Humidity SAW Sensor Sensitivity Enhancement via Electrospraying of Silver Nanowires

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science in Industrial and Systems Engineering.

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Humidity SAW Sensor Sensitivity Enhancement via Electrospraying of Silver Nanowires

Farid Sayar Irani

Abstract

In this research we investigated the influence of surface coatings of silver nanowires the sensitivity of SAW (Surface Acoustic Wave) humidity sensors. Silver nanowires, with PVP (Polyvinylpyrrolidone), which is a hydrophilic capping agent, were chemically synthesized with an average length of $15\mu m$ and an average diameter of $60nm$. Humidity sensors, with a 433 MHz frequency dual-port resonator Rayleigh-SAW devices were coated bye AgNWs (Silver Nanowires) using the electrospray coating method. It was demonstrated that increasing thickness of coated AgNW on the surface of SAW devices results in increased sensitivity. The highest frequency shift (262 kHz) in these SAW devices was obtained with injection of 0.5 ml of the solution with concentration of 0.5 mg/ml in injection rate of 1 ml/h. It also showed the highest humidity sensitivity among the other prepared SAW devices.

Keywords: Humidity sensor, Silver nanowire, Surface Acoustic Wave (SAW) sensor, Electrospray

Gümüş nanotellerin elektrosprey aracılığıyla SAW nem sensör hassasiyeninin geliştirilmesi

Farid Sayar Irani

Öz

Biz bu çalışmada, yüzey akustik dalga nem sensörlerinin (SAW) hassasiyeti üzerinde gümüş nanotellerin yüzey kaplamalarının etkisini araştırdık. Ortalama 60 nm çapında ve 15 μm uzunluğunda üzerleri polyvinylpyrrolidone (PVP) ile çevrili olan gümüş nanoteller kimyasal olarak sentezlendi. Nem sensörleri, 433 MHz frekansında çift girişli rezonatör Rayleigh-SAW cihazıyla, elektrosprey kaplama metoduyla gümüş nanoteller ile kaplandı. Sensör üzerindeki gümüş nanotellerin kaplama kalınlığının artması sensörün hassasiyetinin artmasına yol açmıştır. Bu sensörler ile en yüksek frekans kayması (262 kHz) 0.5 ml hacminde, 0.5 mg/mL gümüş nanotel konsantrasyonunda ve 1 mL/h enjeksiyon hızı uygulandığında elde edilmiştir. Bu çalışma daha önce SAW sensörleriyle hazırlanan nem sensörleri arasındaki en yüksek hassasiyeti göstermiştir.

Anahtar Sözcükler: Nem sensörü, Gümüş nanotel, Yüzey Akustik Dalga sensörü, Elektrosprey

I dedicate this work to my beloved parents, whose encouragement and support helped me to reach the point where I am

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Abbreviations

LAH	**L**ist **A**bbreviations **H**ere
SAW	**S**urface **A**coustic **W**ave
PVP	**P**oly(**V**inyl **p**yrrolidone)
LOD	**L**imit**O**f **D**etection
LOQ	**L**imit **O**f **Q**uantitation
RH	**R**elative **H**umidity
PPM	**P**arts **P**er **M**illion
QCM	**Q**uartz **C**rystal **M**icrobalance
QTF	**Q**uartz **T**uning **F**orks
FBAR	**F**ilm **B**ulk **A**coustic **R**esonators
MEMS	**M**icro**e**lectro**m**echanical **S**ystem
EG	**E**thylen **G**lycol
IDT	**I**nter-**Digital** **T**ransducer

Chapter 1

General Introduction

1.1 Sensing and Sensors

Analytical chemistry and analytical techniques are necessary tools in the exploration of the world surrounding us [1]. Intellectual information structure can produce theories which needs a dependable input data. Therefore the quality of this information is crucial [2]. A sensor is a device, which measures a chemical or physical quantity and converts it into a signal that can be read by an observer or by an instrument, thus sensors can be classified according to the type of energy transfer that they detect, for example, electromagnetic and chemical [3]. Essential qualities for and effective sensors are mentioned in following:

- Selectivity: be able to detect one specific species among presence of various chemical species,
- Reproducibility: it is key that the sensor can be trusted to give the same signal/output value for a certain set of conditions over the course of its lifetime.
- Accuracy: giving a correct concentration of the species being detected, ensuring that the output value that the sensor provides is as close as possible to the true value.
- Sensitivity or the limit of detection (LOD): the minimum signal that can be taken as a meaningful measurement, and

- Limit of quantitation (LOQ): the signal, at which quantitative results can be reported with a high degree of confidence, should be known.
- Reversibility: ideally the sensing process should proceed equally well in both the forward or reverse direction i.e. when the analyte is removed the sensor's response should return to the baseline.
- Stability: the characteristics of sensor should be stable when it is utilized in different conditions and environments.
- Linearity: over the desired measurement range the sensor's response should be linearly proportional to the concentration of analyte [3, 4].

1.2 Humidity

Humidity is widespread component in our environment which a makes it absolutely vital health, human comfort and several industries and technologies [5].
Humidity measurement determines the amount of water vapor exist in a mixed gas, like air, or a pure gas, such as nitrogen or argon. The most commonly units used in measurement of humidity are Relative Humidity (RH), Dew/Frost point (D/F PT) and Parts Per Million (PPM) [6].

"**Relative Humidity (RH)** is the ratio of the partial pressure of water vapor present in a gas to the saturation vapor pressure of the gas at a specified temperature"

$$RH\% = \frac{P_V}{P_S} \times 100 \tag{1.1}$$

"**Absolute Humidity** units are applicable for the primary measurement results inasmuch as one is able to directly measure the value of the water vapor content."

$$AB = \frac{m_w}{v} \tag{1.2}$$

"**Dew Point**, is the temperature and pressure at which a gas begins to condense into a liquid expressed in °C or °F,"

1.3 Humidity sensors

Using of humidity sensors in industrial processing has increased. Besides, it plays an important role in environmental control. In industries such as semiconductor production,during wafer processing, humidity should be controlled continually when a highly advanced integrated circuit is producing. Humidity control is also applicable in home life such as in microwave ovens during cooking and level of humidity in buildings. Humidity sensors have different applications in medical field as well, such as in respiratory equipment, sterilizers, incubators, pharmaceutical processing, and biological products.

In agriculture humidity control has different applications, in a cereal storage or amount of moisture in soil. In addition green-house air conditioning and dew prevention in plantation protection requires controlling of humidity.

There are other examples of humidity control in industry which show importance of humidity sensor usage in our life, such as film desiccation,oven and dryers atmosphere, chemical gas purification and production of textile and paper.

Humidity measurement in manufacturing industries is crucial because it may affect the business cost of the product and the health and safety of the personnel. [7] Sensor sensitivity is a key factor in obtaining precise measurement results and as a consequence helps control the product costs. [8]

There are three groups of humidity sensors. Electronic sensors, Optic sensors and Acoustic sensors. The most common type of sensors is electronic one.[9]

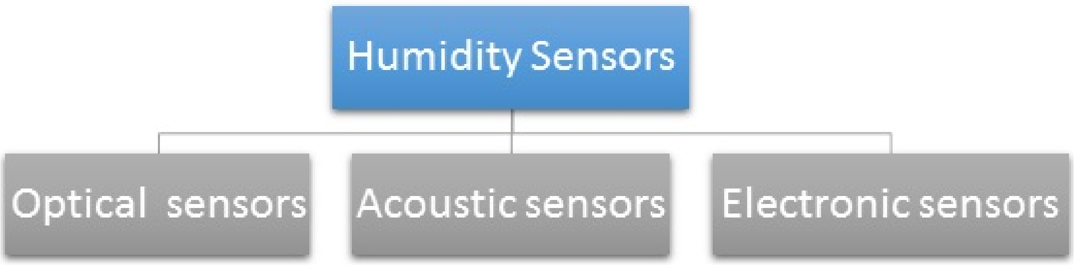


FIGURE 1.1: Types of Humidity Sensors

1.3.1 Electronic Sensors

These days electronic sensors re used more than any other types of sensors in the world-wide market. The first generation of mechanical humidity sensors were changed to electrical sensors during a longtime. The detection in these sensors is based on changes in resistance or capacitance of humidity-sensitive film.

Although electronic sensors have two main advantages which are low price of the interrogation module and the relatively simple design. They have several disadvantages like their response time which is almost long and varies from several tenth of seconds to minutes. They need regular calibration and measurement would be difficult for relative humidity below 5%. In addition, sometimes it is impossible or difficult to use them in environments which are hard to access or atmospheres which are likely to explode and electromagnetic zone

In the electronic sensors, Impedance of the device is changed with absorption of water vapor into a hydrophilic layer. Changes would be measured by the contacts that are applied to the layer.

The sensors response time is typically in the range of 5 to 60 s. The response is good enough for many applications, however, in some other areas, such as breathing sensors, it is too long. The accuracy does not work in high and low RH percentages (around 0% RH and 90% RH) and only in few percentages is reliable.

