Proceedings of the 7th IEEE International
Conference on Nano/Molecular Medicine and Engineering
November 10-13, 2013, Phuket, Thailand

The Effects of Temperature and Humidity Exposure on Reliability of Silicon Nanowires

Uchechukwu C. Wejinya, *Member, IEEE,* Nathan Willems, and Zhuxin Dong, *Member, IEEE*

Abstract— **Material reliability is among the crucial factors that impact material performances before device applications. In order to predict material reliability, accelerated aging study—a study to predict material shelf life when subjected to temperature and humidity, was performed on silicon nanowires. We investigated the effects of process conditions on the diameter and the quality of SiNWs using Atomic Force Microscopy followed by statistical analysis. The experimental results revealed diameter of SiNWs has a linear relationship with changing temperature and humidity. These results are of significant importance and will be a critical design consideration for the use of SiNWs in biomedical implants.**

I. Introduction

NANOWIRES (NWs) are one of the basic building blocks for nanoelectromechanical systems (NEMs). Many different types of NWs exist including metallic NWs – Nickel (Ni), Platinum (Pt), Gold (Au); semiconducting – Indium Phosphide (InP), Silicon (Si), Gallium Nitride (GaN); insulating NWs –Si Dioxide (SiO_2) and Titanium Dioxide (TiO_2). Currently, there are tremendous interests in one-dimensional (1-D) nanostructures, such as nanowires and nanotubes, due to their potential to serve as critical building blocks for emerging nanotechnologies [1-5]. Semiconducting nanowires in particular are of interest because they can function both as nanoscale devices and interconnects for the construction of nanoelectronic systems [6]. Silicon nanowires (Si NWs) are particularly attractive because their diameter and electrical properties can be finely controlled during synthesis [7-9]. Because of this ability to control diameter and electrical properties, Si NWs are ideal for the reproducible assembly of field-effect transistors (FETs) [10-12], logic gates [13] and sensors [14].

Silicon nanowires have also shown superiority over Carbon Nanotubes (CNTs) for use as a one dimensional nanostructure for use in and the assembly of nanoelectrical systems. This comes from the inability to alter the electrical properties of CNTs through doping and the dependence on size for CNT's electrical properties. Due to their flexibility in size and the ability to flexibly alter their electrical properties, Si NWs are thus the subject of intense study by scholars. However, before implementing Si NWs it is important to understand the material's shortcomings which may present serious obstacles to many potential applications including batteries and thermoelectric generators for small scale biomedical implants.

Accelerated aging is the study of material shelf life and is often performed in laboratory settings. It is the most adapted test to predict the lifetime when there is no scientific data available. In this test the material is subjected to excessive oxygen, temperatures, and sunlight in order to accelerate its actual aging [15-16]. The material properties such as the mechanical fatigue, load cycle intake, material stability are evaluated for the prediction of shelf life of the material. Though Europe has favored standard testing methods based on aging at elevated temperatures, slicing and scaling techniques have been the leading approach in North America [17]. Recently, standard test methods in Canada have been adapted by many industries across the US, but these test methods are only defined for the macroscale components. As the test methods involve slicing the material [18-22] which is impossible at the micro- and nano- scale levels, these methods cannot be directly adapted for micro and nano scale materials.

Accelerated aging testing is based on a thermodynamic temperature coefficient formulated by Von't Hof which that states "*for every 10 degree C rise in temperature the rate of chemical reaction will double*." However, since this formulation is based on rate kinetics of a single chemical reaction, not on packages with various kinds of materials, the direct extrapolation of this theory to the aging of packaging materials must be used with caution.

II. Materials and Methods

Si Nanowires (>99%) and acetone (>97%) was purchased from Sigma Aldrich.

