Selective formation of tungsten nanowires

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Abstract
We report on a process for fabricating self-aligned tungsten (W) nanowires with polycrystalline silicon core. Tungsten nanowires as thin as 10 nm were formed by utilizing polysilicon sidewall transfer technology followed by selective deposition of tungsten by chemical vapor deposition (CVD) using WF6 as the precursor. With selective CVD, the process is self-limiting whereby the tungsten formation is confined to the polysilicon regions; hence, the nanowires are formed without the need for lithography or for additional processing. The fabricated tungsten nanowires were observed to be perfectly aligned, showing 100% selectivity to polysilicon and can be made to be electrically isolated from one another. The electrical conductivity of the nanowires was characterized to determine the effect of its physical dimensions. The conductivity for the tungsten nanowires were found to be 40% higher when compared to doped polysilicon nanowires of similar dimensions.

Keywords: tungsten, nanowires, nanostructures, self-aligned, chemical vapor deposition, selective deposition

Background
One-dimensional nanostructured materials such as nanowires, nanorods, and nanotubes have been the focus of intensive research owing to their unique applications in mesoscopic physics and novel nanoscale devices. These nanostructures provide a good platform to investigate the electrical, thermal transport, and mechanical property dependence on dimensionality and size reduction.

Tungsten is a brittle refractory metal that crystallizes in body-centered cubic form. It has high tensile strength and good creep resistance. Due to its high stability, tungsten or tungsten oxide nanowires are promising candidates for a vast range of applications including, smart coatings [1], lithium-ion batteries catalysts [2], electrochromic materials [3,4], and nanostructured sensors [5,6].

Nanowires are unique for sensing applications as they exhibit high sensitivity, long-term stability, and large surface to volume ratios. For sensing applications, tungsten or tungsten oxide nanowires, are known to have a high sensitivity for detecting gasses such as ammonia [7,8], nitrogen dioxide [9,10], hydrogen sulfide [11,12], hydrogen [6,13], pH [5], and etc. at low parts per million and even as low as parts per billion levels.

In semiconductor fabrication, there are various methods that can be used to fabricate patterned nanowires. However, organizing these nanowires into highly ordered arrays can be extremely challenging. Metallic nanowires can be produced with a combination of advanced lithography [14-16], metal etching, chemical mechanical planarization [17], and metal lift-off [18-20]. However, these techniques have limitations and are typically not cost-effective. Metal lift-off with sacrificial resist is a more common solution for producing nanostructures, but the process has resist-imposed limitations namely the thermal stability of the resist which prevents its use in a chemical vapor deposition (CVD) metal process. In this letter, the authors demonstrate a novel method for fabricating tungsten nanowires which allows full integration with standard CMOS fabrication process. The method utilizes selective deposition [21] as an alternative to the conventional growth of nanowires using metal catalyst to form the nanowire structures. The key feature of this method is the ability to selectively deposit and align tungsten nanowires on silicon or polysilicon lines utilizing selective CVD processing. The precursor used, tungsten hexafluoride (WF6), only reacts with silicon or polysilicon lines utilizing selective CVD processing. The precursor used, tungsten hexafluoride (WF6), only reacts with silicon or polysilicon lines utilizing selective CVD processing. The precursor used, tungsten hexafluoride (WF6), only reacts with silicon or polysilicon lines utilizing selective CVD processing. The precursor used, tungsten hexafluoride (WF6), only reacts with silicon or polysilicon lines utilizing selective CVD processing. The precursor used, tungsten hexafluoride (WF6), only reacts with silicon or polysilicon material but will not react with insulating material, such as silicon dioxide or silicon nitride. The method demonstrated here is cost-effective and circumvents the need for state-of-the-art equipments. There are also no lithographic limitations and the nanowires produced are of high resolution. The process is also self-limiting with good control of nanowire diameters that are less than 50 nm. Another advantage of this method is that the tungsten
nanowires can be produced or synthesized at temperatures below 400°C without the need for metallic catalyst, which are commonly used in catalytic reaction synthesis with growth temperatures typically in a range of 700 to 1,000°C [9,22-25]. Hence, our proposed method allows the use of low-temperature substrates such as polymer or glass, which facilitates manufacturing flexibility and reduces costs.

**Method**

Figure 1 illustrates the fabrication process of the tungsten nanowires. All experiments were conducted on 200-mm-diameter silicon wafers. A 200-nm-thick silicon nitride (Si$_3$N$_4$) layer was deposited at 800°C by low-pressure chemical vapor deposition (Figure 1a) to serve as electrical isolation between the nanowires and silicon substrate. This was followed with a 100-nm-thick silicon dioxide (SiO$_2$) layer deposited by plasma-enhanced chemical vapor deposition which was patterned into lines by standard photolithography and etched in CF$_4$ and CHF$_3$ plasma (Figure 1b). A 50-nm-thick undoped polysilicon film is then deposited by low-pressure chemical vapor deposition, PECVD (Figure 1c). Polysilicon spacers were produced by time-controlled etching of the polysilicon layer with HBr and CF$_4$ plasma in a reactive ion-etching system (Figure 1d). The width of the spacers or would be final polysilicon nanowires is in correlation with the deposited thickness of the PECVD polysilicon film and dependent on the directionality of the plasma etch. The silicon dioxide layer was then selectively

