Chapter 10

Carbon Nanostructure-Based Scale Sensors Using Inkjet Printing and Casting Techniques

Hammad Younes, Amal Al Ghaferi and Irfan Saadat

Additional information is available at the end of the chapter

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Abstract

In this chapter, the fabrication and characterization of scale sensor using carbon nanotubes (CNTs) are discussed. Two different methods are used to prepare the carbon nanomaterials for the sensor fabrication: CNT casting and the CNT inkjet printing. In addition, the sensors are integrated into Kelvin architectures. The electrical resistance of the carbon nanomaterial films is measured with and without adding a drop of brine to the surface of the film. The films are characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS). Electrical resistance of the casted CNT films and five layers of CNT inkjet printing are found to be close to 40.0 kΩ and 1.00 kΩ, respectively. Adding one drop of brine solution on the surface of the casted CNT film and five layers of CNT inkjet printing changed the resistance by 50% and 75%, respectively. The resetting process is done for all sensors by soaking in deionized water (DI water) for some time, and the electrical resistance is measured and found to be close to the initial electrical resistance.

Keywords: CNTs, Sensors, inkjet printing, smear casting, scale and electrical resistance

1. Introduction

Carbon nanotubes (CNTs) are an important new class of nano-2-D and nano-1-D materials that have numerous novel and useful properties. Their nanostructures exhibit many interesting and often unique properties, and hence, they can be used in many novel technological and industrial applications. Due to their unique electrical and electronic properties, CNTs are considered for various next-generation device applications, that is nanofluids [1–3], scanning probes

[4], nanocomposites [5–9], grease [10, 11], electron magnetic shielding interface [12–16], solar thermal absorbers [17] and sensors [18–22]. The electrical resistance of the carbon nanomaterials changes when chemicals in the surrounding make covalent or non-covalent interaction with the carbon nanomaterials. This change makes carbon nanomaterials good candidates for chemical sensors. The absorbed molecules act as dopants that cause shifting on the Fermi energy of the carbon nanomaterials. In addition, the bonds formed between absorbed chemicals and the carbon nanomaterials change the band structure of the tube [23].

Scale is the creation of inorganic soluble salts from aqueous brines during oil and gas production, which deposits at the internal surface of the pipelines under the supersaturating conditions [24]. Calcium carbonate ($CaCO_3$) and barium sulfate ($BaSO_4$) are the most insoluble types of inorganic scale formed during the extraction of oil. The deposition can be seen not only in the pipelines but also in water-handling equipment, pumps, valves, and any other parts that interact with water. The deposition of the scale leads to unavoidable damage of the equipment parts. Therefore, suspension of oil operations becomes essential in order to replace the damaged parts. In the petroleum industry, such interruptions lead to extremely high costs [25].

There has been multiple studies and research conducted on scale monitoring, testing, and optimization of inhibitors [26–28]. In general, these studies focused on the development of using new sensor materials that enabled monitoring and offline testing [29–32].

This chapter discusses the sensitivity and selectivity of using carbon nanotubes through two different preparation methods: the smear casted and the inkjet printing, to create sensors that detect scale in oil and gas pipelines. Moreover, the design and the microfabrication method of the sensors are discussed.

2. Experimental

Single-wall carbon nanotubes (SWCNT) were purchased from Sigma–Aldrich, Inc., USA. The CNT inkjet "CNTRENE® 3015 A3-R" used for this printing was purchased from Brewer Science, Inc., USA. DMP2831 Inkjet Printer was used to print the CNT inkjet. The chemical surfactant sodium dodecyl benzene sulfonate (NaDDBS) was purchased from Sigma–Aldrich. Epoxy resins and hardener were purchased from West System Inc, Zayed port, Abu Dhabi. Releasing agents, Frekote, were purchased from Logistics Company Limited, in Dubai, UAE. Sonication was performed using a Branson Digital Sonifier, model 450. Scanning electron microscopy (SEM) images were acquired using the backscattered electron detector on a Zeiss Supra40VP variable pressure system. The electrical conductivity was obtained using Elite 300 Semi-automatic Probe Station & Keithley 4200-SCS Parameter Analyzer. The microstructures of the samples were probed by scanning electron FEI quanta 250 ESEM and the FEI Nova NanoSEM 650. Atomic force microscopy data were obtained using (Asylum MFP-3D, AFM) deflection 1.5 V, scan speed 0.7 Hz, applied voltage 500 V, contact mode imaging.