Depending on whether these sensors work by changing in their resistance or capacitance, they are classified into two groups which are described in the following subsections; [9]

1.3.1.1 Capacitance change-type humidity sensors

They consist of two conductive electrodes and a substrate between them. A polymeric or metal oxide thin film is deposited on the substrate. The materials to make these substrate are normally glass, silicon, or ceramic. In capacitive humidity sensors, the dielectric constant is changed incrementally with increasing of humidity. This change is almost directly proportional to relative humidity of environment around the sensor (see 1.3-a). Basic structure of capacitive type humidity sensor is shown in Figure 1.2.

FIGURE 1.2: Basic structure of capacitive type humidity sensor [10]

Numerous capacitance-change humidity sensors have been designed and produced with interdigitated gold, platinum or silver electrodes. Moreover, different materials such as Organic polymer, porous silicon and alumina are deposited as thin film on a ceramic substrate. [10].

Typically the capacitance of the films, for 1% RH change, varies 0.2-0.5 pF, while this value is between 100 and 500 pF at 50% RH for the bulk capacitance at room temperature [11]. Performance of these sensors at high temperature ambient is as well as low temperature which can tolerate up to 200 °C and they recover perfectly from condensation[12]. Today, about 75% of humidity sensors on the market are capacitive humidity sensors[13]. These sensors have wide application in the commercial, industrial and weather telemetry fields.

Vaisala in Finland [5], with development of thin film in a capacitive humidity sensor obtained a rapid response time of 1 s to reach 90% of out put value.

1.3.1.2 Resistive humidity sensors

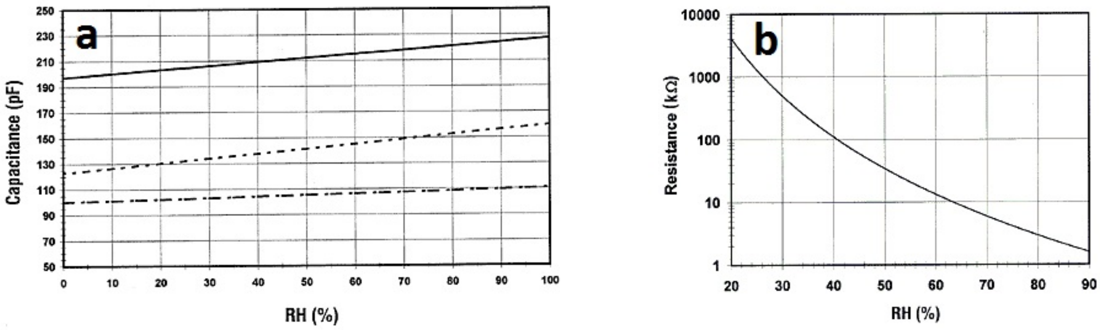
The electrodes in these sensors are mostly made of noble precious metals. They are deposited on a substrate which is usually glass or ceramic, by thick film printing techniques or thin film deposition.

In most of resistive sensors the type of electrodes is interdigitated (interdigital). The thin film which is sensitive against humidity is coated between these electrodes [10].
In these sensors resistance value responds exponentially against changes in humidity.

Figure 1.3 exhibits basic structure of resisitive type humidity sensor.

FIGURE 1.3: Basic structure of resistive type humidity sensor

The impedance change is typically an inverse exponential relationship to humidity, and almost varies from 1 $K\Omega$ to 100 $M\Omega$ (see Figure 1.4) [10].



[10]

FIGURE 1.4: "(a)A near-linear response is seen in this plot of capacitance changes against applied humidity at 25 °C (b) The exponential response of the resistive sensor at 25 °C"

In resistive sensors, an increase in electrical conductivity happen when ionic functional groups dissociate by absorption of water vapor molecules. The response time for most of these sensors varied from 10 to 30 s for a 63% step change. The typical resistive elements impedance ranges from 1 $k\Omega$ to 100$M\Omega$ [14].

1.3.2 Optic Sensors

This sensor use an optical fiber as a sensing element for measuring. These kind of sensors are known as intrinsic sensors.

The first optical fiber commercially produced during the 80th decade. After that, many researches were conducted on optical sensors and its potentiality. Electronic sensors have difficulty or they are unable to work in certain environment or applications. Optical

sensor could be a viable alternative for electronic sensors.
Optic sensors could be a viable alternative to electronic sensors in places using corrosive material. Moreover, because of their lack of electricity, there is no spark surrounding them and it would be safe to monitoring inflammable liquid or gases [15].
The great advantage that optical sensors have over electrical sensors, is that nearby electric or magnetic fields can not have adverse effect on it [**?**].

The other advantages of optical sensors is their fast response in compare to electrical sensors. Moreover, there is no electric contact that sensed substance could damage it [16].

25 years ago, the first research on optical sensors was started. In most of fiber optic humidity sensors a hygroscopic material is used which is usually diposited on a section or on the tip of the optical fiber. Optical properties of these materials are changed by humidity, as a result, a feature of the light which passes from them get modified and turned to a detectable signal [17].

In a research, Bedoya [18] has discussed an optical humidity sensor contain an indicator dyes and works based on its optical properties.

1.3.3 Acoustic Sensors

Humidity measurement by acoustic methods is categorized as one of the mechanical methods.This technique is based on vibration frequency of acoustic devices when water molecules are absorbed or adsorbed. Different methods have existed for measurement of humidity in acoustic sensors which are based on "surface acoustic waves (SAW), the change in the resonance frequency of a quartz crystal microbalance (QCM), quartz tuning forks (QTF) and film bulk acoustic resonators (FBAR) technology which are in category of mass-sensitive humidity sensors" [19].

Mass sensors have major advantages in compare to other types of sensors. Their design and production is very simple. They have low weight, and the power they require is very low. Besides, in this measurement, the results which are obtained are based on frequency shift which is accurate and totally reliable [19].

1.3.3.1 QCM

QCM is the most popular mass sensor which is very stable and sensitive. An extremely small mass change on nano gram scale could be measured by these sensors through variation in frequency of a quartz crystal resonator [20, 21].

1.3.3.2 QTF

Earlier a cost-effective and plain alternative for QCM sensors were QTFs. Their sensitivities are comparable As resonant frequency in QTF is affected by mass adsorption, sensitivity is comparable with QCM. However, QTF has several advantages such as more stable resonant frequency and significantly lower cost. In addition, since QTF working frequency is extensively lower than QCM (up to a hundred kHz for QTF and from one to several dozens of MHz for QCM), simpler electronics are used. [22].

Xiaofeng Zhou et al. [23] demonstrated sensitivity of QTF improve by coating a layer of ceramic film on it, while it has no response against humidity variation. Water vapors are adsorbed on the large surface of QTF film surface with capillary pores. Increase in humidity level leads to decrease in resonant frequency of QTF.

1.3.3.3 FBAR

"FBAR and QCM have the same mechanism of action the QCM is produced in a top-down process and FBARs in a bottom-up process using thin-film technology." Therefore, thinner FBARs can be developed, which higher resonance frequency would be obtained. Resulted frequencies from FBARs are varied form MHz to GHz.

An alternative is the Shear Horizontal-Surface Acoustic Wave (SH-SAW) device which includes a pair of inter-digitated transducers (IDTs). They can detect the surface shear horizontal waves which are produced by converting electrical to acoustic energy and vice versa.

1.3.3.4 Plate Acoustic Waves (Lamb waves)

Recently, Lamb wave devices have also gained attention due to their high velocity, high quality factor (Q), and large coupling [24].

1.3.3.5 Surface Acoustic wave (SAW)

Surface acoustic wave (SAW) resonators are a type of sensors with high sensitivity to changes occurred on/in the surface, including temperature, humidity, mass loading, electrical field etc. . [25]
Sensing in resonating device occurs when a layer of material is deposited between emitting and detecting IDTs on the surface of the device, due to changes in mechanical properties of the device which result in alter in the amplitude and velocity of the propagating wave [26].

In general, the material which are used in SAW sensors are Organic molecules or polymers. Velocity of surface waves is changed when these materials absorb water molecules. Hence, using new hydrophilic materials have gained great attention. Moreover, Many studies have done in order to improve the surface quality of the sensor [9].

Hoang-Si Hong with Gwiy-Sang Chunget al. [27–29] have used AlN films as a piezoelectric substrate and cover it with different nanostructured metal oxide as a sensitive layer to fabricate SAW-based umidity sensors. AlN films because of their attractive characteristics such as superior temperature, the high-acoustic velocity and chemical stability is a good choice as a piezoelectric substrate in SAW applications.The results of experiments showed that the obtained velocity on an uncoated AlN film was about 5136 m/s and on a metal oxide coated AlN film was 5032 m/s [27].
"Surface acoustic wave sensors are a class of microelectromechanical systems (MEMS) which rely on the modulation of surface acoustic waves to sense a physical phenomenon."

