Semiconductor Optoelectronics, *Vol. 42 No. 2 (2023), 490-497*
https://bdtgd.cn/

Semiconductor Optoelectronics
ISSN: 1001-5868

ENHANCEMENT OF ELECTRON FIELD EMISSION FROM SILICON NANOWIRES THROUGH HYDROGEN PLASMA TREATMENT

Karanam Madhavi[1*], V C Veeranna Gowda[1], G Vijayakumar[1], Hanumantha Raju N[1]
[1]Department of Physics, Maharani Cluster University, Bangalore-560001,India.

ABSTRACT
Silicon nanowires (SiNWs) are promising materials for applications in the area of microelectronics due to their unique electrical and novel physical properties at the nanometer scale. SiNWs are fabricated by the silver-assisted chemical etching method and are exposed to hydrogen plasma created by an electron cyclotron resonance (ECR) system at a microwave power of 800 watts. The plasma treatment had been carried out on the surface of SiNWs from 0 minutes to 30 minutes with a time interval of 5 minutes. Scanning electron microscopy (SEM) analysis revealed that SiNWs were found to become thinner with post-deposition hydrogen plasma treatment and approximately 50% reduction was observed in the diameter of SiNWs before and after plasma treatment for 30 minutes. This is an essential property for the enhancement of field emission in nanowires. The electron field emission (EFE) characteristics of the SiNW films were studied based on the current-voltage measurements and analyzed using the Fowler-Nordheim (F-N) equation. The results evidenced that the field enhancement factor (β) significantly increased with the application of hydrogen plasma treatment on the surface of SiNWs and the turn-on field for triggering the EFE process considerably decreased from 9.83 V/µm to 6.5 V/µm after plasma treatment, which is most essential for low-power operational applications.
Keywords: Nanowires; Hydrogen Plasma; Electron Cyclotron Resonance; Electron Field Emission; Turn-On Field;

1. Introduction:

One-dimensional nanostructures play an important role in fabricating optoelectronic and electronic devices [1]. Silicon nanowires (SiNWs) have attracted increasing attention in a diverse array of nanodevice-related applications such as vacuum microelectronic devices, X-ray sources and field emission displays [2]. SiNWs have been fabricated through many methods such as vapor-liquid-solid (VLS) growth, PECVD and metal-assisted chemical etching (MACE), etc. [3-5]. Amongst, MACE method is cost effective method to fabricate uniform SiNWs [6]. Field emission is considered as one of the interesting phenomena in the field of science and technology. Field emission properties of many other nanomaterials like carbon nanotubes [7], titanium dioxide nanotubes [8], and tin oxide nanotubes [9] have been studied over the past few years. Many methods like ion implantation [10], Hydrogen (H_2) plasma surface treatment on diamond [11], and metallic coating [12] have been utilized to enhance the electron field emission. SiNWs are treated as active-electron field emitters due to their low work function and unique sp^3-bonded crystal structure [13]. Modification techniques like H_2 plasma treatment on SiNWs [14] and mo-modified Si field emitters [15] have been utilized to improve the EFE in SiNWs. However, hydrogen plasma treatment through electron cyclotron resonance (ECR) has not been reported much. Thus in the present work, ECR plasma sources have been utilized to apply H_2 plasma treatment on the surface of the SiNWs which is very popular and has many advantages [16]. Later, electron field emission (EFE) characterization was carried out on SiNWs and was analyzed using Fowler-Nordheim (F-N) theory [17]. In this article, the influence of post-hydrogen plasma treatment on the aspect ratio and EFE properties by modifying as-grown SiNWs to plasma-treated SiNWs (30 min) have been investigated.

2. Experimental Methods &Characterization

2.1 Chemicals and materials:

The analytical grade chemicals such as hydrofluoric acid (HF), hydrogen peroxide(H_2O_2), silver nitrate ($AgNO_3$), Sulphuric Acid (H_2SO_4) are purchased from Sigma Aldrich and utilized without any purification. The p-type silicon substrates employed in this work are of high quality.