Casted technique: The epoxy used was a pre-polymer consisting of bisphenol A attached to an epoxide group. Sodium dodecylbenzenesulfonate (NaDDBS) surfactant was added to epoxy with a weight ratio of four times carbon nanotubes and mixed manually for 5 min. The mixture was then sonicated until the surfactant was dissolved completely, and a clear solution was obtained. About 0.5% of carbon nanotubes were added to the mixture and sonicated again. The mixture was then mixed manually for 5 min with hardener by weight ratio of 10:2.63. Glass plate was coated with a layer of releasing agent (Frekote), and the mixture was casted on the glass plate by smear casting technique. The sample was cured at room temperature for 24 hours.

Carbon nanotube inkjet printing: CNT inkjet was used as it is, but the printing recipe was optimized in order to have a uniform continuous printing. CNT inkjet was printed on glass/silicon oxide substrates.

3. Results and discussion

3.1. CNT casting

3.1.1. Preparation of carbon nanotube-based scale sensor

As it has been discussed earlier, two types of preparation techniques for the CNTs have been used: smear casted and inkjet printing. The smear casting CNT nanocomposites were prepared by dispersing 0.5 wt% of CNTs in epoxy polymer using ultrahigh tip sonicator. Kelvin structure was then fabricated as can be seen in **Figure 1**.

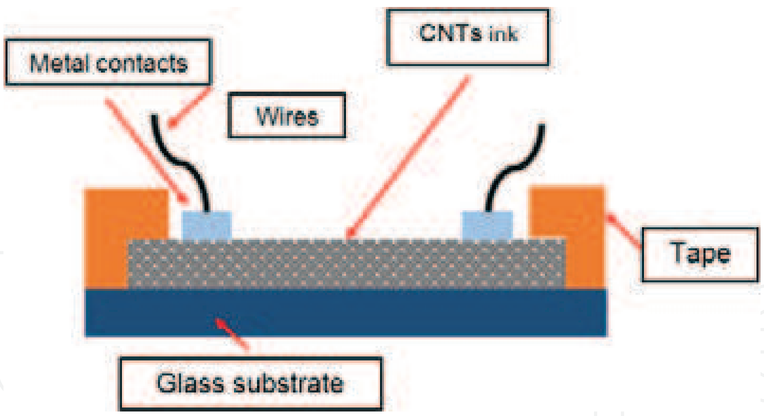

Figure 1. Kelvin structure for sensor device.

3.1.2. Characterization of carbon nanotube-based scale sensor

Figure 2 is a cross-sectional SEM image of the nanocomposites and shows that CNTs disperse very well in the epoxy polymer and make network structure essential for electrical conductivity. The electrical resistance of the prepared CNTs was measured just after the preparation and defined as resistance of original samples. The electrical resistance for samples were measured again after adding brine and defined as resistance with brine.

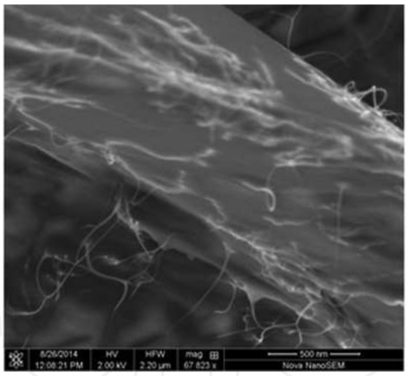

Figure 2. Images of cross section of the 1.0 wt% of CNTs in epoxy.