The sensor takes and electrical signal and convert it into a mechanical waves which, unlike an electrical signal, a physical phenomena can influence it easily. Then the altered wave would be converted back to electrical signal by device. Measuring the difference between input and output electrical signals, in amplitude, phase, frequency, and time-delay, illustrate the presence of the desired phenomenon.[30]

The SAW velocity can be affected due to three basic interactions, i.e. operational mechanisms, namely: [30]

- The change in the film mass due to the adsorption of gas molecules in the film material. This effect is referred to as the mass-loading effect
- The change in the conductivity of the film due to the interaction between the associated electric field with the SAW in the piezoelectric substrate and the charge carriers in the film material. This is brought about by interaction with the target gas molecules. This effect is referred to as the acoustoelectric effect
- The change in the mechanical properties of the film material due to the adsorption of gas molecules which might induce a swelling in the film. This swelling induces a change in the shear and bulk modulus of the film and/or induces a change in the film thickness. This effect is referred to as the viscoelastic effect

"These 3 effects can contribute to the change in the SAW velocity according to the formula": [31, 32]

$$\frac{\Delta V}{V_0} = -Cmf_0\Delta(\frac{m}{A}) + 4C_\epsilon\frac{f_0}{V_0^2}\Delta(hG') - \frac{k^2}{2}\Delta[\frac{\sigma_0^2}{\sigma_0^2 + V_0^2C_0^2}] \tag{1.3}$$

in which Cm and C_ϵ are the coefficients of mass sensitivity and elasticity of the substrate, respectively, (m/A) is the change in mass per unit area, f, is the fundamental frequency of the SAW device, h is the film thickness, G' is the real part of the shear modulus, K2 is the electromechanical coupling coefficient (a measure of the piezoelectric strength of the substrate material), $\sigma 0$ is the sheet conductivity of the film, $c_0 = \epsilon_p + \epsilon_a$ is the capacitance per unit length of the SAW substrate material with ϵ_p, and ϵ_a being permitivities of the substrate and free space respectively, and k is the wave number ($k = 2\Pi/\Lambda, \Lambda$ is the acoustic wavelength)

The mass loading Δm can be calculated as

$$\Delta m = C_sV_f$$

where C_s is the concentration of the solution of the sensitive material, and V_f is the volume of the sensitive material. Due to mass loading, a frequency shift occurs, which can be calculated as follows:

$$\Delta f = k^2 f_0^2 \frac{\Delta m}{A}$$

where k is the constant of the piezoelectric substrate, f_0 is the unperturbed resonant frequency of the SAW oscillator, and A is the sensitive film area [31, 32].

1.4 Humidity sensing material

In order to build a sensor with a high sensitivity for a certain gas, the chemical coating material should be chosen carefully to assure interaction between the target gas and the chemical coating material [30].

Humidity sensing materials can be grouped into two types; ceramics and polymers. Both groups could stay stable in different conditions and could work in environments with various temperatures [33].

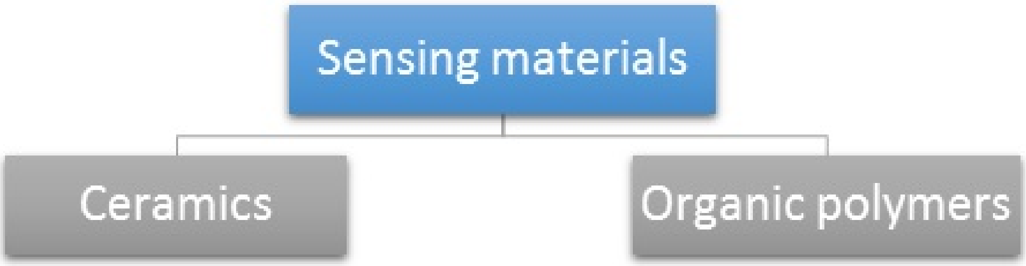


Figure 1.5

Polymeric materials or porous ceramics have been widely used to enhance the performance of the humidity sensors, as they increase the capability of absorbing water molecules either through their specific material properties or their significantly increased surface areas. [25]

1.4.1 Polymer Sensing Material

Compare to ceramics sensing materials, polymeric materials have several advantages. They have higher sensitivity and lower humidity hysteresis. Its construction requires low cost and it has flexibility and easy process-ability [34].

A good sensitivity was achieved with humidity sensors coated with polymeric material were obtained in 2009 using silicon-containing polyelectrolyte [35]. "A silicon-containing polyelectrolyte with crosslinking structure was deposited on a surface acoustic wave (SAW) resonator operating at 433MHz to construct a humidity sensor by the method of electrospray and heat treatment."

1.4.2 Ceramic Sensing Materials

Ceramics are chemical inert materials which make them great in various applications. They can be used either as a film or porous bodies. In humidity sensing, porous ceramics, because of larger capacity for adsorption of water, has more sensitivity than a film-type one.

The porous microstructure and the surface reactivity with water greatly impacts the performance of a ceramic humidity sensor [36]. Volume of pores in ceramic and distribution of them are known to be of foremost importance in order to gain a high humidity sensitivity [37]. "Changes in impedance of porous ceramics, resulting from various environmental humidities, are associated with the water adsorption mechanism on the oxide surface" [38, 39]. High porosity and a large surface area are advantageous to the sensitivity [40]. Some studies have also noted the importance of distribution of pores and its influence on the humidity-sensitive electrical response [37, 41].
In a work, P.M. Faiaet al. [42] used an emulsion of titania powders to fabricate a ceramic thick film humidity sensor by spin coating technique in a low speed.

1.5 Nanomaterial Based Humidity Sensors

Various nanomaterials such as nanoparticles and nanowires of different materials and carbon nanotubes are being used in Humidity sensors. Nanostructured materials as a sensor-sensitive material has attracted great attention in recent years because of their unique physical properties and applications.

The nanoparticles' physical and chemical properties are different of their bulk form, especially in metallic nanostructures. Because of this feature, they have become very interesting. With increasing in surface area of the nanomaterials, active interfaces increase, thus sensitivity would be increased and response and recovery times would be decreased. Nano-sized semiconductor metal oxides have generated low-cost gas and humidity sensing materials. Different kind of nanomaterials are utilized in different humidity sensors, such as different nano-structure of ZnO [43–46] SnO_2 nanowires [47], $BaTiO_3$ nanofiber [48] and TiO_2 nanotube [49] Ag nano-particles [25] carbon nanotube/Nafion composite [50].

Hoang-Si Hong and his coworkers [43] described the fabrication and characterization of zinc oxide (ZnO) nanorods based surface acoustic wave (SAW) humidity sensors. In this work the SAW resonance frequency over a relative humidity (RH) varied in a range from 10% to 90% at 25 °C were investigated. A 750 kHz frequency shift was obtained from the SAW sensor coated with ZnO nanorods as sensing layer. This value was increased in compare with the frequency shift of the ZnO seed layer/IDTs/AlN/Si structure.

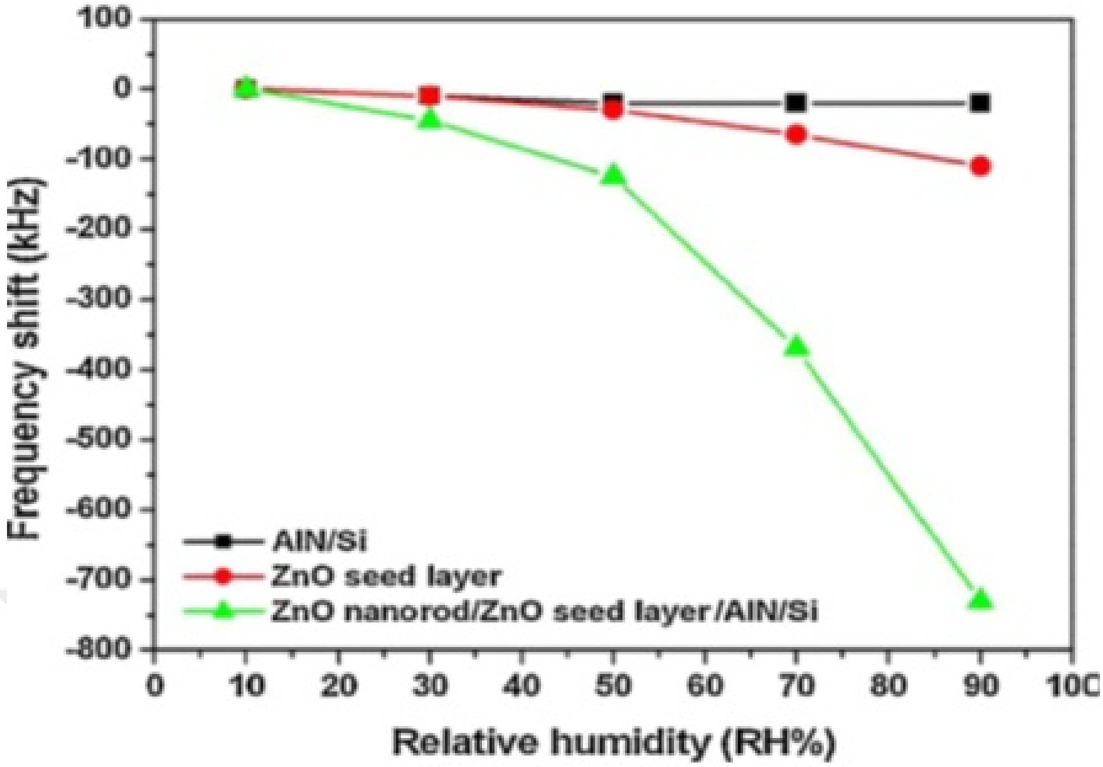


Figure 1.6: "Relationship between the frequency shift of different SAW structures (AlN/Si, ZnO seed layers/AlN/Si, and ZnO nanorods/ZnO seed layers/AlN/Si) and the corresponding relative humidity (10–90% RH) at room temperature (25 °C)" [43]

In the other research D. J. Li,a C. Zhao et al. [25] enhanced a SAW humidity sensor with silver nano particles. Smooth Ag film deposited by chemically deposited with high porosity onto the SAW devices gains good humidity sensitivity of 800 kHz at 75% RH.

