FABRICATION, CHARACTERIZATION AND HUMIDITY SENSING PROPERTIES OF RADIO FREQUENCY MAGNETRON SPUTTERED CALCIUM COPPER TITANATE (CCTO) THIN FILM

MOHSEN AHMADIPOUR

UNIVERSITI SAINS MALAYSIA

2018

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by

MOHSEN AHMADIPOUR

Thesis submitted in fulfilment of the
requirements for the Degree of
Doctor of Philosophy

July 2018

ACKNOWLEDGMENT

In the Name of Allah, the Most Gracious and the Most Merciful…

All praise is for Allah alone, giving me his blessing and the strength to complete my Ph.D. research project entitled: “Fabrication, characterization and humidity sensing properties of radio frequency magnetron sputtered calcium copper titanate (CCTO) thin film”

I would like to take this opportunity to express my greatest thankfulness to my respected main supervisor, Prof. Dr. Zainal Arifin Ahmad who provided me a good chance to conduct my research under his valuable guidance, as well as motivating and supporting me right which enable me to realize my idea into an invention. Moreover, I would lie to give my grateful to my co-supervisor, Prof. Ir. Dr. Mohd Fadzil Ain for his support and endurance in helping and guiding me to complete this research.

My grateful thanks also go to Universiti Sains Malaysia (USM) to provide funding (Fellowship-APEX 91002/JHEA/ATSG4001) for me to complete my Ph.D. My great appreciation also go to, all staffs in School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (USM) which has provided a great and comfortable environment for me to carry out my research. I would like to appreciate to those who involved in accomplished this study.

Last but not least, my heartiest gratitude to my family for their unconditional love, motivation and support that have been a great support either directly or indirectly in the completing of this study. I would like to dedicate this thesis to my parents.

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: MATERIALS AND METHOD

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: CONCLUSION AND FUTURE WORK

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
AH	Absolute Humidity
AC	Alternating Current
CCTO	Calcium Copper Titanate
CSTF	Chiral Sculptured Thin Film
DC	Direct Current
D/F PT	Dew/Frost point
DRAM	Dynamic Random Access Memory
EMF	Electromagnetic Field
EDAX	Energy Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FOCS	Fiber Optical Chemical Sensors
FWHM	Full Width at Half Maximum
GPIB	General Purpose Interface Bus
IDE	Interdigitated Electrodes
IDC	Inter Digital Capacitors
ICDD	International Centre for Diffraction Data
MOCVD	Metal Oxide Chemical Vapor Deposition
MLCC	Multilayer Capacitor
MEMS	Microelectromechanical Systems
NDT	Nondestructive Testing
NFFP	Near Field Fabry Perot
PLD	Pulse Laser Deposition

ppm	Parts Per Million
PVD	Physical Vapor Deposition
QCM	Quartz Crystal Microbalances
RF	Radio Frequency
RMS	Root Mean Square
Ra	Roughness
SPR	Surface Plasmon Resonance
S_H	Humidity Sensitivity
XRD	X-ray Diffraction

LIST OF SYMBOLS

Δ	Delta
$\tan \delta$	Dielectric Loss
ε_r	Dielectric constant
δ	Dislocation Density
ε	Micro Strain
nm	Nanometer
Pv	Partial Pressure
Ps	Saturated Pressure
s	Second
Sccm	Standard Cubic Centimeters Per Minute
θ	Theta
V	Volt
λ	Wavelength

PEMBUATAN, PENCIRIAN DAN SIFAT PENDERIAAN LEMBAPAN FILEM NIPIS KALSIUM KUPRUM TITANAT (CCTO) YANG DI SPUTER MENGGUNAKAN MAGNETRON FREKUENSI RADIO

