Sains Malaysiana 40(1)(2011): 5–8

Characterization of Ge Nanostructures Embedded Inside Porous Silicon for Photonics Application

(Pencirian Nanostruktur Ge Terbenam di dalam Silikon Berliang untuk Aplikasi Fotonik)

A.F. ABD RAHIM*, M.R. HASHIM & N.K. ALI

ABSTRACT

In this work we prepared germanium nanostructures by means of filling the material inside porous silicon (PS) using conventional and cost effective technique, thermal evaporator. The PS acts as patterned substrate. It was prepared by anodization of silicon wafer in ethanoic hydrofluoric acid (HF). A Ge layer was then deposited onto the PS by thermal evaporation. This was followed by deposition of Si layer by thermal evaporation and anneal at 650°C for 30 min. The process was completed by Ni metal deposition using thermal evaporator followed by metal annealing of 400°C for 10 min to form metal semiconductor metal (MSM) photodetector. Structural analysis of the samples was performed using energy dispersive x-ray analysis (EDX), scanning electron microscope (SEM), X-ray diffraction (XRD) and Raman spectroscopy (RS). EDX spectrum suggests the presence of Ge inside the pores structure. Raman spectrum showed that good crystalline structure of Ge can be produced inside silicon pores with a phase with the diamond structure by (111), (220) and (400) reflections. Finally current-voltage (I-V) measurement of the MSM photodetector was carried out and showed lower dark currents compared to that of Si control device. Interestingly the device showed enhanced current gain compared to Si device which can be associated with the presence of Ge nanostructures in the porous silicon

Keywords: Ge; porous; Raman spectroscopy; silicon thermal evaporation

ABSTRAK

Di dalam kajian ini nanostruktur Ge disediakan dengan mengisi Ge ke dalam liang Si menggunakan kaedah konvensional dan kos efektif iaitu penyejatan haba. Si berliang bertindak sebagai substrat yang beracuan. Si berliang disediakan melalui proses anodisasi wafer Si di dalam larutan asid HF bersama etanol. Lapisan Ge diendapkan di atas liang Si ini menggunakan teknik penyejatan haba. Kemudian proses diteruskan dengan endapan lapisan Si menggunakan teknik yang sama dan dipanaskan pada suhu 650°C selama 30 min. Proses ini disempurnakan dengan mengendap logam Ni sebagai sesentuh menggunakan teknik penyejatan haba dan diikuti dengan pemanasan logam sentuh pada suhu 400°C selama 10 min bagi membina pengesan cahaya logam-separuh pengalir-logam. Analisis struktur bahan kajian dilaksanakan menggunakan teknik EDX, SEM, XRD dan spektroskopi Raman. Spektrum EDX mencadangkan kehadiran Ge di dalam struktur liang Si. Spektrum Raman menunjukkan struktur hablur yang baik bagi Ge dapat dihasilkan di dalam liang Si dengan kehadiran fasa berbentuk intan dengan pantulan pada satah (111), (200) dan (400). Akhirnya pengukuran arus voltan untuk pengesan cahaya yang dibina menunjukkan arus gelap yang rendah berbanding arus gelap peranti kawalan Si. Menariknya, peranti pengesan cahaya ini menunjukkan peningkatan gandaan arus berbanding peranti Si dan ini boleh dikaitkan dengan kehadiran struktur nano Ge di dalam liang Si.

Kata kunci: Ge; penyejatan haba; Si berliang; spektroskopi raman

INTRODUCTION

Ge nanostructures have attracted world-wide attention due to their interesting quantum effects both in electronics and photonics application (Jin et al. 2006). A variety of techniques have been employed to grow such structures, the most popular one is self-assembled growth nanometer islands in highly strained system using sophisticated Molecular Beam Epitaxy (MBE) or Low Pressure Chemical Vapor Deposition (LPCVD) techniques (Cheng et al. 2008; Chen et al. 2004; Krasil'nik et al. 2002; Schittenhelm et al. 1995). However these techniques require sophisticated machine and the cost is very high. Covering or filling the pore network of a PS layer to produce a silicon nanocomposite is a promising process for new potential optoelectronics applications. Recent work has shown that the presence of Ge islands ranging from few nanometers to a micron on Si substrates and underneath the metal contact enhanced the photo detection of Metal Semiconductor Metal (MSM) photodetector (Baharin & Hashim 2007). The Ge islands were grown using conventional thermal evaporator.

