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Citation: Applied Physics Letters **87**, 213115 (2005); doi: 10.1063/1.2136217
View online: http://dx.doi.org/10.1063/1.2136217
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/87/21?ver=pdfcov
Published by the AIP Publishing

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(Received 3 June 2005; accepted 27 September 2005; published online 17 November 2005)

Field-emission studies on Si nanowires (Si NWs) grown by the vapor-liquid-solid (VLS) technique are presented. The field-emission properties of the Si NWs were characterized in ultrahigh vacuum following several postgrowth processes such as catalyst etching, *in situ* annealing, and cesiation. The average threshold field of cesiated Si NWs was found to be $\sim 7.76 \pm 0.55$ V/μm and showed a significant improvement over that of as-grown NWs (average threshold field ~ 11.58 V/μm). The superior field-emission characteristics are attributed to the combination of cesiation and quality of the NWs' surface grown via hydrogen reduction of silicon tetrachloride. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2136217]

One-dimensional (1D) nanostructures (nanotubes and nanowires) have gained attention over the past few years for their potential use as electron field emitters in displays, x-ray sources, sensors, and other vacuum microelectronic devices.[1–4] Nanostructures of different materials systems have been characterized for their field-emission properties.[5–11] Silicon has been the backbone of the microelectronics industry for decades and it would be desirable to have silicon field emitters to facilitate integration onto silicon substrates along with the driving circuitry.

We report the electron field-emission characteristics of silicon nanowires (Si NWs) grown by the vapor-liquid-solid (VLS) technique[12] and the reduction of threshold field via postgrowth processing steps such as *in situ* annealing and *in situ* cesiation. The NWs were grown on n^+-Si $\langle 111 \rangle$ substrates by atmospheric pressure chemical vapor deposition (APCVD) of $SiCl_4 + H_2$ (mole ratio $SiCl_4 : H_2 = 0.02$) in the temperature range of 850–950 °C. A thin Au film (5–20 nm) was used as the catalyst for VLS growth. The average NW diameter was ~ 100 nm and the average areal density was 3×10^7 cm^{-2}. Figure 1 shows a scanning electron microscope (SEM) image of a Si NW sample used in this study. The field-emission measurement was carried out in a homebuilt ultrahigh-vacuum (UHV) system using a spherical Au ball (500 μm diam) as the anode. The sample holder was equipped with a heater for *in situ* annealing and the chamber contained a cesium (Cs) evaporation source to perform *in situ* cesiation. The data were acquired using LABVIEW® and a homebuilt current amplifier was used to measure the field-emission current. A recessed window allowed for measuring the interelectrode separation with an accuracy of ~ 5 μm using a long working distance objective lens (Mitutoyo 10×). All field-emission measurements were performed in vacuum with a base pressure of $< 5 \times 10^{-9}$ Torr.

Field-emission measurement was carried out on as-grown samples and subsequent measurements were performed at the end of each of the following postgrowth processing steps: (a) catalyst removal (Au-selective etching), (b) *in situ* annealing, and (c) *in situ* cesiation. The *I–V* characteristics (truncated to current value of 30 μA) of the Si NWs for different postgrowth processing steps are shown as follows: as-grown case [Fig. 2(a)], Au-selective etching + *in situ* annealed case [Fig. 2(b)], and finally, Au-selective etching + *in situ* annealed + *in situ* cesiated case [Fig. 2(c)]. The *I-V* curves in all cases were obtained after repeated forward and reverse sweeps until subsequent sweeps were almost identical. The threshold field is defined as the electric field required for an emission current density of 10 mA/cm^2, corresponding to the saturation current density of a phosphor in displays. The emission area in our case was calculated ac-