Figure 3 is an SEM image of the surface of smear casted CNTs. There are many white spots on the surface of the sample, so we selected one of the largest (marked with a red cross) to carry on the EDS, as shown in **Figure 4**. As it can be seen, the sample has sodium and chlorine, which indicates the presence of sodium chloride on the surface.

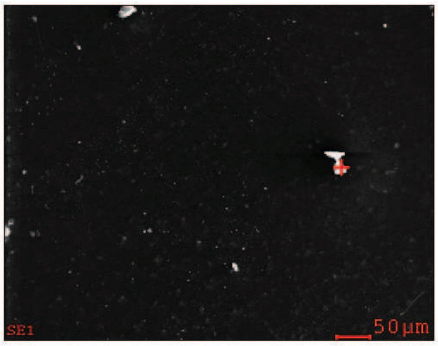

Figure 3. SEM image of the surface of smear casted CNTs showing a spot of NaCl.

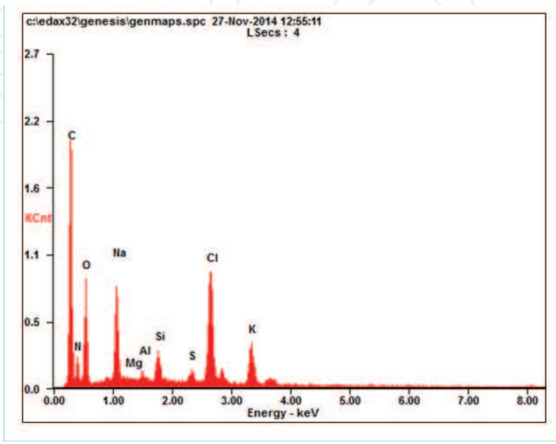

Figure 4. EDS spectrum for casted CNTs on a glass substrate.

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Conductive atomic force microscopy (C-AFM) was carried out for sample A, which is original, and for sample B that has brine. **Figure 5** shows that sample A has more tubes than B, which means that C-AFM of casted CNTs affirm that the material A is more conductive than B, and this matches the resistance curve depicted in **Figure 6**.

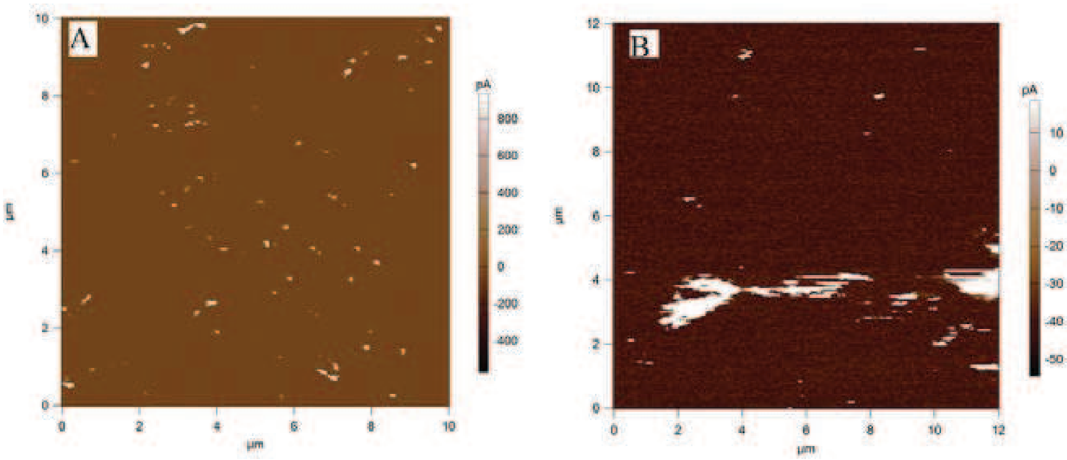

Figure 5. CAFM for current mapping of rough casted CNTs, A: original sample B: with brine sample.