This triggers the idea that inexpensive technique such as thermal evaporator could be utilized to grow Si/SiGe based nanocrystalline structure for optoelectronic applications. The idea of this work is to utilize the conventional technique (thermal evaporation) to grow Ge nanostructres on low cost Si patterned substrate, which is porous silicon.

EXPERIMENTAL PROCEDURES

An n-type <100>-oriented silicon wafer with a resistivity of 1-10 Ωcm was used to fabricate PS substrates. The substrates were cleaned in a wet chemical etch process, using RCA cleaning method. After cleaning, the sample was anodized at a current density of 10 mA/cm^2 in an HF-ethanol solution (HF:C_2H_5OH=1:4) for 20 min to form PS. The anodization was carried out under illumination of a 100 W incandescent white light, 20 cm away from the samples. A Ge with 99.999% purity commercial source was then deposited onto the PS by thermal evaporation in a vacuum condition with a background pressure of 3.4×10^{-5} torr. This is followed by deposition of Si capping layer by the same method. After that the sample was annealed at 650°C for 30 min. The process was completed by Ni metal deposition using thermal evaporator to form MSM structure followed by metal annealing of 400°C for 10 min. Structural analysis of the sample was performed using energy dispersive x-ray analysis (EDX), scanning electron microscope (SEM), X-ray diffraction (XRD) and Raman spectroscopy (RS). This Ge inside PS with Si capping layer is referred as Si/Ge/PS throughout the text.

RESULTS AND DISCUSSION

Figure 1(a) shows SEM image of the Si/Ge/PS formed using the conventional thermal evaporator system. A uniform circular network distribution of pores is observed with size of 100 nm to 2.5 μm. Also observed are clusters with near spherical shape clinging around the pores believed to be Ge or GeO_2. The EDX spectrum in Figure 1(b) suggests the presence of Ge or GeO_2 on and inside the pore structure. Interestingly the Ge peak is quite prominent, suggesting that it cannot come from the scattered clusters on the porous structure, but instead they could come from those located or embedded in the porous. Figure 2(a) shows Raman spectrum of PS and Si/Ge/PS samples. The PS spectrum shows a strong peak at 515 cm^{-1} which show a broader and shifted to lower frequency compared to standard spectrum peak of crystalline Si(c-Si) sub at 520 cm^{-1} (Lei et al. 2005). The stronger Raman intensity of PS is due to change of its optical constant (Yang et al. 1994). Similarly the Si/Ge/PS sample shows a peak at 515 cm^{-1} but with lower intensity compared with that of PS probably due to the Si emission can be partially covered by the Ge inside the porous. Besides that a sharp Raman peak at 298 cm^{-1} is observed which reflects Raman active transverse optical mode (TO) of the introduced Ge which indicate the growth of Ge microcrystals with good crystallinity after annealing (Liu et al. 1998; Maeda et al. 1991). No evidence of Si-Ge alloy mode is observed between 300 cm^{-1} and 520 cm^{-1} indicating that intermixing at Ge/Si interfaces is small. The Raman spectrum showed that good crystalline structure of the Ge can be produced inside silicon pores.

