical Engineers of Japan, the Institute of Image Information and Television Engineers, The Society for Information Display.

Kazuya Tada graduated the Department of Electrical Engineering, Nara National College of Technology, Japan in 1992, and received B.S., M.S. and Ph.D. degrees in Electronic Engineering from Faculty of Engineering, Osaka University, Japan in 1994, 1996 and 1998, respectively. In 1998, he joined the faculty of Department of Electrical Engineering, Himeji Institute of Technology, where he is currently a research associate. His research interests are in the electronic and optical properties of conducting polymers and their composites, and application of them to electronic devices such as LEDs, photocells and FETs. He is a member of the Institute of Electrical Engineers of Japan and the Physical Society of Japan.

Tooru SONODA was born in Osaka on October 3, 1975. He graduated from Department of Electronic Engineering, Osaka University in 1998. He is now Master course student of Department of Electronic Engineering, Graduate School of Engineering, Osaka University and now studying conducting polymer-inorganic composite and layered systems.



Katsumi Yoshino was born in Shimane on December 10, 1941. He graduated in 1964 from Department of Electrical Engineering, Faculty of Engineering, Osaka University, where he obtained a Doctor of Engineering Degree in 1969. In that year, he became an Research Associate in Electrical Engineering, Osaka University. He was promoted to Assistant Professor in 1972 and Associate Professor in 1978. In 1988, he became a Professor in Electronic Engineering. He is also now Professor of Tohoku University. He has been engaged in research on organic functional materials such as conducting polymers. He received an Applied Physics Society Award , Osaka Scientific Award, Book of Year Award and Outstanding Achievement Award from the Institute of Electrical Engineers of Japan in 1981, 1990, 1997 and 1998, respectively. He authored or co-authored more than 32 books. He is a member of the Institute of Electrical Engineers in Japan, Japan Physical Society, Applied Physical Society, and Polymer Society.