ABSTRAK

Penderia lembapan jenis-rintangan berasaskan filem nipis CCTO yang mampu mengesan kelembapan dalam julat 30%-90% dengan tempoh yang singkat telah berjaya dihasilkan menggunakan teknik magnetron percikan frekuensi radio (RF). Penderia lembapan filem nipis CCTO berasaskan pengukuran rintangan tidak pernah dilaporkan. Tujuan kajian ini untuk menghasilkan suatu penderia lembapan yang kecil dan berstruktur mudah untuk mengurangkan kos pembuatan, meningkatkan sifat-sifat penderian lembapan dan akhirnya untuk membuktikan potensi besar CCTO untuk digunakan dalam penderian lembapan. Filem nipis CCTO dengan ketebalan 200 nm, 400 nm dan 600 nm telah dimendapkan masing-masing di atas substrat Al_2O_3 yang dianalisis menggunakan FESEM-EDAX, XRD dan AFM untuk memahami mikrostuktur dan morfologinya. Sebelum CCTO dimendapkan, proses pembuatan telah dilakukan menggunakan penguapan terma untuk menyediakan elektrod argentum terinterdigit konduktor tinggi. Penderia lembapan filem nipis CCTO telah diuji secara elektrik di dalam berbagai lembapan relatif (RH) (30% hingga 90%) pada suhu bilik. Keputusan menunjukkan bahawa rintangan semua sampel berkurangan dengan peningkatan ketebalan filem nipis CCTO apabila didedahkan dalam lembapan. Tambahan pula, tempoh respon pantas iaitu kurang dari 1 min telah diperhatikan untuk kedua-dua filem nipis yang dimendapkan di atas substrat-substrat Al_2O_3. Untuk peranti yang menggunakan 200 nm filem nipis CCTO di atas substrat Al_2O_3, sifat-sifat penderian lembapan (Tempoh respon = 10 s, Tempoh pemulihan = 450 s, Kesensitifan = 75.6%) telah diperhatikan apabila didedahkan pada kelembapan. Apabila pengukuran diulangi selepas sebulan, filem nipis CCTO menunjukkan kestabilan yang luar biasa. Mekanisme yang mungkin di antara lembapan dan filem nipis CCTO telah dicadangkan di mana proses penderiaan lembapan berkaitan dengan penyerapan dan nyahserapan air di atas permukaan filem pada RH rendah, molekul air tidak akan melitupi permukaan sepenuhnya dan hanya boleh menyerap pada tapak-tapak yang ada di permukaan CCTO. Selanjutnya, serapan air tidak akan menyediakan elektron kepada lapisan-lapisan penderiaan dan akan merendahkan sifat penderiaan penderia lembapan filem nipis CCTO. Pada RH tinggi, kandungan air yang banyak telah diserap, maka ketumpatan cas pembawa bertambah dan menjadikan sifat-sifat penderiaan meningkat. Oleh itu, prestasi sifat-sifat keelektrikan filem nipis CCTO tercapai untuk keperluan penderia lembapan yang baik. Tambahan pula, keupayaannya untuk mengesan lembapan relatif di dalam julat 30%-90% melayakkan filem nipis CCTO ini untuk digunakan sebagai penderia lembapan berprestasi tinggi dan praktikal dalam masa yang terdekat.

FABRICATION, CHARACTERIZATION AND HUMIDITY SENSING PROPERTIES OF RADIO FREQUENCY MAGNETRON SPUTTERED CALCIUM COPPER TITANATE (CCTO) THIN FILM

ABSTRACT

Resistance-type humidity sensor based on CCTO thin films which are capable of sensing of humidity in the range of 30%-90% and short period of time have been successfully fabricated by using radio frequency (RF) magnetron sputtering technique. The CCTO thin film humidity sensor based-on resistance measurement has never been reported before. The aim of this study is to fabricate a humidity sensor with small size and simple structure in order to reduce the fabrication cost, to enhance of CCTO thin film humidity sensing properties, and finally to prove the great potential of CCTO as a humidity sensing application. CCTO thin film with 200 nm, 400 nm, and 600 nm thicknesses were deposited on alumina (Al_2O_3) substrates, respectively and physically analyzed by field emission scanning electron microscopy which is connected with energy dispersive X-ray spectroscopy (FESEM-EDAX), X-ray diffraction (XRD) and atomic force microscopy (AFM) in order to understand their microstructure and morphology. Prior to CCTO deposition, the fabrication process was assisted by thermal evaporator to prepare the highly conductive interdigitated silver electrode. The CCTO thin film humidity sensor electrically tested in different relative humidity (RH) (30% to 90%) at ambient temperature. Results exhibited that resistance of all samples decreased with increasing the CCTO thin film thickness and also upon exposure to humidity. In addition, a quick response time i.e., approximately less than 1 min was observed for both CCTO thin films. For device based on 200 nm CCTO thin film, high humidity sensing properties (Response time = 10 s, Recovery time = 450 s, Sensitivity = 75.6 %) was observed upon exposure to humidity. When the measurements were repeated after a month, the CCTO thin film showed remarkable stability. The possible mechanism between humidity and CCTO thin film was proposed whereby the humidity sensing process is correlated to adsorption and desorption water on the films surface at low RH, water molecule will not cover the surface completely and can only chemisorb on the available site of the CCTO surface. Furthermore, water adsorbing will not provide electrons to sensing layers and will significantly lower the sensing properties of CCTO thin film humidity sensor. At high RH, the larger content of water is adsorbed, so the density of charge carrier becomes higher and hence the sensing properties increases. Thus, the performance of the CCTO thin film electrical properties achieved the requirement for good humidity sensor. Moreover, its ability to detect relative humidity in range 30%-90% qualified this CCTO thin film as a very promising potential to be applied as a practical and high performance humidity sensor in the near future.