Seed Solution: 40 mg of SiNWs was measured using an electronic balance with a resolution of 10 μg and suspended in 1 mL of acetone to make a seed concentration of 40 mg/mL. From the seed concentration, the final working concentration of 0.1 mg/mL was prepared by mixing 250 μL to 1 mL. In order to ensure a uniform dispersion, the seed solution was sonicated in a sonicator for 1 hour and then the final working concentration was prepared. The final working concentrations was again sonicated for 1 hour and then dispersed onto the glass slide. The acetone was evaporated using a hotplate. The SiNWs dispersed glass slides were then subjected to variable temperatures at a constant humidity and at variable humidity with constant temperature. A Microclimate Environmental Chamber (Manufactured by Cincinnati Sub Zero model No. MCBH 1.3) was employed for the study. In the first part of the experiment, keeping the relative humidity constant, the temperature was ramped between 50°C and 200°C with a step increment of 50°C for 30 minutes. In the second part, the temperature was kept constant and the relative humidity varied between 20% RH and 90% RH with a ramping of 10% RH. The samples were then analyzed for dimensional changes using Atomic Force Microscopy (AFM). The chips were treated for 30

978-1-4799-2690-9/13/$31.00 © 2013 IEEE

minutes and then dried in a dry box until the relative humidity fell below 3%. The AFM was utilized to obtain surface images of the treated SiNWs. The changes in the dimensions of the SiNWs were recorded.

The initial diameters and lengths of the silicon nanowires before exposure to the environmental chamber were 40 nm and 1 – 20 µm respectively for 99% of the SiNWs. The melting point (mp) of the SiNWs is 1410 °C. In order to accurately determine the diameter of the treated SiNWs, an Atomic Force Microscope (AFM) is employed. The AFM used in the experiment is the Agilent 5500-ILM microscope. The scanning and characterization was done under Acoustic AC (tapping) imaging mode as shown in Fig. 1. The AFM probe utilized during imaging has a resonant frequency of 190 kHz and a spring constant (F_c) of 48 N/m. During intermittent contact, the tip is brought close to the sample so that it lightly contacts the surface at the bottom of its travel, causing the oscillation amplitude to drop. Hence, the influence of the cantilever tip during the dimension measurement can be neglected since it will not change the shape in this mode of contact.

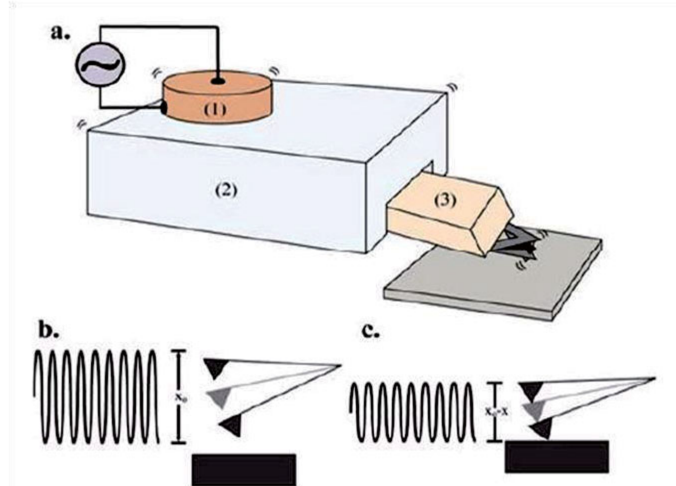

Fig. 1. AFM probe motion under Acoustic AC Mode: a. (1) AC applied to the nose cone; (2) the base body of the cantilever beam; (3) the cantilever bean with its tip; b. & c. the cantilever driven to oscillate in sinusoidal motion.

A small scanner (max scan size 9 µm × 9 µm) with Aluminum (Al) coated tip was used for scanning the samples. Prior to the experiments, the tip sensitivity was calculated. The sensitivity (S) of the tip is the ratio of deflection of cantilever to the applied amplitude. The tip was calibrated for sensitivity with respect to a mica surface and the tip sensitivity is 66.4 nm/V. A setpoint voltage (V) of 0.4 V was used for the accelerated aging study. Thus the applied tip force F_{tip} was obtained as 1.275 µN using Equation (1). The SiNWs samples were then loaded into the AFM for scanning and measurement of the diameter changes. In order to maintain the surface integrity, the AC mode (Non-contact/ Intermittent Contact) scanning was used. Fig. 2 below shows a cross section of a SiNW after 30 minute exposure to 80 ^{o}C.