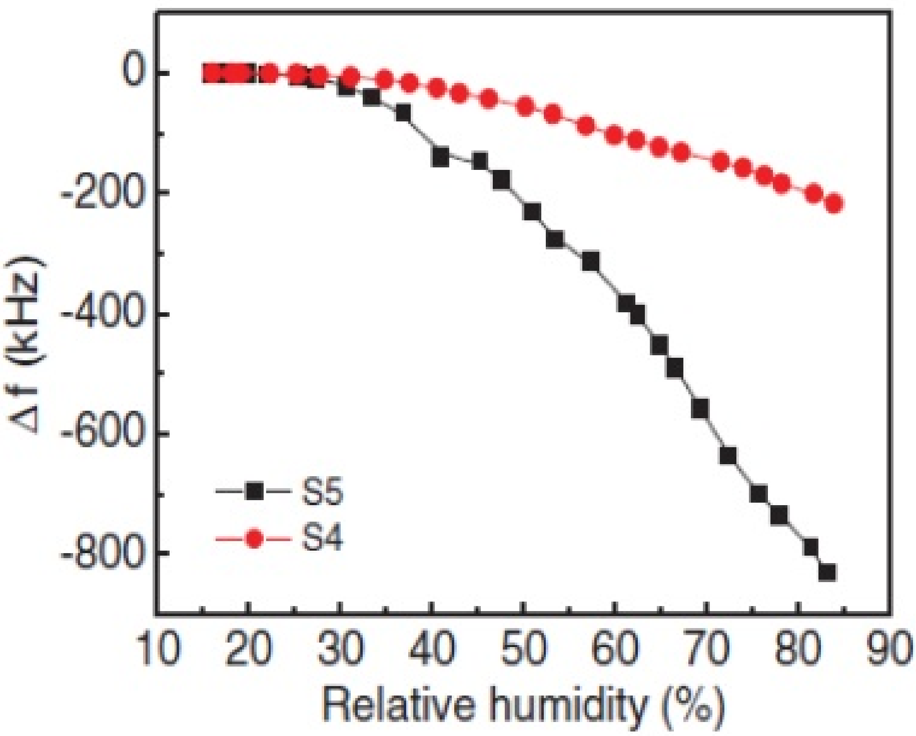


FIGURE 1.7: Variations of resonant frequency shift as a function of relative humidity silver nanoparticles with annealing in 400 °C in N_2 1 hr for Sample S4 and S5.

In a good example of using nanomaterials as a sensitive films in humidity sensors, Lei Sheng et al. [50] obtained an very high sensitivity of 400 kHz/%RH by using a multi-walled carbon nanotube/Nafion (MWCNT/Nafion) composite material. The response time was very short and about 3 s at 63%. The sensitivity of SAW sensor, with MWCNT/Nafion composite, was much higher than simlar research such as the SAW sensor with polymeric material (silicon-containing polyelectrolyte) as sensing layer. [35]

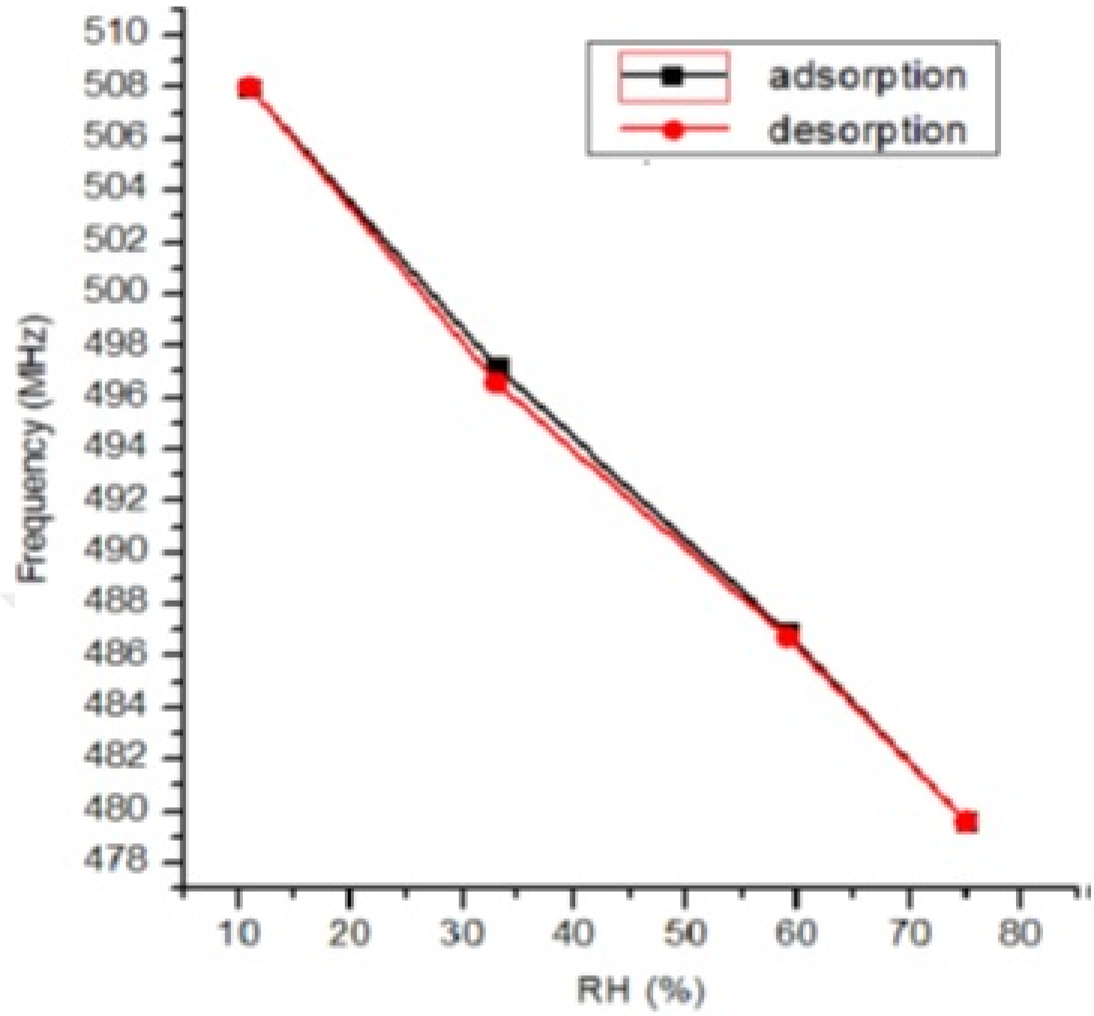


FIGURE 1.8: Graph of impedance change against humidity percentage in a resistive humidity sensor

Silver and its nanostructures are utilized as different sensors, including gas sensors (such as ammonia sensors) [51]. Silver nanowire, due to its high surface-to-volume ratio, good conductivity and a fast, simple, and cheap synthesis method has received great attention in different applications, such as sensing devices. In this research, we tried to enhance the sensitivity of SAW sensors against humidity with coating of silver nanowires, and a poly(vinylpyrrolidone) (PVP) as a capping layer, on the surface of device.

Chapter 2

Experimental

2.1 Introduction

In this research it is tried to enhance sensitivity of SAW sensors while expose to humidity with coating of silver nanowire. For this purpose Silver nanowires were chemically synthesized through the method which Sahin Coskun et al. have mentioned in their article [52] and it was coated on saw device by electrospray coating technique.
Whereas amount of materials which are coated on device has a great influence on the sensor response, so effects of different parameters including time of coating, concentration of solution and rate of injection were investigated.