2.2 Cleaning of silicon substrates:

The cleaning of silicon wafers of thickness 500 μm is very important before the fabrication of SiNWs. The RCA procedure is followed to clean the silicon wafers. This procedure follows with the ultrasonication of substrates in acetone and rinsing with deionized water to remove the organic contamination. Subsequently, samples are dipped in 2% HF aqueous solution for 2 minutes at 60^0 to remove the surface oxide formation followed by rinsing with deionized water. Furthermore, the samples are dipped in H_2O: HCL: H_2O_2 solution for 10 minutes at 70^0 followed by a gentle wash with deionized water to remove the ionic impurities [13].

2.3 Fabrication of SiNWs:

The cleaned silicon samples have been used to synthesize SiNWs by MACE method. It begins with pre-immersion treatment. In the pre-immersion treatment, the cleaned silicon wafers are immersed in H_2SO_4 & H_2O_2 solution of ratio of 3:1 for 10 minutes followed by rinsing with deionised water. After pre-immersion treatment, the Ag-nanoparticles were deposited on the silicon wafer by immersing silicon samples in the aqueous solution comprising 0.02 M $AgNO_3$ & 4.8 M HF for 40 sec. These Ag-deposited silicon wafers were dipped in an etching bath consisting of HF & H_2O_2 for 60 minutes followed by immersion in nitric acid and then in 5% HF-solution to remove the native oxides on silicon wafers respectively. After the fabrication process, the SiNW samples are rinsed with de-ionized water and dried [18].

2.4 Plasma treatment:

To apply the plasma treatment, samples are loaded in the ECR plasma chamber at a constant distance from the plasma region by maintaining the gas pressure of $1x10^{-3}$ mbar at an H_2 flux of 84 sccm under constant microwave power of 800 watts. Plasma exposure on SiNWs samples had been carried out for 0 min,5 min, 10 min, 15 min,20 min, 25 min and 30 min [19].

2.5 Field emission measurement:

The field-emission properties of SiNWs were analysed in a vacuum chamber with a base pressure of 1 X 10^{-5} Pa. Inside the vacuum chamber, the phosphor was deposited on a conducting material to serve as anode and the sample holder in which the sample loaded is connected to the cathode. The distance between the sample and electrode is calculated by digital micrometer and in our work, it is adjusted to 100 μm. The bias is applied between anode and sample and EFE properties are studied by Keithley-electrometer.

The morphology and cross-section of the prepared SiNWs is studied using SEM (JSM-6701F, JEOL).