$$F_{tip} = S \times F_C \times V \quad (1)$$

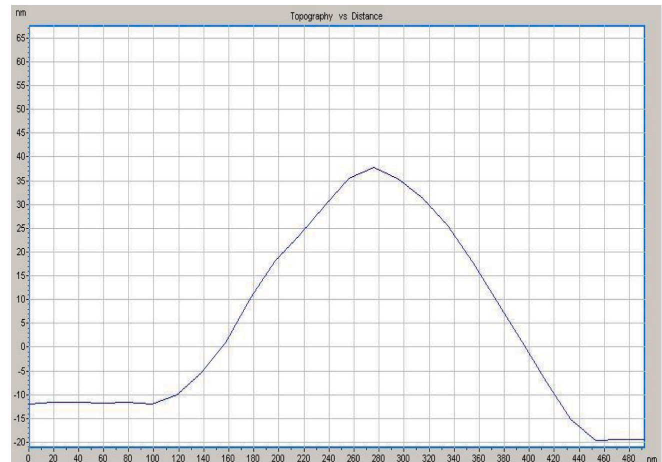

Fig. 2 A cross section of a SiNW after a 30 minute exposure to a 80 ^{o}C environment which shows a diameter of ~45nm

The SiNWs were first located by using a wide scan area (8 µm × 8 µm) and smaller scan areas were chosen for measurements based off of the number of SiNWs present in the area and the amount of surface debris which could create difficulties when taking cross sections of the SiNWs. The scan areas of the SiNWs after environmental chamber treatment are shown in Fig. 3. As depicted in Fig. 3, nanowires were all over the glass plane and once the nanowires were located, a traverse is drawn across the nanowire in order to obtain a two dimensional graph of the nanowire. The dimensional data can then be obtained from the graph. The peak of the curve from the baseline is the diameter of the nanowires and a traverse is drawn along the nanowires to obtain its length.

III. Current Results

In order to obtain precise and accurate results, dimensional data of 20 nanowires was collected and then averaged. The average length and diameter of the SiNWs after exposure to the environmental chamber, i.e, to temperature and humidity are given in Tables I and II respectively. The plots of the data in these tables are shown in Figs. 4 and 5 respectively. From Tables I and II, it can be seen that the diameters changed with aging treatments.

In the case of SiNW samples in the temperature exposure experiment, the swelling is likely caused by oxidation of the Si at the surface. TEM imaging measurements of a SiNWs aged at 50°C showed that the oxide layer thickness had increased to 14.22 ± 1.12 nm, which is significant.