2.2 Instruments and Chemicals

Chemicals which were used in this research: Poly(vinylpyrrolidone) (MW 55,000), silver nitrate ($AgNO_3$), and isopropyl (99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), Ethylene glycol (EG), sodium chloride (NaCl 99%), acetone, and ethanol were purchased from Merck Co., Kenilworth, New Jersey, USA.

Instruments which were used in this research:

The following instruments and devices were used: a hotplate and stirrer, a syringe and syringe pump (kdScientific, Holliston, Massachusetts, USA), a centrifuge device (hettich, Buckinghamshire, UK), a sonication device, an electrospray device (which consists of two parts—a sensor holder, which rotates with a specific rate and is exposed to a negative charge, and a second part, an injector to spray the material with a positive charge), a SAW device (SAW Components GmbH, Dresden, Germany), an oscilloscope (Tektronix, Beaverton, Oregon, USA) to measure the frequency shift before and after coating, a sensor measurement setup (which includes 7 SAW devices, one of which is used as a reference that is closed with a lid to block the influence of the gases, and the other six of which are exposed to humidity at the same time), an optic microscope (Carl Zeiss, Oberkochen Germany), and a Scanning Electron Microscope (SEM) with a maximum resolution of 2 nm (JEOL JSM.6335F, Peabody, Massachusetts, USA) .

2.3 Synthesis of AgNW

First, 10 mL of a 0.45 M EG (ethylene glycol) solution of PVP was prepared, and 7 mg of NaCl was added afterward. The solution was poured into a two-necked round flask to be stirred and heated at 170 °C. A second solution was prepared, and 0.12 M $AgNO_3$ was added to 5 mL of EG. This was injected dropwise into the PVP solution by an injection pump at a rate of 5 mL/h. The mixture was stirred and heated at the same temperature for an additional 30 min after injection. The solution color changes to a yellowish-brown. The final solution was cooled to room temperature, while it was stirring. After keeping the solution in a stable state for 2 days, the supernatant was decanted and the solid layer was washed and centrifuged 5 times with acetone and 5 times with ethanol [52]. After all purification processes, the final precipitate, silver nanowires (AgNWs) with a capping layer of PVP, was dispersed in isopropyl. Before dispersion in isopropyl, the weight of the solid precipitate was measured with a precision digital scale in order to reach a specific concentration of the solution.

2.4 SAW device preparation

A 433 MHz frequency dual-port resonator Rayleigh-SAW device (SAW Components GmbH, Dresden, Germany) mounted on a TO-39 socket was employed. This was washed via dipping in acetone and ethanol, each for 5 min. The reference frequency was measured with an oscilloscope to compare with its frequency after coating.

2.5 Electro-spray coating

The electro spraying system consists of a two-compartment setup with a sample holder in which sensors are placed on it and spins at 1000 rpm, exposing the sensors to a negative discharge cloud and the positive electrospray mist. A schematic diagram and its photograph are given in Figures 7 and 8.

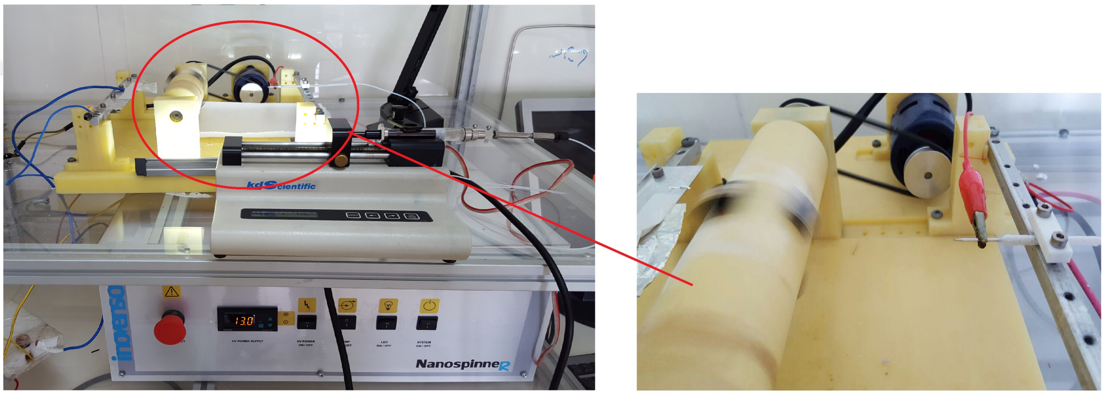


FIGURE 2.1: Photograph of the electrospraying system

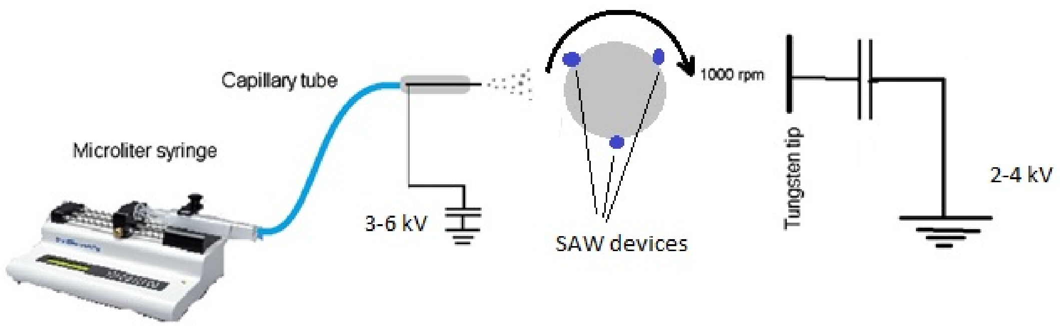


FIGURE 2.2: Graph of impedance change against humidity percentage in a resistive humidity sensor

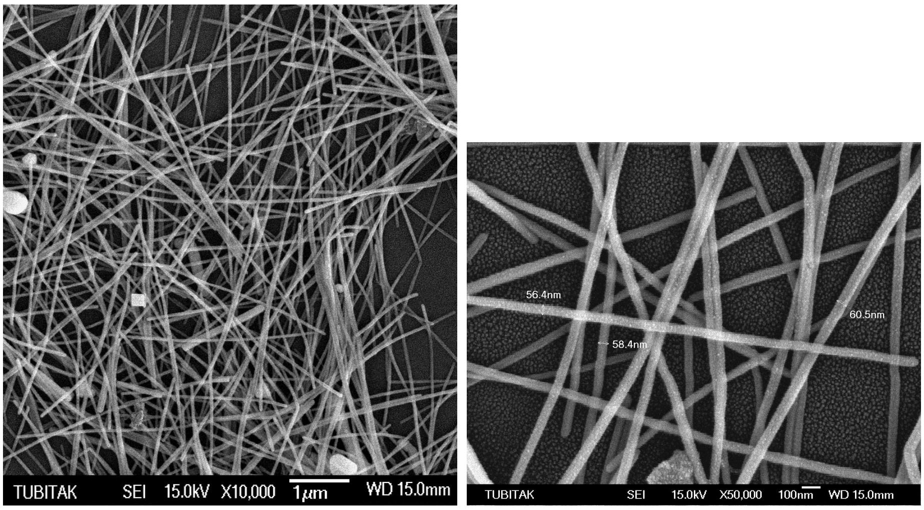
A syringe was filled with the solutions and placed in the syringe pump. The solution was injected at a constant rate into the sensors that were mounted on the rotator. As mentioned above, in order to obtain sensors with different sensitivities, we changed the amount of coating material on the SAW device. To that end, seven different SAW sensors were created by changing the injection rate, the volume, and the concentration of the injected solution. The details for these seven sensors are given in Table 1.

TABLE 2.1: Parameters of AgNW-coated SAW sensors by the electrospray method

No	Rotator	Volume	Injection Rate	Concentration	Frequency Shift
S1	1000 rpm	0.75 mL	2 mL/h	0.25 mg/mL	240 KHz
S2	1000 rpm	0.25 mL	2 mL/h	0.5 mg/mL	165KHz
S3	1000 rpm	0.25 mL	2 mL/h	0.25 mg/mL	123 KHz
S4	1000 rpm	0.25 mL	1 mL/h	0.25 mg/mL	91 KHz
S5	1000 rpm	0.25 mL	1 mL/h	0.75 mg/mL	220 KHz
S6	1000 rpm	0.5 mL	1 mL/h	0.5 mg/mL	262 KHz
S7	1000 rpm	0.25 mL	1 mL/h	0.5 mg/mL	158 KHz
S8	1000 rpm	0.5 mL	1 mL/h	0.25 mg/mL	188 KHz
S9	-	-	-	Uncoated SAW Device	-