3. Results and Discussion:

3.1 SEM analysis

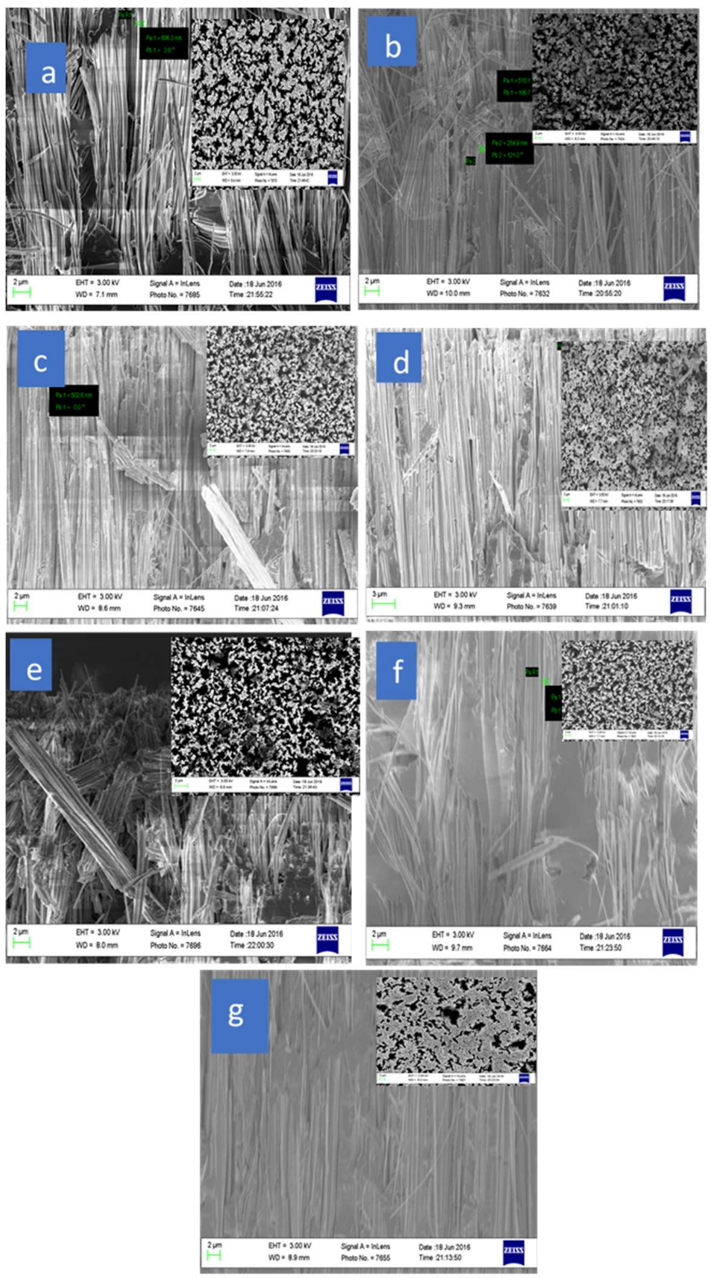

Figure 1: Morphology & Cross section of SiNWs (a) as fabricated SiNWs (b) after plasma exposure for 5 min (c) 10 min (d) 15 min (e) 20 min (f) 25 min (g) 30 min

SEM images in Figure 1 illustrate the morphology and cross-section of fabricated samples and after being treated with H_2 plasma treatment for different intervals of time. It has been calculated from the cross-section of the SEM images that the average diameter of SiNWs was increased with the increase of plasma exposure time. It is noticed that the diameter of fabricated SiNWs is 606 nm, and it is decreased to 303 nm after plasma treatment for 30 min, whereas the variation in length of SiNWs is very less which lies in the range of 80 µm -130 µm. The decrease in size of SiNWs is due to the hydrogen plasma exposure which passivates the dangling bonds on the surface and removes the oxide layer around the shell of SiNWs [19]. From SEM analysis, the aspect ratio of the SiNWs (length/diameter) is measured and is found to be enhanced with hydrogen plasma exposure which is displayed in Table 1. This enhancement in the aspect ratio of plasma-treated SiNWs is essential for the field emission studies of SiNWs.

Table: 1

Plasma exposure time (in minutes)	**Aspect ratio**
0	130:01:00
5	342:01:00
10	237:01:00
15	219:01:00
20	356:01:00
25	376:01:00
30	432:01:00