![Figure 1](image_url)  
*Figure 1 Fabrication process flow to selectively form tungsten nanowires with polysilicon core*
etched in buffered hydrofluoric acid (HF) resulting in 50-nm polysilicon nanowires formed on silicon nitride (Figure 1e). The etch rate of SiO$_2$ in buffered HF was approximately 70 nm/min while the etch rate of Si$_3$N$_4$ in the same solution was approximately 2 nm/min, showing high selectivity. The fabricated polysilicon nanowires are comparable to that in literature from sidewall transfer technology [26-28]. Finally, the tungsten nanowires were formed by selectively depositing tungsten by CVD at 400°C onto the exposed polysilicon nanowires (Figure 1f). More information on the CVD conditions is detailed in the next section.

**Results and discussions**

The tungsten nanowires exhibited good adhesion to the polysilicon core and the underlying silicon nitride surface, where nanowire thickness down to 10 nm was achieved (Figure 2). The tungsten deposition is confined to the polysilicon regions; hence, the nanowires are electrically isolated from one another without requiring processing such as etching. There is also no limit to the length of the nanowire that can be produced with this method.

The selective tungsten deposition chemistry confining the tungsten to only polysilicon regions, is based on the reduction of the tungsten hexafluoride (WF$_6$) precursor by the exposed polysilicon as described in Eq. 1; hence producing the selectively formed tungsten nanowires

$$2WF_6(g) + 3Si(s)\overset{\text{R}}{\rightarrow}2W(s) + 3SiF_4(g)$$

Tungsten deposition was performed at 400°C with 10 sccm of WF$_6$ precursor with 500 sccm of Argon carrier gas for 5 min, yielding a layer of approximately 10 nm thick with a resistivity of approximately 13 $\mu\Omega$cm. The sheet resistance of a blanket 10-nm-tungsten layer was measured using a four-point-probe. The by-product from this reaction is silicon tetrafluoride, which is nonreactive with semiconducting material. Argon was used as the carrier gas to aid the removal of these by-products from the wafer surface, thus reducing deposited layer resistivity. The achieved resistivity compares well to published resistivity of 20-$\mu\Omega$cm for a 100-nm-thick tungsten film selectively deposited on bulk silicon [29]. It is proposed that in the future, the underlying polysilicon can be doped to further reduce the resistivity of the nanowire. The tungsten deposition temperature has an impact to the selectivity of the process, where at 450°C nucleation was observed on the silicon nitride surface. When the deposition temperature is at 500°C, selectivity was lost in which tungsten was deposited across the whole substrate on both polysilicon and silicon nitride surfaces.

Electrical resistances of the fabricated tungsten nanowires were characterized to determine the effect of nanowire length and width as shown in Figure 3. The lengths of the measured nanowires were varied from 20 to 500 $\mu$m, and it was observed that the resistance increases almost linearly with length. Inversely, the measured resistance increases by approximately 10% when the width of the core is reduce from 100 to 50 nm. As we double the number of wires from 20 to 40, the measured resistance reduces by 40% due to the increase in the total measured surface area. Comparing these results to those of doped polysilicon nanowires with similar dimensions, the electrical resistance measured for tungsten nanowires were found to be at least 40% lower (Figure 4).

**Conclusions**

In summary, we have demonstrated a self-align process to produce highly ordered arrays of lateral tungsten nanowires utilizing a combination of sidewall transfer technology and selective tungsten CVD. All nanowires were produced with a polysilicon core. Overall, the
fabrication process does not require sub-micron lithographic techniques, metal catalyst, metal lift-off, extensive etching, or polishing. A 5-min tungsten deposition at 400°C is sufficient to produce 10-nm-thick tungsten nanowire with high selectivity and good adhesion to the underlying layers. The measured electrical resistances for these wires were found to increase almost linearly with length of the nanowires and are 40% more conductive when compared to doped polysilicon nanowires of the same dimensions. We believe the process is easily scalable to assemble tungsten nanowires with sub-50-nm polysilicon core.