CHAPTER ONE

INTRODUCTION

1.1. Research background

Humidity measurement and control are important in numerous medical, industrial, and agricultural applications. In the medical field, humidity control is required during pharmaceutical processing. In industry, many engineering processes including semiconductor manufacturing and gas purification depend on well-ordered levels of humidity. In agriculture, greenhouse and incubation need humidity control. Humidity control is also important in humans' daily lives. The ideal indoor relative humidity (RH) should be 40% to 60%. Lower RH levels cause discomfort and health difficulties such as chapped lips, bleeding nose, and dry throat (Fenner & Zdankiewicz, 2001). Higher RH levels, on the other hands, cause fungus growth. All of these applications plus much more make humidity control more important nowadays.

The first humidity sensor (hygrometer) was created in 1450 by Bicolas Cryfts, while used wool to measure the humidity changes in the air (Mohammed & Mahmud, 2015). After hundreds of years of development, many kinds of humidity sensor were invented, such as psychrometer and lithium chloride (LiCl) dew point sensor. These methods are referred to as classical humidity measurement techniques. Compared to modern instruments, these devices have a large size, slow response, and often have low accuracy. The development of miniaturized humidity sensors is growing on par with the demand for them (Hartzell & da Silva, 2007; Dubourg et al., 2017) due to having several advantages compared to the classical measurement such as integration, small size, low cost, low power consumption, and high performance (Kim et al., 2009a).

Many parameters are involved to fabricate a good humidity sensor, including hysteresis (< 5%) (Wang et al., 2013; Zhuang et al., 2017; Ding et al., 2018), response time (< 60s) (Hu et al., 2014; Ruiz et al., 2015; Rahim et al., 2018), recovery time (few minutes) (Yun et al., 2014; Wang et al., 2016; Su & Syu, 2017; Zhao et al., 2017). Generally, for humidity sensing applications, many scientists used the impedance (resistance) and capacitance as the monitoring object for the determination of the sensor performance (Bernard et al., 2005; Su & Chang, 2018), and many attempts have been aimed to enhance the sensing performance by enhancing the response values of sensor (Zhan et al., 2000; Wan et al., 2004; Hartzell & da Silva, 2007; Qiu & Yang, 2007; Durrer et al., 2008; Kaur et al., 2008; Lee et al., 2008; Wang et al., 2017; Zhang et al., 2018). For the past few years, numerous types of ceramic have been extensively examined as humidity sensing materials (Hu et al., 2008; Sharma & Islam, 2016; Sikarwar et al., 2016). Humidity sensors based on ceramic materials have certain benefits in contrast to other types of humidity sensors, including shows better chemical resistance, thermal stability and can survive in harsh chemical environments. Newly, a metal oxide such as CCTO (Li et al., 2010) has been established to own excellent humidity sensing properties. CCTO is a novel electroceramic material presented with high dielectric constant (ε_r), nearly 10^5 for single crystal and 10^4 for bulk material at ambient temperature (Subramanian et al., 2000). It belongs to a family of $ACu_3Ti_4O_{12}$ (A

= Ca, Sr, Ba, $Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$) type metal oxide presenting of pseudo-cubic perovskite-related structure (space group: Im3) (Subramanian et al., 2000).