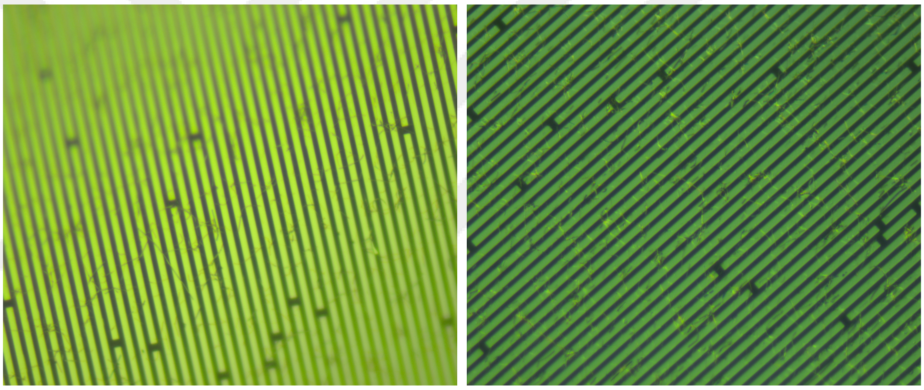
2.6 Characterization of AgNW

The morphology and size of the polyol-synthesized silver nanowires were investigated via SEM analysis, and the results are shown in Figure 9. The few silver nanoparticles that can be seen in Figure 9a are normal and inevitable in polyol synthesis. These nanoparticles have no significant effect on our experiments and results. The nanowires have an average length of 15 μm and an average width of 60 nm (Figure 9b). All wires are covered with a PVP capping agent, and no agglomeration is evident in the SEM photos. To observe the morphology of AgNWs on the surface of the SAW device and the inter-digital transducers (IDTs), we used an optic microscope with high magnification power and resolution. Figure 4 shows two different AgNW-coated IDT transducers (Sensors S6 and S7). Both photos show few silver nanowires on top of the fingers and between them. There is no connection between most of them, which demonstrates the very low electrical connectivity of the film. Although the amount of material sprayed on the surface of Sensor S7 (figure 10-b) is different in comparison to Sensor S6 (figure 10-a) , the difference is not distinguishable on the images. The reason lies in the weight difference at the microgram or nanogram scales.



(a) Figure 9a (b) Figure 9b

FIGURE 2.3: SEM images of silver nanowires (AgNWs): (a) the existing nanoparticles among the nanowires; (b) the dimensions of the nanowires.



(a) Figure 10a (b) Figure 10b

FIGURE 2.4: Optic microscope photos of IDTs coated with AgNWs by the electrospray coating method. (a) Sensor S6; (b) Sensor S7.

2.7 Sensor Measurement

Sensors testing were done by an experiment which an isothermal gas were exposed at 22 °C, and consisted of seven steps of exposure to the humidity, which took 70min in total, and a subsequent purging with pure air, after each step of exposure and one time at the start of the experiment (80 min in total) to reset the baseline. During the measurements, the humidity concentration was increased from 20% to 80% in seven steps. Each step of exposure and purging was lasts for 10 mins.

The system which sensors were tested with, is homemade and it is able to test 6 sensors at a same time. The sensors are placed in a chamber with volume of 4 ml and the temperature control in it. A multiplexing technique was using to read the frequencies of each sensor during the test. An uncoated SAW sensor is also used as a reference which is covered with a lid to block the effect of gases on thin film.

11.jpg 11.jpg

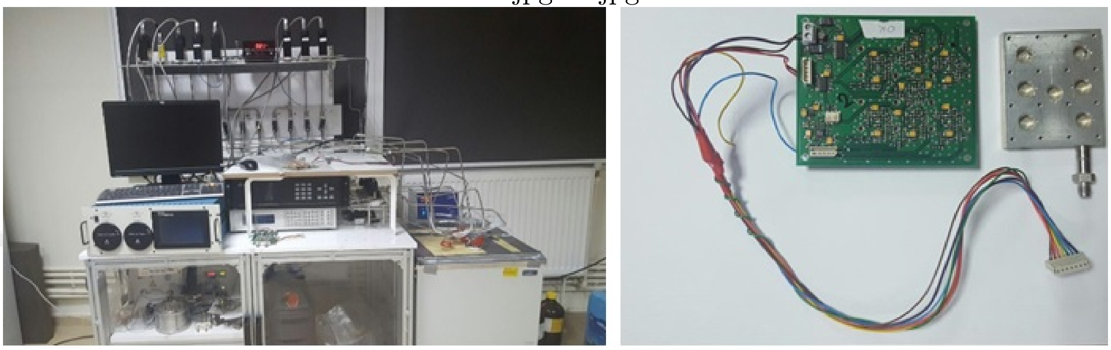


FIGURE 2.5: A photograph of SAW sensor measurment system and the cahmber

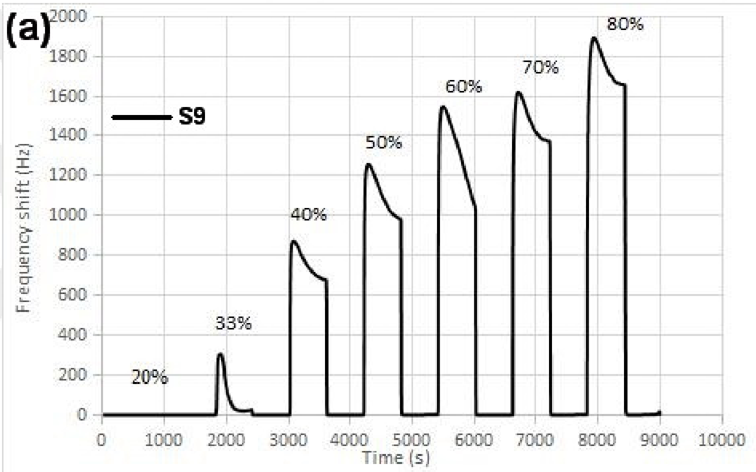
Chapter 3

Results and Discussion

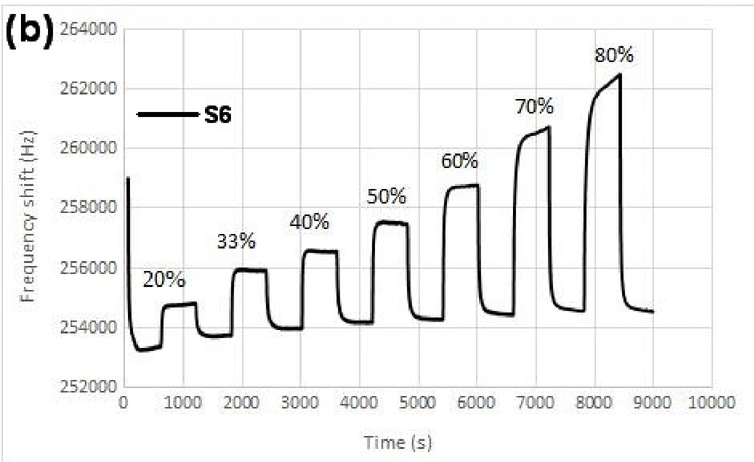
As was explained, the frequency shift in SAW devices is altered by change in parameters such as conductivity and mass of sensing film. Thus, several SAW sensors with different coating loads of silver nanowires were prepared. The sensors response against humidity was investigated and their characterization dependency on the mass and conductivity of the sensing film was illustrated. To that end, seven different SAW sensors were made by changing the injection rate, the volume, and the concentration of the injected solution. The details for these sensors are given in Table 2.1.

In the primary investigation, it was concluded that no frequency shift was obtained from SAW devices with a high load of AgNWs, which is conductive. A conductive SAW device, which was obtained in the experiments, resulted from spraying 3 mL of the AgNW solution with a concentration of 0.5 mg/mL at an injection rate of 2 mL/h. This was also observed in the work of Cihat Tasaltin et al. [40], as they state that the active range of the acoustoelectric effect of the SAWs (the highest change of wave velocity) was found to be in the range of $0.4 < \frac{\sigma_s}{(V_0 C_s)} < 1.7$. This range also includes the maximum point of insertion loss (IL). $\sigma_s = \sigma h$ is the surface conductivity, and $C_s = \epsilon_p + \epsilon_0$ is the concentration of the solution of the sensitive material (the total dielectric potential associated with the SAW and the carriers of the electric charge in the gas-sensitive film leads to a decrease in the velocity.). V_0 is the sound velocity in the crystal without any sensitive coated materials. The desired frequency shift was obtained from other sensors with coat that was less thick. However, they were not conductive. The comparison of the measured frequencies with the duration of electro-spraying and the concentration of the sprayed solution showed a direct correlation.

Sensor measurements were performed against humidity. The measurements were done twice for each of the sensors. The concentration humidity varied in a range from 20% RH to 80% RH. One uncoated sensor was tested as well to compare the results of the coated sensors against it and to check the sensitivity improvement. The acquired data was gathered in a spread sheet in order to draw the frequency graph versus the time for each sensor (Figure 3.1(a)). The graph for Sensor S6, which was coated with a higher volume and concentration of AgNW solution, is shown in Figure 3.1(b). The graph shows frequency shift responses to the changes in humidity percentage.



(a) (a)



(b) (b)

Figure 3.1: (a) An uncoated SAW sensor (S9) and (b) an AgNW-coated SAW sensor (S6) response against humidity in seven different humidity percentage in the range of 20%–80% RH. The baseline corresponds to 0% RH.