Authors' contributions
DCSB coordinated the research work, conceived the fabrication process flow and conducted the electrical characterization for the nanowires. RMS conducted the selective tungsten deposition experiments. SAMB fabricated the polysilicon nanostructures and HWM, designed the nano-resistor layout and participated in the electrical characterization of the nanowires. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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References
1. Hong K, Xie M, Hu R, Wu H. Diameter control of tungsten oxide nanowires as grown by thermal evaporation. Nanotechnology 2008, 198.
2. Gu Z, Li H, Yang W, Xia Y, Yao J. Large-scale synthesis of single-crystal hexagonal tungsten trioxide nanowires and electrochemical lithium intercalation into the nanocrystals. J Solid State Chemistry 2007, 180:1.
3. Yao SJ, Lim JW, Sung YE, Jung YH, Choi HG, Kim DK. Fast switchable electrochromic properties of tungsten oxide nanowire bundles. Appl Phys Lett 2007, 90:173126.
4. Shim HS, Kim JW, Sung YE, Kim WB. Electrochromic properties of tungsten oxide nanowires fabricated by electrospinning method. Solar Energ Mat Sol Cell 2009, 93:12.
5. Fenster C, Smith AJ, Abis A, Milenkovic S, Hassel AW. Single tungsten nanowires as pH sensitive electrodes. Electrochem Comm 2008, 10:8.
6. Choi J, Kim J. Highly sensitive hydrogen sensor based on suspended, functionalized single tungsten nanowire bridge. Sensors Actuator B Chem 2009, 136:1.
7. Neri G, Miceli G, Bonavita A, Ispale S, Rizzo G, Niederberger M, Pinna N. Tungsten Oxide Nanowires-Based Ammonia Gas Sensors. Sensor Lett 2008, 64.
8. Zhao YM, Zhu YQ. Room temperature ammonia sensing properties of W18O49 nanowires. Sensor Actuator B Chem 2009, 137:1.
9. Ponzoni A, Corini E, Speraviglieri G, Zhou J, Deng SZ, Xu NS, Ding Y, Wang ZL. Ultrasensitive and highly selective gas sensors using three-dimensional tungsten oxide nanowire networks. Appl Phys Lett 2008, 88:203101.
10. Ko R, Wang S, Wen Z, Lin J, Fan G, Shu W, Liu B. Development of gas sensors based on tungsten oxide nanowires in Metal/SiO2/Metal structure and their sensing response to NOx. J Appl Phys 2008, 47:3272.
11. Rout CS, Hedge M, Rao CNR. H2S sensors based on tungsten oxide nanostructures. Sensor Actuator B Chem 2008, 128:2.
12. Parthangal PM, Zachariah MR, Cavigelli RE, Montgomery CB, Turner S. Restructuring tungsten thin films into nanowires and hollow square cross-section microducts. J Mat Res 2005, 20:11.
13. Rout CS, Kulkami GU, Rao CNR. Room temperature hydrogen and hydrocarbon sensors based on single nanowires of metal oxide. J Phys D: Appl Phys 2007, 40:2777.
14. De-Boor J, Geyer N, Wittemann JV, Gösele U, Schmidt V. Nanofabrication of metal nanowires by atomic force electron beam nanolithography system and its application to Si nanofabrication. Jpn J Appl Phys 1995, 34.
15. Traving M, Schindler G, Engelhardt M. Damascus and subtractive processing of narrow tungsten lines: resistivity and size effect. J Appl Phys 2006, 100:094525.
16. Chen YJ, Hsu JH, Lin HH. Fabrication of metal nanowires by atomic force microscopy, nanoscraping and lift-off process. Nanotechnology 2005, 8:1112.
17. Azuelyte V, Solak HH, Ekinci Y, Mackenzie R, Vörös J, Olliges S, Spolenak R. Large area arrays of metal nanowires. Microelectron Engineering 2008, 85:1131.
18. Sonkusale SR, Amsinck CJ, Nakashi DP, Di Spigna NH, Barlage D, Johnson M, Franzon PD. Fabrication of wafer scale, aligned sub-25-nm nanowire and nanowire template using planar edge defined alternate layer process. Physica E: Low Dimensional Systems and Nanostructures 2005, 28:27.
19. Bien DCS, Badaruddin SA, Saman RM. Method of fabricating nanowires. Malaysian Patent Office, MyPO, P 20097036.
20. Gu G, Zheng Bo, Han WQ, Roth S, Liu J. Tungsten oxide nanowires on tungsten substrate. Nano Lett 2002, 2:8.
23. Wang S, He Y, Zou J, Jiang Y, Xu J, Huang B, Liu CT, Liaw PK: Synthesis of single-crystalline tungsten nanowires by ni-cate-catalyzed vapor-phase method at 850°C. J Crystal Growth 2007, 306:2.

24. Chen GY, Stolojan V, Cox DC, Giusca C, Silva SRP: Growth of tungsten oxide nanowires using simple thermal heating. IEEE Conf. on Emerging Techniques-NanoElectronics 2006, 376.

25. Park B, Yong K: Synthesis and characterization of tungsten oxide nanorods. Surf Rev Lett 2005, 12:5.

26. Hållstedt J, Hellström P-E, Radamson HH: Sidewall transfer lithography for reliable fabrication of nanowires and deca-nanometer MOSFETs. Thin Solid Films 2008, 517(1):117.

27. Law YH, Bain MF, Bien DCS, Mitchell SJN, Gamble HS: Fabrication of self-aligned sub-100nm iron wires by selective chemical vapor deposition. Electrochem Solid State Lett 2006, 9(12):340.

28. Ra HW, Choi KS, Kim JH, Hahn YB, Im YH: Fabrication of ZnO nanowires using nanoscale spacer lithography for gas sensors. Small 2008, 4(8):1105.

29. Li FX, Armstrong BM, Gamble HS: LPCVD of tungsten by selective deposition on silicon. J Mat Sci 2001, 12:303.

cite: Bien et al.: Selective formation of tungsten nanowires. Nanoscale Research Letters 2011, 6:543.

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