Research on CCTO demonstrated that the devices based on CCTO are used to detect gases such as O_2-N_2 (Parra et al., 2010), H_2 (Kim et al., 2006), O_2 (Joanni et al., 2008) and (H_2O) (Li et al., 2010). The detection method is mostly depending on the electrical measurement which provides information on dielectric properties (capacitance-type) of tested devices. However, the sensors still suffered from low sensitivity (3% for O_2-N_2, 1.25% for H_2, 2.6 % for O_2, 3% for H_2O) and high response time (10 min for O_2-N_2, 60 min for H_2, 5 min for O_2, 13 min for H_2O) and recovery time (30 min for O_2-N_2, 60 min for H_2, no study for O_2, 30 min for H_2O). In addition, all of gases sensing measurements (except H2O) were done at high temperature 220 °C, 300 °C, 100 °C for O_2-N_2, H_2 and O_2, respectively.

1.2. Problem statement

Humidity is an unavoidable component in the air attributed to our water-rich environment. Thus, the determine and capability to control the humidity in air is crucial not only for human comfort but is also important in technologies that rely on amount of water in the air, including environmental protection, air quality control, and health sciences (Slunečko et al., 1992; Rittersma, 2002; Ivanov et al., 2004a). In past years, scientists have given extensive attention on the improvement of humidity-sensitive metal oxide materials (Gusmano et al., 1993a; Kleperis et al., 1995; Zhang et al., 2005; Rezlescu et al., 2007; Kotnala et al., 2008; Glot et al., 2009; Si et al., 2010; Fiz et al., 2013; Tawale et al., 2014; Park et al., 2018) that can be functional in humidity control systems. Moreover, different categorizations of sensitive materials for humidity sensors have been utilized, such as electrolytes, organic polymers and porous ceramics (Farahani et al., 2014). Among of them, humidity sensors fabricated by porous ceramics commonly shows superior conductivity and thermal stability in contrast to electrolyte and organic polymer sensors. In reality, furthermost porous ceramic humidity sensors can resist harsh chemical environments. One of the latest examples is CCTO (Subramanian et al., 2000). CCTO has moderate dielectric loss value (tan $\delta = 0.15$) at a broad frequency region (up to 10^6 Hz) at ambient temperature has leads to various possible technological applications including gas sensor, antenna, and capacitor (Fechine et al., 2006; Parra et al., 2010; Schmidt et al., 2012; Pongpaiboonkul et al., 2016; Thiruramanathan et al., 2018). The resistance value of CCTO was also established to decline under exposure to humid air, propose it a promising candidate for application as humidity sensors. In addition, CCTO is unlike other metal oxides (humidity sensor) that require heat treatment to have good humidity sensing performance which results consumption of more energy. Besides, sensors based on CCTO have advantages including lightweight, non-corrosive, and easy to prepare. All those advantages led to fabrication of CCTO thin film humidity sensor.

The unique sensing properties including short response time and recovery time, high sensitivity, good stability can be attained when CCTO is in the form of thin film owing to high porosity and better uniformity in contrast to bulk materials. Therefore, CCTO thin film can be fabricated through frequently used chemical and physical techniques including sol-gel (Kumar, 2011), metal oxide chemical vapor deposition (MOCVD) (Fiorenza et al., 2011), pulse laser deposition (PLD) (Deng & Muralt, 2010), and radio frequency (RF) magnetron sputtering (Prakash et al., 2008). Nevertheless, among them, RF magnetron sputtering has been utilized for various thin films deposition for long period of time and gained an inclusive attention due to allows high uniformity for large-area processing, long-term stability and strong adhesion, and provide special control ability for the deposition.

However, there have been only a few reports about the CCTO thin films sensors prepared by RF sputtering. Foschini et al. (Foschini et al., 2013) described that the sputtering is a useful method to prepare good quality of polycrystalline and homogeneous morphology of CCTO thin film. It is studied for its ε_r. Joanni et al. (Joanni et al., 2008) stated a deposition of CCTO thin films on Si/SiO_2/Ti/ Pt substrates to investigate its gas sensing properties (capacitance-type). Li et al. (Li et al., 2010) had studied the CCTO humidity sensor and obtained high sensitivity, but the long response and recovery times.