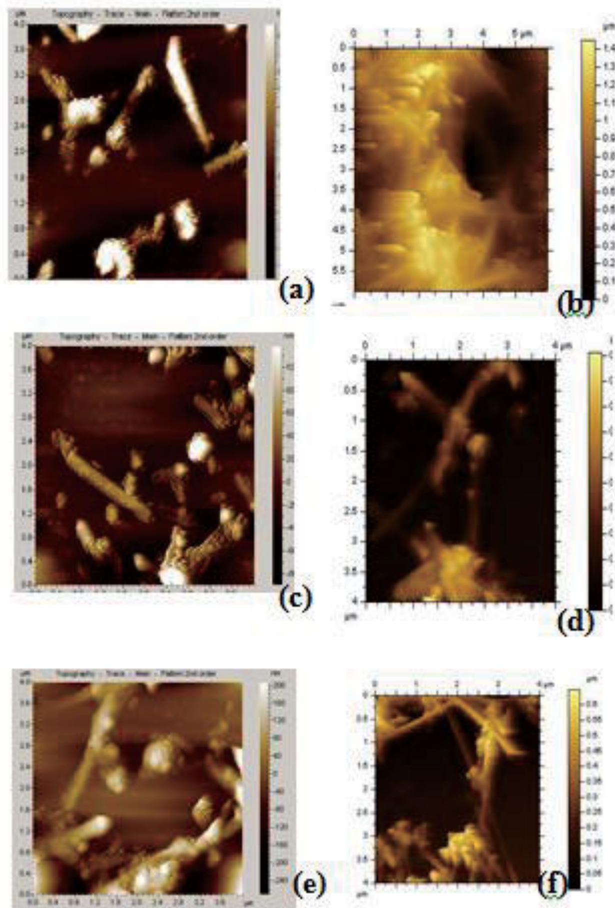

Fig. 3 (a) Scan image of nanowires after treatment at 70% RH. (c) Scan image of nanowires after treatment at 80% RH. (e) Scan image of nanowires after treatment at 90% RH. (b) Scan image of the nanowires after treatment at 50°C. (d) Scan image of nanowires after treatment at 100°C. (f) Scan image of nanowires after treatment at 150°C.

TABLE I
AVERAGE DIMENSIONAL DATA COLLECTED FROM AFM AFTER TREATMENT AT DIFFERENT TEMPERATURES.

Temperature (°C)	Average Diameter (nm)	Length (µm)
22	37.21	1.22
30	41.43	1.31
40	47.17	1.41
50	46.90	1.44
60	49.54	1.15
70	49.11	1.19
80	48.41	1.33
90	49.92	1.11
100	52.33	1.25
110	54.47	1.39
120	56.61	1.48
130	58.60	1.39
140	61.47	1.38
150	64.50	1.46

TABLE II
AVERAGE DIMENSIONAL DATA COLLECTED FROM AFM AFTER TREATMENT AT DIFFERENT RELATIVE HUMIDITY.

Humidity (%RH)	Average Diameter (nm)	Length (µm)
20	39.45	1.42
30	43.35	1.21
40	45.70	1.44
50	47.70	1.22
60	49.21	1.05
70	51.95	1.30
80	54.65	1.42
90	60.15	1.00

Further research is needed to model the mechanics for changes in physical and mechanical properties as the systems age. Future tests for these samples include a chemical profiling of the SiNW surface after high humidity and acid exposure via energy dispersive X-ray spectroscopy (EDX) in order to pave the way for specific removal of post exposure build up. Due to the expansive nature of SiNWs when exposed to process conditions typical to biomedical applications, biomedical devices using SiNWs should be designed with disposability in mind if such a selective build up removal is not available.

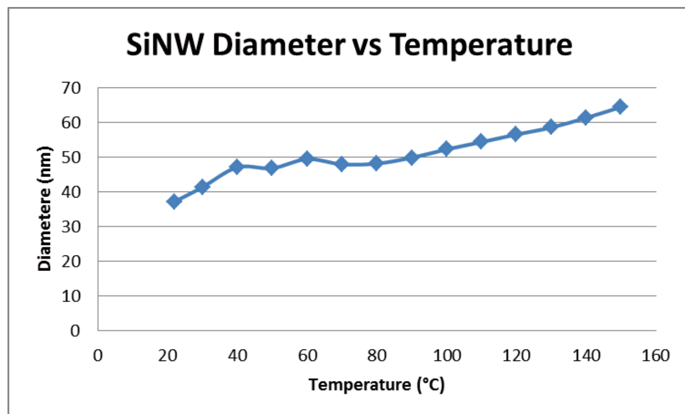

Fig. 4. Average diameter of the SiNWs as a function of temperature.