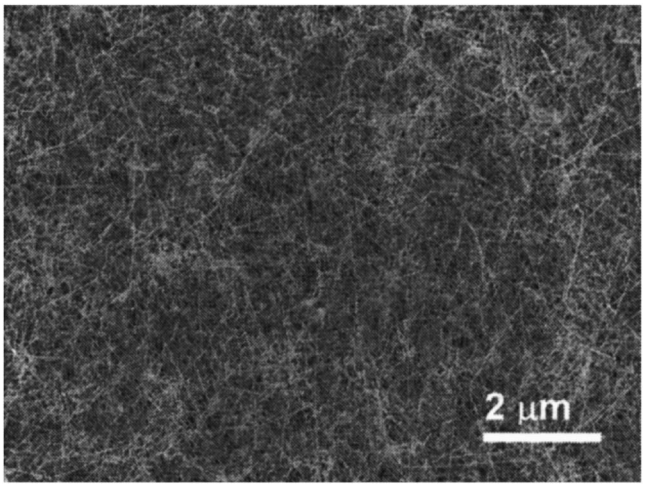

FIG. 1. SEM image of Si NWs grown by APCVD of $SiCl_4 + H_2$ (mole ratio $SiCl_4 : H_2 = 0.02$) at 850 °C using a 20-nm Au film as a catalyst. The average NW diameter ~ 100 nm.

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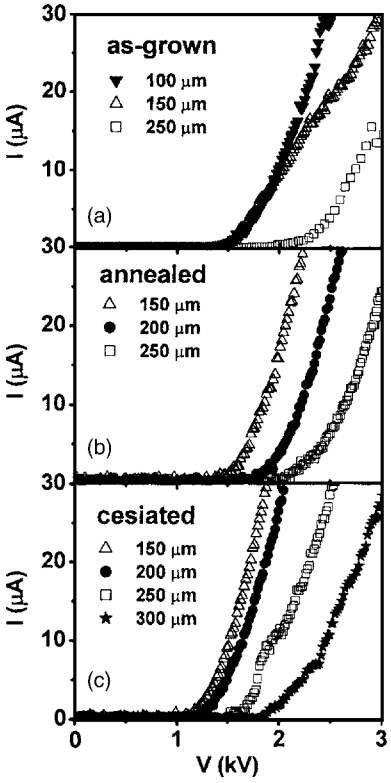

FIG. 2. *I-V* characteristics for different electrode separations (truncated to current value of 30 μA) of Si NWs for (a) as grown, (b) Au-selective etched + *in situ* annealed, and (c) Au-selective etched + *in situ* annealed + *in situ* cesiated cases.

cording to a modification of the formula in Ref. 13, and is given by $A=2\pi(R+Z/2)Z(2^{(1/n)}-1)$, and is valid for $Z<2R$, where R=radius of anode, Z=interelectrode spacing, and $n=(V/I)dI/dV$. The quantity dI/dV in our case was obtained by differentiating the smoothed *I-V* curves obtained from experiment (shown in Fig. 2).

Field-emission measurement on the as-grown sample was performed initially and the average threshold field was found to be 11.58 V/μm. Catalyst removal was performed by etching the sample in aqua regia (HNO_3:HCl=1:3) for 10 min to selectively etch away Au and this was confirmed by energy dispersive x-ray spectroscopy (EDS) in a SEM (LEO 1530). After the Au-selective etch, the sample was reloaded into the vacuum chamber for field-emission measurements. All subsequent postgrowth processes were performed *in situ*. The field-emission measurement on Au-selective etch alone yielded similar *I-V* characteristics as the as-grown case (not shown) and the same threshold field, indicating that the Au-Si Schottky barrier did not play a deterministic role in the field-emission characteristics of the Si NWs. *In situ* annealing was carried out by passing a dc current of 1.2 A (equivalent to a current density of 16 A/cm^2) for 4 s. Based on the color of the sample (red hot) we estimated the temperature was raised to 700 °C. The sample was then rapidly cooled down. The field-emission measurement was carried out after a reasonable time (>30 min) had elapsed from the point it was heated so as to avoid any thermionic contribution to the emission current. This procedure removed the surface adsorbates[14] as evidenced from the smooth *I-V* characteristics [shown in Fig. 2(b)]. The plot of emission current density, J, versus electric-field strength, E, for the Au-selective etched + *in situ* annealed case is shown