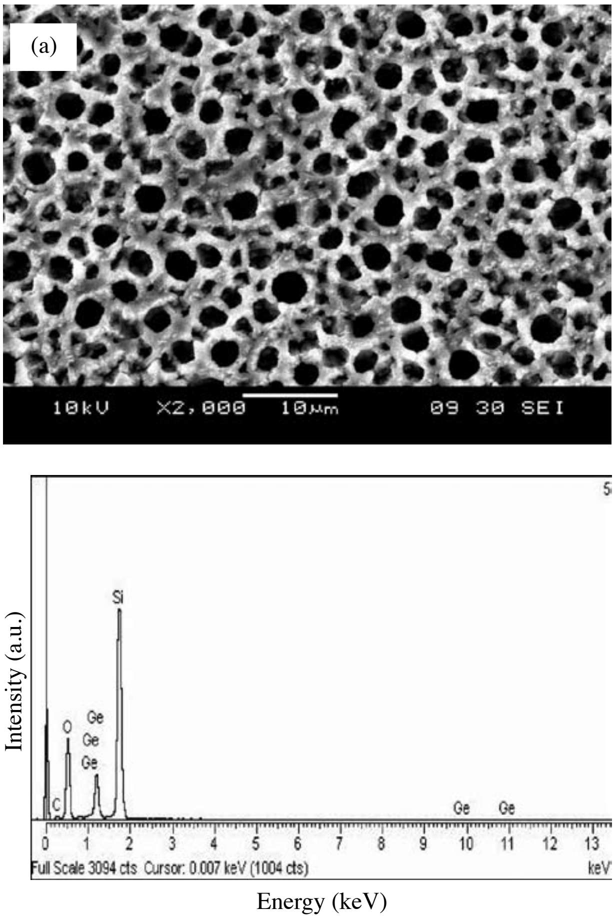

FIGURE 1. (a) SEM of Si/Ge/PS sample showing uniform circular pore network and (b) EDX spectra of Si/Ge/PS sample

Figure 2(b) shows the measured XRD of the c-Si and Si/Ge/PS samples. XRD spectrum of Si/Ge/PS revealed the presence of a Ge phase with the diamond structure by (111), (220) and (400) reflections (Caldelas et al. 2008). We can see that the dominant peak at $2\theta= 69.24^\circ$ is the (422) diffraction from Si substrate. XRD pattern of fresh silicon showed a very sharp peak at $2\theta = 69.2^\circ$ showing the single crystalline nature of the wafer. This peak becomes very broad for Si/Ge/PS sample, which suggests the formation of pores on the crystalline silicon surface (Jayachandran et al. 2001).

Figure 3 shows measured dark and photo currents for the fabricated Ni MSM photodetector of Si/Ge/PS and conventional Si devices. For completeness both forward and reverse biased characteristics are shown. It can be seen that both forward and reverse currents for Si/Ge/PS are not exactly symmetrical, where the reverse bias showing higher currents. (Balagurov et al. 2001) suggest that the higher reverse currents are probably due to oxidation of porous surface. This agrees with the previous EDX spectrum which showed the presence of oxygen in the sample. The asymmetric I-V behaviors are expected since the contacts are made on the porous structure. Specifically, it can be seen that the dark currents for Si/Ge/PS device at forward and reverse

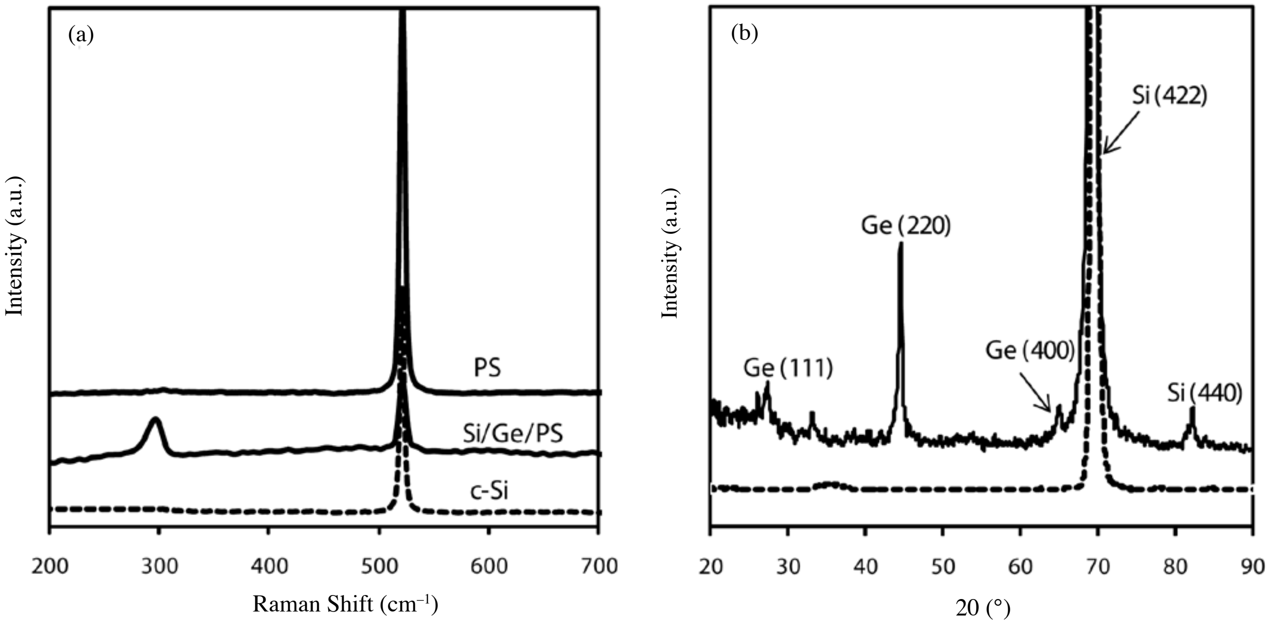

FIGURE 2. (a) Raman spectra of PS, Si/Ge/PS and c-Si and (b) XRD spectra of the Si/Ge/PS (solid line) and crystalline Si(dotted line) samples