Frequency vs. RH% graph, which indicates sensor sensitivity, for Sensor S6 and the uncoated one, is shown in Figure 13. It shows that the sensitivity of the SAW sensor with a AgNW-coated surface is higher than the uncoated SAW sensor. For Sensor S6, the frequency shift in 80% RH is about 6.5 kHz, which is three times greater than the uncoated sensor at 80% RH.

13.jpg 13.jpg

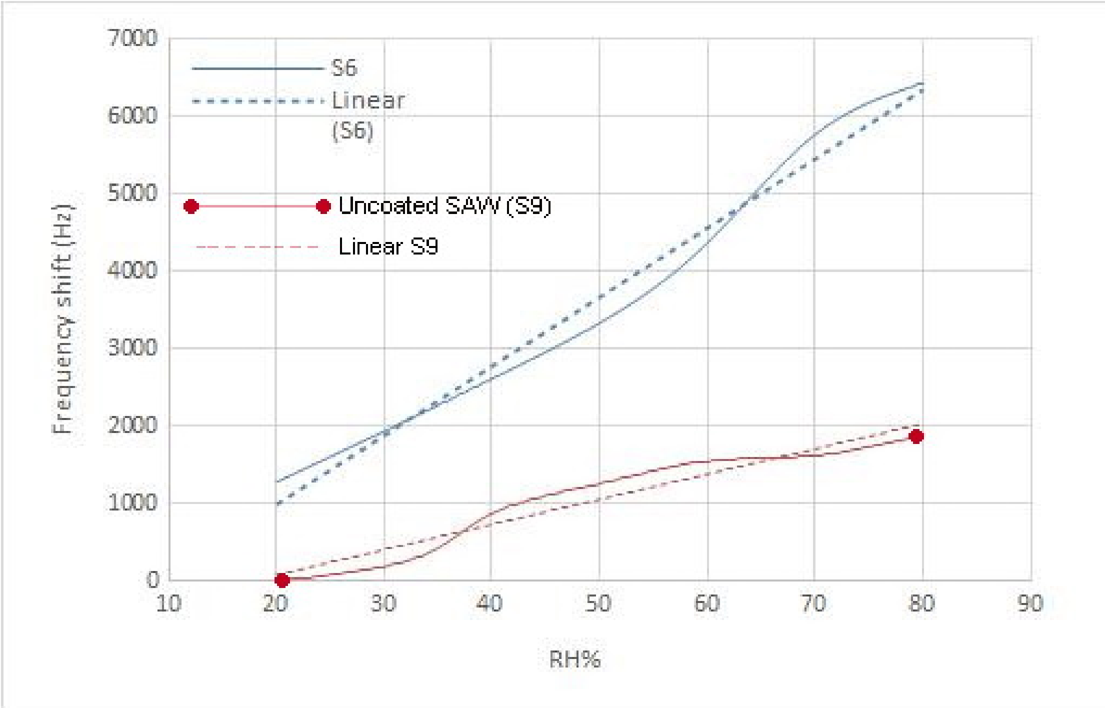


Figure 3.2: Sensitivity graphs of Sensor S6 and the uncoated SAW device.

The sensitivity graph for all seven sensors is shown in Figure 3.3. Considering the data in Table 1 and Figure 3.3, it can be concluded that the sensitivity increases as the amount of coated AgNWs on the sensor grows.

14.jpg 14.jpg

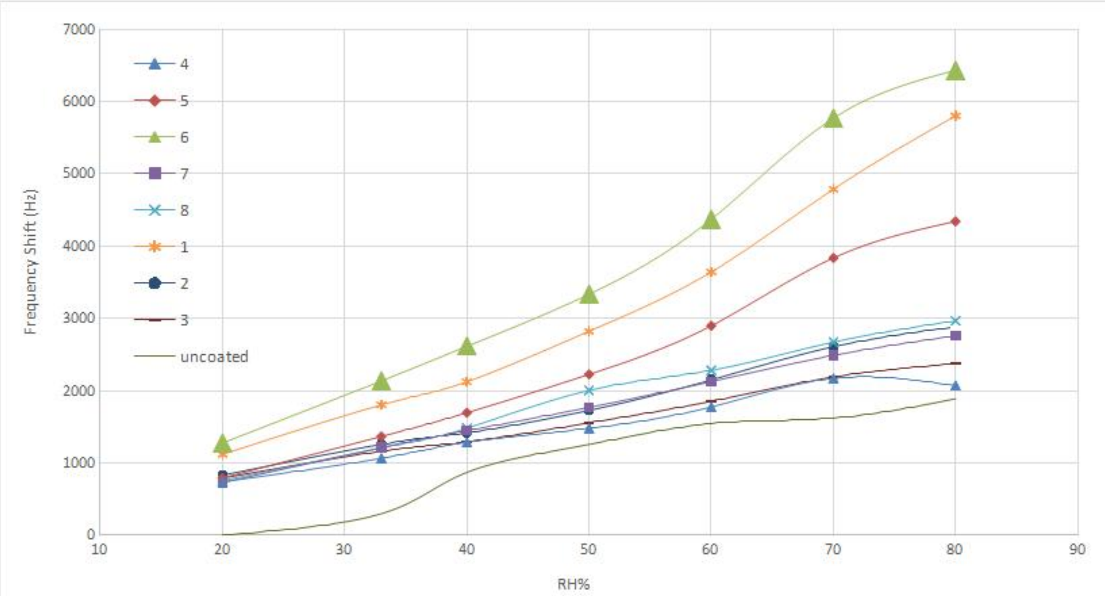


Figure 3.3: Sensitivity of all AgNW-based SAW sensors against humidity.

Chapter 4

Conclusion

The results of this research showed sensitivity of SAW sensor against humidity could be enhance by coating proper material on its surface. Polyol synthesized AgNWs because of its hydrophilic capping agent (PVP) and its high surface-to-volume ratio were used for this purpose. In order to obtain ideal samples with various amounts of nanomaterials on the surface of sensor, electrospray coating method was used. Sensor measurement results demonstrated that with increasing thickness of coated AgNWs on the sensor the sensitivity increases. It is also concluded that mass loading is a dominant factor in AgNW-based SAW humidity sensors.

Bibliography

[1] TL Yeo, T Sun, and KTV Grattan. Fibre-optic sensor technologies for humidity and moisture measurement. *Sensors and Actuators A: Physical*, 144(2):280–295, 2008.

[2] H. Günzíer and A. Williams. Handbook of analytical techniques. *Evolution*, 1:1–2, 2001.

[3] P. Hauptmann. *Sensors: principles and applications.* Prentice-Hall, Inc., 1993.

[4] D Woermann. J. janata: Principles of chemical sensors. plenum press, new york and london 1989. 317 seiten. *Berichte der Bunsengesellschaft für physikalische Chemie*, 94(4):543–543, 1990.

[5] N. Yamazoe and Y. Shimizu. Humidity sensors: principles and applications. *Sensors and Actuators*, 10(3-4):379–398, 1986.

[6] Zh. Chen and Ch. Lu. Humidity sensors: a review of materials and mechanisms. *Sensor letters*, 3(4):274–295, 2005.

[7] BC Yadav, R. Srivastava, CD Dwivedi, and P. Pramanik. Moisture sensor based on zno nanomaterial synthesized through oxalate route. *Sensors and Actuators B: Chemical*, 131(1):216–222, 2008.

[8] F. Sayar Irani and B. Tunaboylu. Saw humidity sensor sensitivity enhancement via electrospraying of silver nanowires. *Sensors*, 16(12):2024, 2016.

[9] S. A. Kolpakov, N. T. Gordon, Ch. Mou, and K. Zhou. Toward a new generation of photonic humidity sensors. *Sensors*, 14(3):3986–4013, 2014.

[10] H. Farahani, R. Wagiran, and M. Nizar Hamidon. Humidity sensors principle, mechanism, and fabrication technologies: a comprehensive review. *Sensors*, 14(5): 7881–7939, 2014.

[11] J. Fontes. *Sensor Technology Handbook*, pages 271–284, 2005.

[12] C. Laville and C. Pellet. Comparison of three humidity sensors for a pulmonary function diagnosis microsystem. *IEEE sensors journal*, 2(2):96–101, 2002.

[13] ZM. Rittersma. Recent achievements in miniaturised humidity sensorsa review of transduction techniques. *Sensors and Actuators A: Physical*, 96(2):196–210, 2002.

[14] Y. Sakai, Y. Sadaoka, and M. Matsuguchi. Humidity sensors based on polymer thin films. *Sensors and Actuators B: Chemical*, 35(1):85–90, 1996.

[15] M. Consales, A. Buosciolo, A. Cutolo, G. Breglio, A. Irace, S. Buontempo, P. Petagna, M Giordano, and A Cusano. Fiber optic humidity sensors for high-energy physics applications at cern. *Sensors and Actuators B: Chemical*, 159(1): 66–74, 2011.