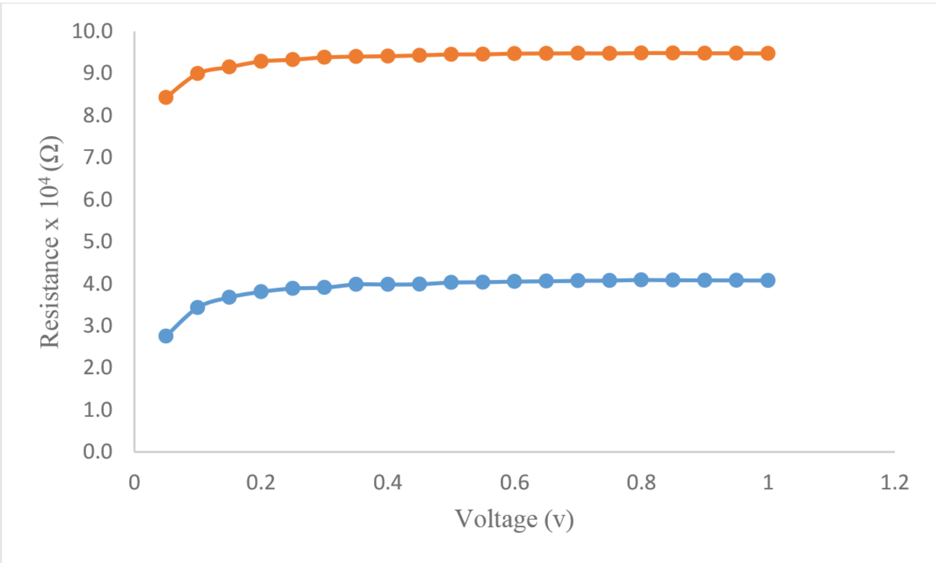

Figure 6. Electrical resistance of 0.5 wt% of smear casted CNTs.

3.1.3. Electrical resistance of carbon nanotube-based scale sensor

Figure 6 shows the resistance of the casted sample with sweeping voltage from 0 to 1.0. The resistance of the material seems to be very consistent with the swept voltage. Once one drop of brine solution was added to the surface of the smear casted CNTs, the resistance increased from 4.0 E+4 to almost 9.5 E+4 Ω. Chemical doping can induce strong changes in conductance. Such modifications can be easily detected by electron current signals, and these properties make CNTs extremely small sensors that are very sensitive to the surrounding chemicals.

3.2. CNT inkjet printing

3.2.1. Preparation of carbon nanotube-based scale sensor

The CNT inkjet “CNTRENE® 3015 A3-R” used for this printing was purchased from Brewer Science, Inc., USA. DMP2831 Inkjet Printer was used to print the CNT inkjet. About 1×1 cm^2 of CNT inkjet printing was printed on Si substrate. Ebeam evaporator was used to deposit 200 nm Al as metal contact using a shadow mask. The printing was carried out at different temperatures and a second curing cycle was applied to the printed samples to ensure a very staple printing.

3.2.2. Characterization of carbon nanotube-based scale sensor

After optimizing the printing recipe, it was critical to study the effect of the CNT printed layers on the electrical resistance; hereafter the sensor performance was assessed. About 3, 4, 5, and 6 layers of CNT inkjet were printed on Si substrates. The samples were characterized by measuring the electrical resistance of 4-point Kelvin-like structures and taking SEM and AFM images. **Figure 7** shows that 3, 4, 5, and 6 layers of CNT have the following electrical resistance, respectively: 5.5 kΩ, 4.2 kΩ, 1 kΩ, and 0.6 kΩ. This led us to conclude that while increasing number of printing passes, the electrical resistance decreases because the addition of CNT passes generates more paths for the electrons to go through and thus increases the conductivity.