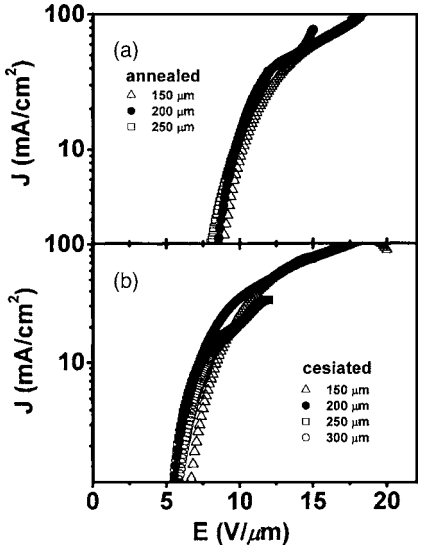

FIG. 3. *J-E* characteristics of the Si NWs for different electrode separations for (a) Au-selective etched + *in situ* annealed and (b) Au-selective etched + *in situ* annealed + *in situ* cesiated cases.

in Fig. 3(a), from which we deduce a threshold field of $\sim 9.9\pm0.3$ V/μm, indicating that the threshold field decreased upon *in situ* annealing. From the simplified Fowler–Nordheim (F–N) equation,[4] $J=(A\beta^2E^2/\phi)\exp(-B\phi^{3/2}/\beta E)$, where $A=1.56\times10^{-10}$ AV^{-2} eV and $B=6.83\times10^3$ V eV$^{-3/2}$ μm^{-1}, β was estimated to be $\sim$500 using the work function of intrinsic Si (ϕ=4.5 eV) (Ref. 15).

In situ cesium evaporation was then carried out in UHV using a Cs source from SAES Getters.[16] The cesium was evaporated for 5 min corresponding to a nominal coverage of 5 ML. As can be seen from the *J-E* characteristics of the cesiated Si NWs [Fig. 3(b)], the average threshold field reduced to $\sim 7.76\pm0.55$ V/μm, which is lower compared to prior reports on silicon NWs (Refs. 17 and 18) and Si microstructures.[19] The superior field-emission characteristics can be explained based on the fact that the Si NWs were grown by H_2 reduction of $SiCl_4$, in which the by-product HCl is simultaneously etching the Si surface as the growth proceeds,[20] rendering NWs with a superior surface quality.

Figure 4 shows the F–N plot for different postgrowth processing conditions at an electrode separation of 250 μm. From the F–N equation, the ratio of slopes in the F–N plot of the cesiated sample to that of the as-grown sample is equal to $(\phi_{\text{cesiated}}/\phi_{\text{as-grown}})^{3/2}$. From Fig. 4 we deduce that

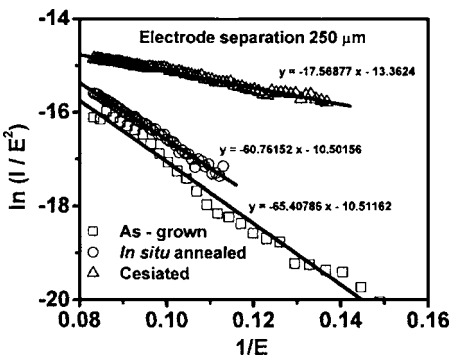

FIG. 4. F–N plot for different postgrowth processing conditions with respective linear fits. The decrease in slope in the Au-selective etched + *in situ* annealed + *in situ* cesiated case indicates the lowering of the work function.

$(\phi_{\text{cesiated}}/\phi_{\text{as-grown}})=0.4147$, indicating that there is a clear reduction in the work function of the Si NWs' surface after cesiation.[21]

In conclusion, we have reported field-emission studies on VLS-grown Si NWs and studied the effects of various postgrowth processing steps on their field-emission characteristics. The cesiated Si NWs exhibit a low-threshold field ($\sim 7.76 \pm 0.55$ V/μm) compared to most silicon nanostructures,[17–19] with the exception of carbon-coated Si cones.[22] This low-threshold field emission from cesiated Si NWs is comparable to that reported from various 1D materials,[5–11] including carbon nanotubes,[13] and Si has the added advantage of being potentially integrated with microelectronic driving circuitry, making vacuum microelectronic devices, including displays based on Si NWs, viable in the future. Further improvement in the field-emission characteristics can be obtained by incorporating the Si NWs into a triode structure, as compared to the diode device reported in this study.

The authors gratefully acknowledge support of this work by the Texas Advanced Technology and Research Programs, NSF Grants No. DMR-0210383, DMR-0306239, and DMR-0312491, and the Advanced Materials Research Center.

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