3.2 Field emission studies:

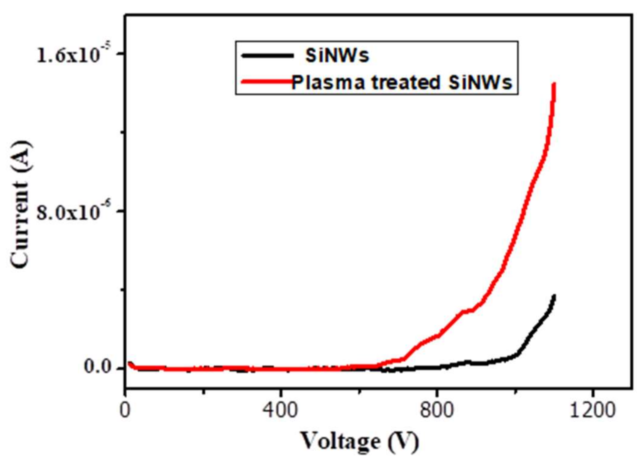

Figure 2: I-V characteristics of SiNWs

The EFE measurements have been carried out at room temperature. Figure 2 shows the I-V characteristics of SiNWs and plasma-treated SiNWs. The emission current is noted as a function of the applied voltage from 0 V to 1200 V. The Turn-on field (the field required to detect a current of 0.01 mA/cm^2) is calculated from the I-V data. It was found to be 9.83 V/µm & 6.5 V/µm for the SiNWs and plasma-treated SiNWs respectively. It is noticeable that turn on-field of plasma-treated SiNWs is smaller. These results indicate that the electrons can emit easily from the tip of the plasma exposed SiNWs which shows the increase of sharpness of SiNWs and also the decrease of diameter which is proved through enhancement of aspect ratio of SiNWs from the SEM analysis. These results demonstrated that hydrogen plasma treatment enhances the field emission characteristics of SiNWs. The other EFE parameter is the field enhancement factor β can be determined by F-N equation [20] i.e.

$$I = \frac{aE_{effe}^{2}}{\phi} \exp\left(-\frac{b\phi^{3/2}}{E_{effe}}\right)$$

Where a & b are constants that depend on the work-function ϕ of the material. For silicon a = -1.54$\times 10^{-3} AeV\, V^{-2}$ $and\ b = 6.83\ \times 10^{3}\ eV^{-3/2} \mu\, V^{-1}, E_{\ eff}$ is the effective electric field, $E_{eff} = \beta E_0$, where β is field-enhancement factor and $E_0 = \frac{V}{d}$ is the average effective electric-field, V is the voltage applied, d is the distance between silicon nano wire tip and anode. Then F-E equation can be written as

$$\ln\left(\frac{I}{V^2}\right) = \ln\left(\frac{a\beta^2}{\phi d^2}\right) - \frac{b\phi^{3/2} d}{\beta V}$$

Plotting $\ln\left(\frac{I}{V^2}\right)$ versus $\left(\frac{1}{V^2}\right)$ yields a straight line which is called F-N plot with the slope of ($-\frac{b\phi^{3/2} d}{\beta V}$) and with the intercept of $\ln\left(\frac{a\beta^2}{\phi d^2}\right)$ [21]

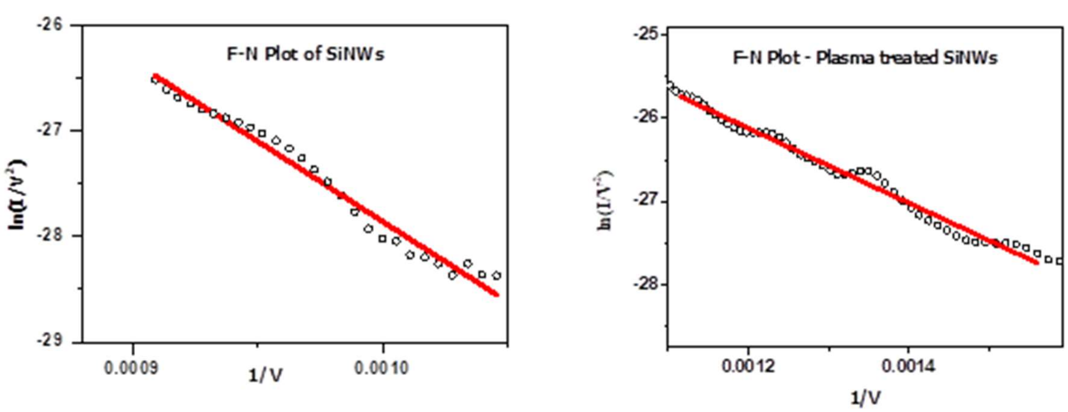

Figure 3: F-N PLOT (a) SiNWs (b) Plasma-treated SiNWs

Figure 3 (a) and 3 (b) display the F-N plots of SiNWs and plasma-exposed SiNWs respectively.