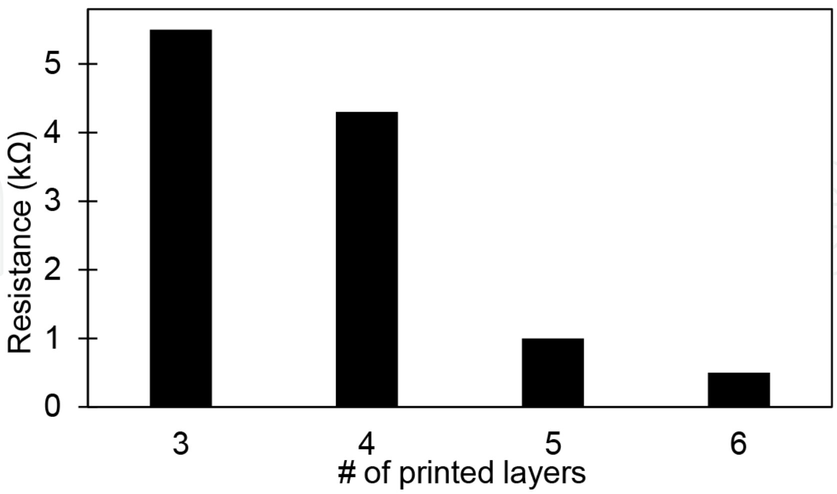

Figure 7. Electrical resistance as a function of voltage of multilayer CNT inkjet printing.

Figures 8 and **9** show SEM images for CNT inkjet printing of one and five layers of printing. The SEM images show that the CNTs are making network structures. SEM images of the five

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layers of CNT printing (**Figure 8**) shows more CNTs and thicker network structure than that of one layer of CNT printing (**Figure 7**), as expected.

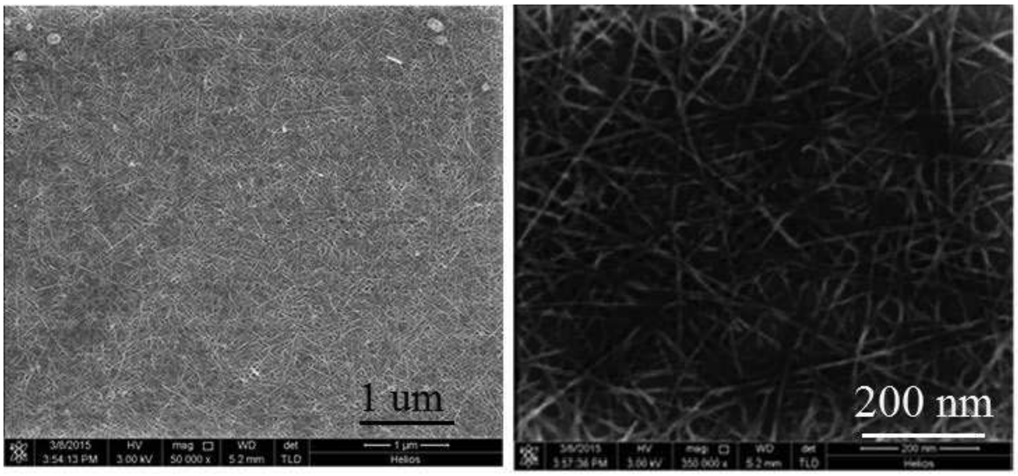

Figure 8. SEM images for one layer of CNT inkjet printed on Si substrate.