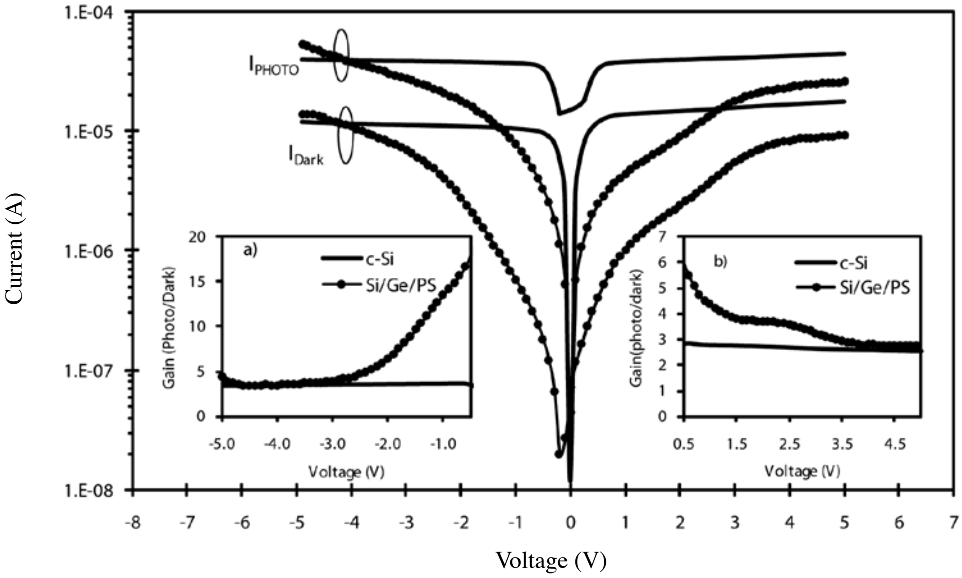

FIGURE 3. I-V characteristics of MSM photodetector for control Si device (Solid line) and Ge inside porous silicon (Si/Ge/PS) (symbol), insets show current gains at –ve bias and (b) +ve bias

biased of 1V are lower than Si device by a factor of 13.7 and 18.25, respectively. While photo currents for Si/Ge/PS at forward and reversed biased of 1V exhibit lower values compare to Si device by a factor of 8.65 and 4.84. However, in any photodetector devices, the current gain which is the ratio of detector light current-to-dark current is often quoted for performance evaluation of the device. In relation to this, the insets in Figures 3(a)-(b) present current gain for both reverse and forward bias of the devices. Interestingly it can be seen that Si/Ge/PS device exhibited enhanced current gain compared to conventional Si device where the gain for Si/Ge/PS is 13.51 while for Si device is 3.58 at reversed biased of 1V. The current gain at forward bias of 1 V shows similar trend where the gain is higher for Si/Ge/PS compare to Si device. The larger enhancement of the current gain of Si/Ge/PS could be related to the presence of Ge nanostructures in the porous silicon. Further investigation is needed to confirm this effect.

CONCLUSIONS

It is possible to grow Ge nano/microstructure on low cost porous silicon by using a simple and low-cost method of thermal evaporation and thermal annealing. SEM spectrum showed that uniform circular pores structure can be produced using simple anodic dissolution of Si substrate. Raman spectrum showed that good crystalline structure of the Ge can be produced inside silicon pores. EDX suggests the presence of Ge inside the pores structure. XRD showed the presence of a Ge phase with the diamond structure by (111), (220), and (400) reflections. Finally, the presence of Ge inside porous silicon has been shown to suppress the dark current. While the gain for the Si/Ge/PS photodetector also increased by a factor of four at reversed bias of 1V, as compared to conventional Si MSM.