The curves indicate that experimental data fitted well with the F-N model very well [21]. The field enhancement factor β was calculated from the slope, where slope = $-\frac{b\phi^{3/2}d}{\beta}$,where ϕ=4.15 eV, d=100 µm, b= -6.83×10^{3} $eV^{-3/2}$ μm^{-1}. The field enhancement factor β of SiNWs/plasma treated SiNWs is 351 and 1214 respectively. The enhancement in the β shows superior EFE quality in plasma treated SiNWs. Thus, low turn on field and enhancement of field emission factor are the evidences to believe that hydrogen plasma treatment could improve the EFE property of SiNWs. Table 2 lists the EFE parameters attained from the F-N plots.

Table: 2

EFE parameters	SiNWs	H_2 Plasma treated SiNWs
Turn on field V/µm	9.83	6.5
Field enhancement factor (β)	351	1214

4.Conclusions:

MACE provides a simple approach to prepare the SiNWs. It is observed from the SEM images that the vertically aligned SiNWs are formed along the whole surface of the silicon wafer. The H_2 plasma treatment on SiNWs enhanced the aspect ratio and field emission characteristics. A low turn-on field of 6.5V/µm and enhancement of β from 351 to 1214 is achieved through H_2 plasma treatment for 30 minutes on the surface of the SiNWs. Further optimization of parameters may lead to improvement in the EFE properties.

Conflicts of Interest: Authors declare that there were no conflicts of interest

Funding Sources: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

5. References:

[1] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, One-Dimensional Nanostructures: Synthesis, Characterization, and Applications, Adv. Mater, 15 (5) (2003) 353-389, https://doi.org/10.1002/adma.200390087

[2] Yu-Fen Tzeng, Hung-Chi Wu, Pei-Sun Sheng, Nyan-Hwa Tai, Hsin Tien Chiu, Chi-Young Lee, I Nan Lin, Stacked Silicon Nanowires with Improved Field Enhancement Factor, ACS Appl. Mater. Interfaces 2 (2) (2010) 331-334, https://doi.org/10.1021/am900490m

[3] Kadambaka S, Tersoff J, Reuter M C, Ross FM, Diameter-Independent Kinetics in the Vapor-Liquid-Solid Growth of Si Nanowires, Phys. Rev. Lett. 96(9) (2006) 096105(1-4). https://doi.org/10.1103/PhysRevLett.96.096105

[3] Wang Y, Schmidt V, Senz S, Gosele U, Epitaxial growth of silicon nanowires using an aluminum catalyst, Nat.Nanotechnol 1(2006)186-189. https://doi.org/10.1038/nnano.2006.133

[4] Nafis Ahmed, P. Ramasamy, P. Balaji Bhargav, A. K. Sivadasan, S. Amirthapandian, Sandip Dhara,C.Balaji, Crystallization of PECVD grown Si nanowire and its characterization using confocal Raman and EELS studies, J. Mater. Sci. Mater. Electron 32 (2021) 204–209. https://doi.org/10.1007/s10854-020-04754-0

[5] Zhipeng Huang, Nadine Geyer , Peter Werner , Johannes de Boor , Ulrich Gösele, Metal-Assisted Chemical Etching of Silicon: A Review, A. Adv. Mater. (2011) 23285–308. https://doi.org/10.1002/adma.201001784,

[6] Hochbaum, A. I.Gargas, D.Hwang, Y. J. Yang, P, Single crystalline mesoporous silicon nanowires. Nano Lett., 9 (2009) 3550-3554. https://doi.org/10.1021/nl9017594

[7] Se-Jin Kyung, Yong-Hyuk Lee, Chan-woo Kim, June-Hee Lee, Geun-Young Yeom, Field emission properties of carbon nanotubes synthesized by capillary type atmospheric pressure plasma enhanced chemical vapor deposition at low temperature, J. Carbon 44 (8) (2006) 1530-1534. https://doi.org/10.1016/j.carbon.2005.12.020

[8] R. P. Antony, T. Mathews, K. Panda, B. Sundaravel, S. Dash and A. K. Tyagi, Enhanced Field Emission Properties of Electrochemically Synthesized Self-Aligned Nitrogen-Doped TiO_2 Nanotube Array Thin Films, J. Phys. Chem. C 116 (2012) 16740-746. https://pubs.acs.org/doi/abs/10.1021/jp302578b