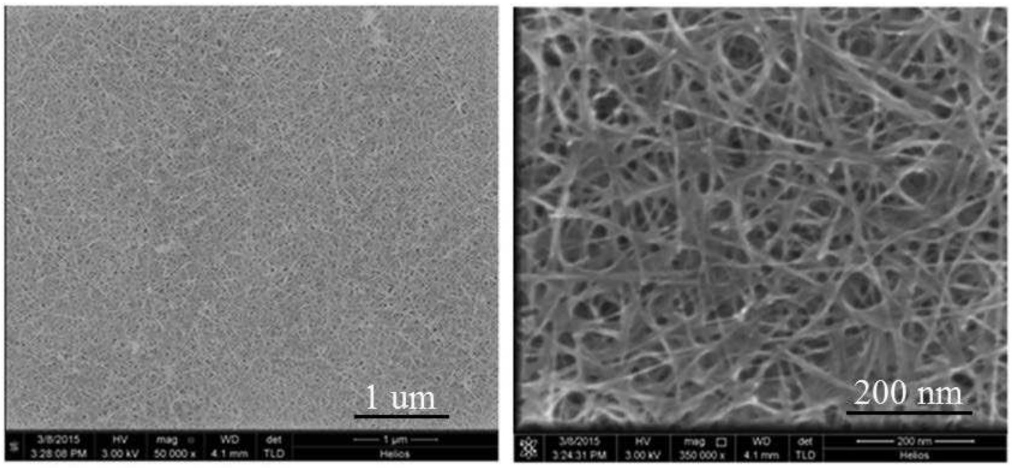

Figure 9. SEM images for five layers of CNT inkjet printed on Si substrate.

The ultimate goal of this study was to fabricate a sensor that can be used in oil and gas pipelines, which is a very hostile environment. Therefore, the sensor should be stable enough to sustain consistent results within the harsh conditions found in the pipelines. The stability of the CNT inkjet printed on silicon substrate was tested by immersing it in a solvent for some time and then obtaining SEM images, to examine the effect of the solvent on the printing.

Images obtained using tapping-mode AFM (**Figures 10** and **11**) indicate that exposure to water for 72 hours does not have pronounced effects on the topography of the sample, in the case of inkjet-printed CNT films. The roughness of the inkjet-printed CNT decreased as a result of the exposure (**Figure 8**) by 26.3%. The roughness analyses were carried out on images obtained using tapping-mode AFM topography scans.

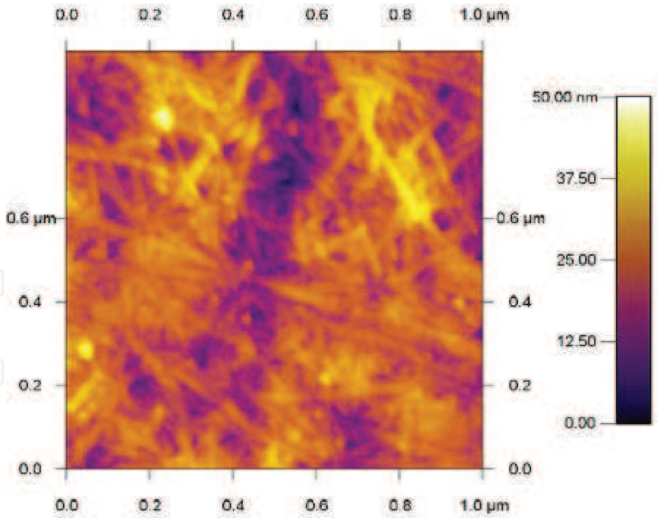

Figure 10. AFM images of five layers of CNT inkjet printed on silicon oxide substrate.