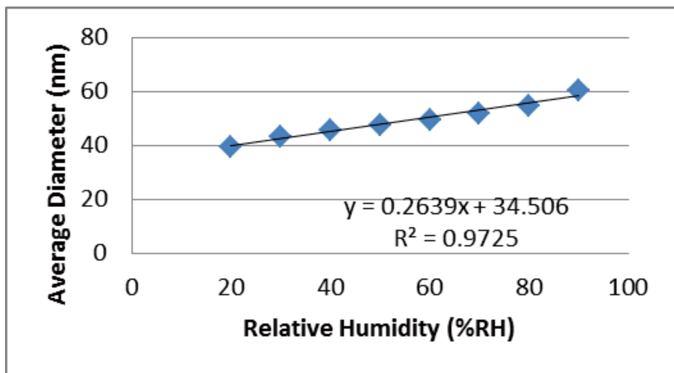

Fig. 5. Average diameter of the SiNWs as a function of relative humidity

REFERENCES

[1] [1] C. M. Lieber, Solid State Commun. 107 (1998) 607-616.
[2] J. Hu, T. W. Odom, C. M. Lieber, Acc. Chem. Res. 32 (1999) 435-445.
[3] C. Dekker, Phys. Today 52(5) (1999) 22-28.
[4] J. Voit, Rep. Prog. Phys. 57 (1994) 977-1116.
[5] C. Kane, L. Balents, M. P. Fisher, A. Phys. ReV. Lett. 79 (1997) 5086.
[6] (a) J. Hu, T. W. Odom, C. M. Lieber, Acc. Chem. Res. 32 (1999) 435-445. (b) C. M. Lieber, Sci. Am. 285 (2001) 50-56. (c) C. M. Lieber, MRS Bull. 28 (2003) 486-491.
[7] A. M. Morales, C. M. Lieber, Science 279 (1998) 208-211.
[8] Y. Cui, L. J. Lauhon, M. S. Gudiksen, J. Wang, C. M. Lieber, Appl. Phys. Lett. 78 (2001) 2214-2216.
[9] Y. Cui, X. Duan, J. Hu, C. M. Lieber, J. Phys. Chem. B 104 (2000) 5213-5216.
[10] J. Y. Yu, S. W. Chung, J. R. J. Heath, Phys. Chem. B 104(50) (2000) 11864-11870.
[11] Y. Cui, C, M. Lieber, Science 291 (2001) 851-853.
[12] Y. Cui, Z. Zhong, D. Wang, W. U. Wang, C, M. Lieber, Nano Lett. 3 (2003) 149-152.
[13] Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K. Kim, C. M. Lieber, Science 294 (2001) 1313-1317.
[14] Y. Cui, Q. Wei, H. Park, C. M. Lieber, Science 293 (2001) 1289-1292.
[15] K. J. Hemmerich, "General Aging Theory and Simplified Protocol for Accelerated Aging of Medical Devices" Proceedings of MDM-West January, 1997.
[16] G. Clark, "Shelf Life of Medical Devices" Guidance Document, Division of Small Manufacturers Assistance, CDRH, FDA, April 1991.
[17] S. N. Singh, M. Ntiru, K. Dedecker, “Long Term Thermal Resistance of Pentane Blown Polyisocyanaurate Laminate Boards” Proceedings of Polyurethanes Conference (2002) 19-26.
[18] CAN/ULC-S770-03. Standard Test Method for Determination of Long-Term Thermal Resistance of Closed- Cell Thermal Insulating Foams (2003) Underwriters Laboratories of Canada, Ontario, Canada.
[19] J. E. Christian, A. Desjarlais, R. Graves, T. L. Smith, “Five-year Field Study Confirms Accelerated Thermal Aging Method for Polyisocyanurate Insulation” Proceedings of the Polyurethane (1995) 314-322.
[20] M. T. Bomberg, M. K. Kumaran, “Laboratory and Roofing Exposures of Cellular Plastic Insulation to Verify a Model of Aging” ASTM-STP 1224 (1994) 151-167.
[21] M. K. Kumaran, M. T. Bomberg, Journal of Thermal Insulation 14 (1990) 43-57.
[22] L. Ross, J. Clinton, J. Hogan. “Polyiso Insulation: Leading the Way to Long Term Thermal Resistance (LTTR) Values” Proceedings of the Polyurethane Expo (2002) 370-373.

Author contact info: U. C. Wejinya is with the Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701 USA (corresponding author to provide phone: 479-575-4800; fax: 479-575-6982; e-mail: uwejinya@uark.edu).

Z. Dong is with the Department of Civil & Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, IN USA (e-mail: zdong1@nd.edu).

N. Willems is with Microelectronics and Photonics Graduate Program, University of Arkansas, Fayetteville, AR 72701 USA (e-mail: nmwillem@uark.edu).