ACKNOWLEDGMENTS

A.F. Abd Rahim wishes to thank Universiti Teknologi MARA for financial assistance. Support from the USM Research University Postgraduate Research grant no: 1001/PFIZIK/842066 is acknowledged.

REFERENCES

Baharin, A. & Hashim, M.R. 2007. Study of electrical characteristics of Ge islands MSM photodetector structure grown on Si substrate using conventional methods. *Semiconductor Science and Technology* 22(8): 905-910.

Balagurov, L.A., Bayliss, S.C., Andrushin, S. Ya., Orlov, A.F., Unal, B., Yarkin, D.G. & Petrova, E.A. 2001. Metal/PS/c-Si photodetectors based on unoxidized and oxidized porous silicon. *Solid-State Electronics* 45(9): 1607-1611.

Caldelas, P., Rolo, A.G., Gomes, M.J.M., Alves, E., Ramos, A.R., Conde, O., Yerci, S. & Turan, R. 2008. Raman and XRD studies of Ge nanocrystals in alumina films grown by RF-magnetron sputtering. *Vacuum* 82(12): 1466-1469.

Chen, P.S., Pei, Z., Lee, S.W., Tsai, M.J. & Liu, C.W. 2004. Nanostructures and optical properties of self-assembled Ge quantum dots grown in a hot wall UHV/CVD system. *Proceedings - 205th Meeting of Electrochemical Society*, May, San Antonio.

Cheng, M.H., Ni, W.X., Luo, G.L., Huang, S.C., Chang, J.J. & Lee, C.Y. 2008. Growth and characterization of Ge nanostructures selectively grown on patterned Si. *Thin Solid Films* 517(1): 57-61.

Jayachandran, M., Paramasivam, M., Murali, K.R., Trivedi, D.C. & Ragharan, M. 2001. Synthesis of porous silicon nanostructures for photoluminescent devices. *Materials Physics and Mechanics* 4: 143.

Jin, Chang-Beom, Jee-Eun Yang, & Moon-Ho Jo. 2006. Shape-controlled growth of single-crystalline Ge nanostructures. *Applied Physics Letters* 88(19): 193105-3.

Krasil'nik, Z.F., Lytvyn, P., Lobanov, D.N., Mestres, N., Novikov, A.V., Pascual, J., Ya Valakh, M. & Yukhymchuk, V.A. 2002. Microscopic and optical investigation of Ge nanoislands on silicon substrates. *Nanotechnology* 13(1): 81-85.

Lei, Zhen-Kun, & Kang, Yi-Lau, Cen Hao, Hu Ming & Qiu Yu. 2005. Residual stress on surface and cross-section of porous silicon studied by micro-raman spectroscopy. *Chinese Physics Letters* 22(4): 984-986.

Liu, Feng-Qi, Zhan-Guo Wang, Guo-Hua Li & Guang-Hou Wang. 1998. Photoluminescence from Ge clusters embedded in porous silicon. *Journal of Applied Physics* 83(6): 3435-3437.

Maeda, Yoshihito, Nobuo Tsukamoto, Yoshiaki Yazawa, Yoshihiko Kanemitsu & Yasuaki Masumoto. 1991. Visible photoluminescence of Ge microcrystals embedded in SiO[sub 2] glassy matrices. *Applied Physics Letters* 59(24): 3168-3170.

Schittenhelm, P., Gail, M. & Abstreiter, G. 1995. Self-organized MBE growth of Ge-rich SiGe dots on Si(100). *Journal of Crystal Growth* 157(1-4): 260-264.

Yang, Min, Daming Huang, Pinghai Hao, Fulong Zhang, Xiaoyuan Hou & Xun Wang. 1994. Study of the Raman peak shift and the linewidth of light-emitting porous silicon. *Journal of Applied Physics* 75(1): 651-653.

A.F. Abd Rahim* & M.R. Hashim
School of Physics
Universiti Sains Malaysia
11800 Penang, Malaysia

A.F. Abd Rahim*
Faculty of Electrical Engineering
Universiti Teknologi MARA
13500 Permatang Pauh, Penang
Malaysia

N.K. Ali
Faculty of Electrical Engineering
Department of Electronic Engineering
Universiti Teknologi Malaysia
81310 Skudai, Johor
Malaysia

*Corresponding author; email: alhan570@ppinang.uitm.edu.my

Received: 7 December 2009
Accepted: 13 July 2010