However, previous works show that the quality of CCTO sensor is not yet efficient since it has high response time (5-60 min), recovery time (30-60 min), and low sensitivity (1.25%-3%). In addition, the measurement is based on capacitance type and mostly was done at high temperature (100-600 °C). But CCTO has several advantages as a humidity sensing material; however, its inherent swelling properties that become an obstacle which cannot stick strongly on the patterned substrate during the deposition process. Therefore, the investigation of CCTO thin film, deposition parameter, and thickness effect become very important to obtain the most suitable fabrication parameter. Later, the selected fabrication parameters will be used to fabricate CCTO based humidity sensor to detect 30% - 90% RH.

The humidity sensing detection method is very important to explore the device response and sensing characteristic. Most of the research on the metal oxide humidity sensing device demonstrates that the detection method is solely based on electrical measurement such as voltage characteristic and resistivity (Chen & Lu, 2005). This electrical measurement is able to provide real-time result observation. In this study, current-voltage characteristic will be used to evaluate the device sensing activities. The device able to be used in the humidity sensing activity is supported by the surface analysis study in order to verify the presence of water molecules on the CCTO humidity sensor surface.

Thus, this research will focus on the fabrication of CCTO thin film humidity sensor by RF magnetron sputtering. The CCTO films were fabricated with different thicknesses on Al_2O_3 substrate, respectively. The fabricate films were characterized by field emission scanning electron microscopy which is connected with energy dispersive X-ray spectroscopy (FESEM-EDAX), X-ray diffraction analysis (XRD), atomic force microscopy (AFM). For laboratory test scale, the CCTO humidity sensing properties such as response, recovery, sensitivity, and stability was tested by measuring the change in output voltage of CCTO when exposure to different RH at ambient temperature.

1.3. Research objectives

The objectives of this research are:

- To fabricate CCTO thin film sensor on aluminum oxide (Al_2O_3) substrate by using RF magnetron sputtering for sensing RH at ambient temperature.

- To characterize the microstructure, and chemical composition, surface morphology, and phase of RF magnetron sputtered CCTO thin film.
- To test the CCTO thin film humidity sensing properties by applying direct current (DC) voltage at ambient temperature.
- To propose sensing mechanism of CCTO film to humidity.

1.4. Project approach

This research will embark based on the following approach

- This study was divided into three main parts; sensor fabrication, physical characterizations, and electrical testing. Sensor fabrication was carried out at ambient temperature using the RF magnetron sputtering. Initially, the 1 mm thick Al_2O_3 substrate was ultrasonically cleaned with acetone, alcohol and deionized water for 30 min, respectively, in order to remove surface impurities. In the deposition process, the deposition ratio was varied in the range of 0.27 Å/s to 0.84 Å/s and deposition time was 120 min with power 150 W to achieve the thickness between 200 to 600 nm.
- The physical characterization of the fabricated devices was performed by using field emission scanning electron microscopy linked with energy dispersive X-ray spectroscopy (FESEM-EDAX), X-ray diffraction analysis (XRD), and atomic force microscopy (AFM). The information about the relationship between electrical properties and the molecular structure was utilized to investigate the sensing mechanism of CCTO thin film humidity sensor.
- Electrical properties include response/recovery times, sensitivity, and reliability of the sputtered CCTO thin film was assessed by using a multimeter (Keithley

2611A). The applied voltage was fixed between 2-10 V. The electrical measurement will be performed at the ambient temperature.

1.5. Thesis organization

This thesis is organized as follows. In Chapter 1, research background, problem statement, research objectives, and project approach of the thesis were explained.

Chapter 2, literature review about the definition of humidity, a different type of humidity sensors, humidity sensing materials, humidity sensing mechanism, $CaCu_3Ti_4O_{12}$, deposition techniques used for the preparation of CCTO films.

Chapter 3 presents information on the materials and methodology of this study. The equipment, chemical, consumables and humidity used in this study. Furthermore, the sample preparation and cleaning process was also provided. The parameter involved in the fabrication process step such as thickness was involved in this chapter. In addition, the device characterization which involved physical and electrical characterization and RF magnetron sputtering system was explained.