[16] P. R. Somani, A. Kasi Viswanath, RC. Aiyer, and S. Radhakrishnan. Charge transfer complex-forming dyes incorporated in solid polymer electrolyte for optical humidity sensing. *Sensors and Actuators B: Chemical*, 80(2):141–148, 2001.

[17] L. Han Chen, T. Li, Ch. Chiu Chan, R. Menon, P. Balamurali, M. Shaillender, B. Neu, XM. Ang, P. Zu, WC. Wong. Chitosan based fiber-optic fabry–perot humidity sensor. *Sensors and Actuators B: Chemical*, 169:167–172, 2012.

[18] M. Bedoya, M. T. Díez, M. C. Moreno-Bondi, and G. Orellana. Humidity sensing with a luminescent ru (ii) complex and phase-sensitive detection. *Sensors and Actuators B: Chemical*, 113(2):573–581, 2006.

[19] TA Blank, LP Eksperiandova, and KN Belikov. Recent trends of ceramic humidity sensors development: A review. *Sensors and Actuators B: Chemical*, 228:416–442, 2016.

[20] J. Xie, H. Wang, Y. Lin, Y. Zhou, and Y. Wu. Highly sensitive humidity sensor based on quartz crystal microbalance coated with zno colloid spheres. *Sensors and Actuators B: Chemical*, 177:1083–1088, 2013.

[21] Y. Zhu, H. Yuan, J. Xu, P. Xu, and Q. Pan. Highly stable and sensitive humidity sensors based on quartz crystal microbalance coated with hexagonal lamelliform monodisperse mesoporous silica sba-15 thin film. *Sensors and Actuators B: Chemical*, 144(1):164–169, 2010.

[22] S. Vlassova, O. Schelerb, M. Plaadoa, R. Lõhmusa, A. Kurgb, Kristjan Saala, and Ilmar Kinka. Integrated carbon nanotube fibre–quartz tuning fork biosensor. *Proceedings of the Estonian Academy of Sciences*, 61(1):48–51, 2012.

[23] X. Zhou, T. Jiang, J. Zhang, J. Zhu, X. Wang, and Z. Zhu. A quartz tuning fork-based humidity sensor using nanocrystalline zinc oxide thin film coatings. In *2006 IEEE International Conference on Information Acquisition*, pages 1152–1157. IEEE, 2006.

[24] Ch. Lin, Y. Chen, V. V Felmetsger, D. G Senesky, and A. P Pisano. Aln/3c–sic composite plate enabling high-frequency and high-q micromechanical resonators. *Advanced Materials*, 24(20):2722–2727, 2012.

[25] DJ Li, C Zhao, YQ Fu, and JK Luo. Engineering silver nanostructures for surface acoustic wave humidity sensors sensitivity enhancement. *Journal of The Electrochemical Society*, 161(6):B151–B156, 2014.

[26] C. McMullan, H. Mehta, E. Gizeli, and Ch. R Lowe. Modelling of the mass sensitivity of the love wave device in the presence of a viscous liquid. *Journal of Physics D: Applied Physics*, 33(23):3053, 2000.

[27] H. Hong and G. Chung. Surface acoustic wave humidity sensor based on polycrystalline aln thin film coated with sol–gel derived nanocrystalline zinc oxide film. *Sensors and Actuators B: Chemical*, 148(2):347–352, 2010.

[28] H. Hong and G. Chung. Humidity sensing characteristics of ga-doped zinc oxide film grown on a polycrystalline aln thin film based on a surface acoustic wave. *Sensors and Actuators B: Chemical*, 150(2):681–685, 2010.

[29] H. Hong, D. Phan, and G. Chung. High-sensitivity humidity sensors with zno nanorods based two-port surface acoustic wave delay line. *Sensors and Actuators B: Chemical*, 171:1283–1287, 2012.

[30] N. M Tashtoush. *SAW humidity sensor and an environmental electronic nose system*. PhD thesis, Concordia University, 1996.

[31] AJ Ricco, SJ Martin, and TE Zipperian. Surface acoustic wave gas sensor based on film conductivity changes. *Sensors and Actuators*, 8(4):319–333, 1985.

[32] M Penza, P Aversa, G Cassano, W Wlodarski, and K Kalantar-Zadeh. Layered saw gas sensor with single-walled carbon nanotube-based nanocomposite coating. *Sensors and actuators B: Chemical*, 127(1):168–178, 2007.

[33] A. Power. The preparation and characterisation of silver nanomaterials and their application in sensing techniques, 2011.

[34] J. Shi, Yongfa Zhu, X. Zhang, W. RG Baeyens, and A. M Garcıa-Campaña. Recent developments in nanomaterial optical sensors. *TrAC Trends in Analytical Chemistry*, 23(5):351–360, 2004.

[35] Y. Li, P. Li, M. Yang, Sh. Lei, Y. Chen, and X. Guo. A surface acoustic wave humidity sensor based on electrosprayed silicon-containing polyelectrolyte. *Sensors and Actuators B: Chemical*, 145(1):516–520, 2010.

[36] G. Fu, H. Chen, Zh. Chen, J. Zhang, and H. Kohler. Humidity sensitive characteristics of zn 2 sno 4–liznvo 4 thick films prepared by the sol–gel method. *Sensors and Actuators B: Chemical*, 81(2):308–312, 2002.

[37] Y Shimizu, H Arai, and T Seiyama. Theoretical studies on the impedance-humidity characteristics of ceramic humidity sensors. *Sensors and Actuators*, 7(1):11–22, 1985.

[38] J. Hunter A. Jr and G. A Parks. Electrical conductivity of silica gel in the presence of adsorbed water. *The Journal of Physical Chemistry*, 72(10):3662–3668, 1968.

[39] E McCafferty and AC Zettlemoyer. Adsorption of water vapour on α-fe 2 o 3. *Discussions of the Faraday Society*, 52:239–254, 1971.

[40] E. Traversa and A. Bearzotti. A novel humidity-detection mechanism for zno dense pellets. *Sensors and Actuators B: Chemical*, 23(2):181–186, 1995.

[41] TY Kim, DH Lee, YC Shim, JU Bu, and ST Kim. Effects of alkaline oxide additives on the microstructure and humidity sensitivity of mgcr2o4? tio2. *Sensors and Actuators B: Chemical*, 9(3):221–225, 1992.

[42] TW Grudkowski, JF Black, TM Reeder, DE Cullen, and RA Wagner. Fundamental-mode vhf/uhf minature acoustic resonators and filters on silicon. *Applied Physics Letters*, 37(11):993–995, 1980.

[43] H. Hong, D. Phan, and G. Chung. High-sensitivity humidity sensors with zno nanorods based two-port surface acoustic wave delay line. *Sensors and Actuators B: Chemical*, 171:1283–1287, 2012.

[44] F. Tsai and Sh. Wang. Enhanced sensing performance of relative humidity sensors using laterally grown zno nanosheets. *Sensors and Actuators B: Chemical*, 193: 280–287, 2014.

[45] XL He, DJ Li, J Zhou, WB Wang, WP Xuan, SR Dong, H Jin, and JK Luo. High sensitivity humidity sensors using flexible surface acoustic wave devices made on nanocrystalline zno/polyimide substrates. *Journal of Materials Chemistry C*, 1(39): 6210–6215, 2013.

[46] Sh. Chang, Sh. Chang, Ch. Lu, M. Li, Ch. Hsu, Y. Chiou, T. Hsueh, and I. Chen. A zno nanowire-based humidity sensor. *Superlattices and Microstructures*, 47(6): 772–778, 2010.

[47] Q. Kuang, Ch. Lao, Zh. Wang, Zh. Xie, and L. Zheng. High-sensitivity humidity sensor based on a single sno2 nanowire. *Journal of the American Chemical Society*, 129(19):6070–6071, 2007.

[48] L. Wang, Y. He, J. Hu, Qi Qi, and T. Zhang. Dc humidity sensing properties of batio 3 nanofiber sensors with different electrode materials. *Sensors and Actuators B: Chemical*, 153(2):460–464, 2011.

[49] Y. Zhang, W. Fu, H. Yang, Qi Qi, Y. Zeng, T. Zhang, R. Ge, and G. Zou. Synthesis and characterization of tio 2 nanotubes for humidity sensing. *Applied Surface Science*, 254(17):5545–5547, 2008.

[50] L. Sheng, Ch. Dajing, and Ch. Yuquan. A surface acoustic wave humidity sensor with high sensitivity based on electrospun mwcnt/nafion nanofiber films. *Nanotechnology*, 22(26):265504, 2011.

[51] S. T Dubas and V. Pimpan. Humic acid assisted synthesis of silver nanoparticles and its application to herbicide detection. *Materials Letters*, 62(17):2661–2663, 2008.

[52] S. Coskun, B. Aksoy, and H. E. Unalan. Polyol synthesis of silver nanowires: an extensive parametric study. *Crystal Growth & Design*, 11(11):4963–4969, 2011.