[9] A.C. Deshpande, P.M. Koinkar , S.S. Ashtaputre , M.A. More, S.W. Gosavi , P.D. Godbole, D.S. Joag, S.K. Kulkarni, Field emission from oriented tin oxide rods, Thin solid films, 5154 (5)(2006) 1450-1454. https://doi.org/10.1016/j.tsf.2006.04.034

[10] Thomas Joseph, Palathinkal, Nyan-Hwa Tai, Chi-Young Lee, Huan Niu, Hsiu-Fung Cheng, Way-Faung Pong, I-Nan Lin, Field Emission Enhancement in Ion Implanted Ultra-nanocrystalline Diamond Films, Plasma Process. Polym., 6 (2009) S834–S839. https://doi.org/10.1002/ppap.200930107

[11] KJ Sankaran, K Srinivasu, KC Leou, NH Tai, IN Lin, High stability electron field emitters made of nanocrystalline diamond coated carbon nanotubes, Appl. Phys. Lett. 103 (2013) 251601 (1-4).
https://doi.org/10.1063/1.4850525

[12] Xiao-Ping Wang, Meng-Han Li, Mei-Mei Guo, Li-Jun Wang, Xin-Wei Yang, Ying Yang, Man-Jun Deng, Guang-Ran Yang, Yu-Tao Qian, Effect of metal coating material on field emission of vertically grown layered MoS_2 nanosheets, J. Vaccum ,177 (2020) 109386 (1-4).
https://doi.org/10.1016/j.vacuum.2020.109386

[13] Sumanta Kumar Sahoo, Arumugam Marikani, Morphological Dependence of Field Emission Properties of Silicon Nanowire Arrays, J. Nano, 11 (02) (2016) 1650017(1-4). https://doi.org/10.1142/S179329201650017X,

[14] Au FCK, Wong KW, Tang YH, Zhang YF, Bello I, Lee ST, Electron field emission from silicon nanowires, Appl Phys Lett. 75(1999) 1700–1702. https://doi.org/10.1063/1.124794

[15] Ha JK, Chung BH, Han SY, Choi JO, Drastic changes in the field emission characteristics of a Mo-tip field emitter array having PH3-doped a-Si: H as a resistive layer material throughout vacuum packaging processes in a field emission display. J Vac Sci Technol, 20 (2002) 2080–2084. https://doi.org/10.1116/1.1508817

[16] K. Deenamma Vargheese, G. Mohan Rao, Electron cyclotron resonance plasma source for ion assisted deposition of thin films, Rev. Sci. Instrum.71 (2000) 467-472. https://doi.org/10.1063/1.1150225

[17] Fowler, R. H. Nordheim, L. W. Proc. R. Electron emission in intense electric fields, Soc. London, Ser. A), 119 (1928)173-184, https://doi.org/10.1098/rspa.1928.0091,

[18] Karanam Madhavi, Padma Suvarna R, Monalisa Ghosh, Habibuddin Shaik, G Mohan Rao, Effect of Plasma ion etching towards Super-hydrophobicity, J. Mater, 3 (2016) 1907–1913. https://doi.org/10.1016/j.matpr.2016.04.091

[19] Karanam Madhavi, Monalisa Ghosh, G. Mohan Rao, R Padma Suvarna, Surface modification influenced properties of silicon nanowires grown by Ag-assisted chemical etching with ECR hydrogen plasma treatment, J. Mater. Sci. Mater. Electron, 31(2020) s1904–1911. https://doi.org/10.1007/s10854-019-02709-8

[20] Walt A De Heer, Chtelain A, D Ugarte, A Carbon Nanotube Field-Emission Electron Source, J. Science, 270 (1995) 1179-1180. https://doi.org/10.1126/science.270.5239.1179

[21] A. J. le Fèbre, L. Abelmann, ,J. C. Lodder, Field emission at nanometer distances for high-resolution positioning, J. Vac. Sci. Technol. B (26) (2008) 724–729. https://doi.org/10.1116/1.2894898