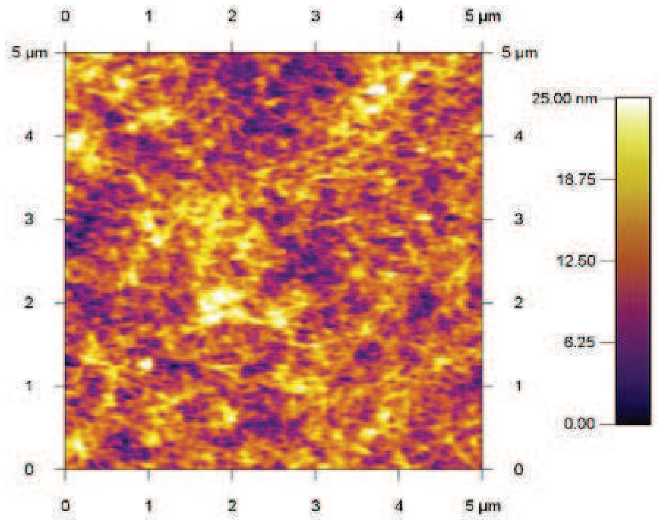

Figure 11. AFM images of five layers of CNT inkjet printed on Si substrate after 72 hours of soaking in DI water.

3.2.3. The resetting process of carbon nanotubes-based scale sensor

Figure 12 shows the ability of the resetting film (made of CNT inkjet printing) to reset the resistance values. The resetting process is the ability of the film to get back to its primitive condition after soaking it in DI water. The electrical resistance of the CNT 5 passes printed film is 1.0E+03 Ω; by dipping the film for one hour in DI water, the electrical resistance decreased to 5.0E+02 Ω. This treatment is needed to remove the left over ink from the surface as mentioned earlier. This value is the resistance of the optimized original sample and is thus used as the reference for the resetting process. Adding one drop of brine solution increases the electrical resistance up to 4.2E+03 Ω and decreases the sweeping voltage to 3.6E+03 Ω. By immersing the film for one hour in DI water, for the resetting process, we are able

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to obtain an electrical resistance very close to the electrical resistance of the original optimized sample.

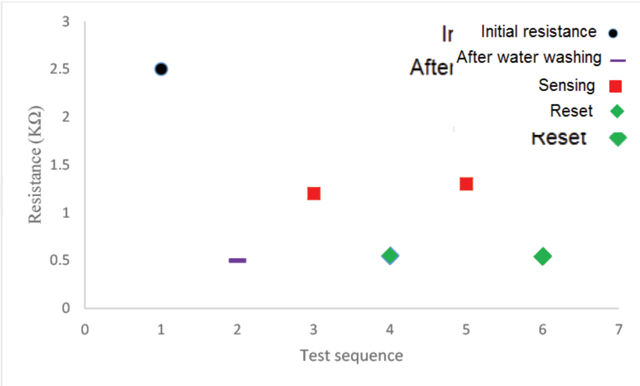

Figure 12. Ability to reset the resistance values for five layers of CNTs printed on silicon oxide substrate.

4. Conclusion

In summary, this chapter discussed the chemical sensing properties of CNTs obtained through smear casting and CNT inkjet printing techniques have been studied and compared. It was shown the ability of these films to be used for sensing salts, which are the precursors for the scale deposition. This was assessed through the modulation of the change in electrical conductance in the presence of various media. The SEM images showed that both CNT smear casted and the CNT inkjet printing were dispersed very well among the matrix and made a network structure. The results of these studies indicated that: (a) in case of casting, adding brine solution on the surface of the CNT casted films increased the resistance from 4.0E+3 kΩ to almost 9.5E+3 kΩ; (b) for the inkjet printing, five printing layers of CNT films was critical to obtain a consistent electrical resistance. Moreover, washing the original CNT inkjet printing sample with water was a precondition step to stabilize the CNT inkjet printing and ultimately get consistent electrical resistance. The resistance of the CNT inkjet printing increased from 0.50 kΩ to 1.50 kΩ once the brine solution was added to the surface of the sample. The CNT inkjet printing sample was found to be stable even after more than 48 hours of soaking in water.

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Author details

Hammad Younes[1*], Amal Al Ghaferi[1] and Irfan Saadat[2]

*Address all correspondence to: hyounes@masdar.ac.ae; hasy193@yahoo.com

1 Department of Mechanical and Material Engineering, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates

2 Department of Electrical Engineering and Computer Science, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates

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