Chapter 4 presents the results and discussion of this study. This chapter covers discussion of results on the humidity sensor fabrication process, physical characterization (FESEM-EDAX, XRD and AFM). In continuation, the electrical properties of CCTO thin film with a different thickness on Al_2O_3 substrate in presence of different RH will be described in detail.

Chapter 5 presents the conclusion, contributions of this study and recommendation for future research.

CHAPTER TWO

LITERATURE REVIEW

2.1. Humidity

Humidity is one of the important constituents of all living organisms on the earth and plays an important role in every part of the earth. Even fewer quantities of it can intensely influence the chemical, physical, mechanical and technological properties of nature. Therefore, it is important to monitor, identify and control the environmental humidity under different circumstances ranging from low temperature to high or in mixtures with other gases (Carr-Brion, 1986; Stetter et al., 2003). Use in intelligent systems and networks as monitoring sensors to specify the soil moisture during irrigation in agriculture, or for recognition of corrosion and erosion in infrastructures and civil engineering are among the applications of humidity sensors (Dean et al., 2012). In reality, the need for protection of environmental conditions has been leading to extensions in various humidity sensor improvements based on the use of physical and chemical methods in presence of organic and inorganic materials (Salehi et al., 2006; Kim et al., 2009a; Aziz et al., 2011; Lei et al., 2011). Development of humidity sensor systems includes enhanced attempts in improvement of transducer performance such as sensing elements (Yadav & Singh, 2010; Lin et al., 2013), fabrication technologies (Gusmano et al., 1993b; Traversa & Bearzotti, 1995), and principle of mechanism (Smetana & Unger, 2008; Karimov et al., 2010).

The conventional materials utilized for sensing elements of the humidity sensors are metal oxides based on the composition of these compounds. The ability of metal oxide materials to recognize humidity is affected by their fundamental chemical and physical properties. The sensing mechanism of the humidity sensor is according to water adsorption on the sensor surface. An exclusive structure of ceramics involving of grains, grain boundaries and pores promotes this process (Shimizu et al., 1989; Tulliani et al., 2013). Humidity sensors use the change of electrical behaviors attributed to surface modifications of the sensing layer with water adsorption.

Several types of humidity sensors are fabricated for sensing of RH (Casalbore-Miceli et al., 2006; Li et al., 2007; Tu et al., 2012; Wong et al., 2012; Rivadeneyra et al., 2016; Tripathy et al., 2016; Shakya et al., 2017; Su & Chang, 2018) Commonly the humidity sensors production and characterization are investigated at various gaseous atmospheres (Basu et al., 2001), N_2 (Torsi et al., 2001; Saha et al., 2008), Ar (Basu et al., 2001; Li et al., 2001), H_2 (Neumeier et al., 2008), O_2 (Basu et al., 2001) or such mixer gas as O_2/N_2 (Rosty et al., 2005) and $Ar/He/N_2/O_2$ (Saha et al., 2008) are utilized as carrier gas besides air. Some humidity sensors are particularly for human breath monitoring (Laville et al., 2001; Rimeika et al., 2009; Akita et al., 2010) or for humidity control in the exhaust gas of industrial textile dryers (Zipser et al., 2000) and in a combustion rig under the conditions of excess air (Hassen et al., 2000). Certain humidity sensors simultaneously with detection of air relative humidity may have other promising applications such as water leakage revealing, mapping on roofs and in-situ humidity measurements on airplane surfaces (Yang et al., 2006), humidity controlling electronic instruments (Zhang et al., 2009).

However, no single sensor is accomplished to be able of covering the entire range of humidity measurement (Islam et al., 2012). Some of the humidity sensors can work at elevated temperatures (Banerjee & Sengupta, 2002; Joseph et al., 2004; Islam et al., 2012; Mohan et al., 2012) or identify trace humidity (Chen et al., 2009a; Chen et al., 2010). The criteria for good humidity sensors are good sensitivity over a wide range of the water content and ambient temperature, short response/recovery time, good reproducibility, very small deviation, low cost and maintenance, resistance to contaminants, easy fabrication, and long life (Islam & Saha, 2006; Majumdar & Banerji, 2009; Su & Lin, 2012). In some cases, low weight and compatibility with a microprocessor may also be needed (Estella et al., 2010).

Many of the concerns related to the design of humidity sensors are attributed to the restrictions in the sensor materials selection and in their compatibility with the fabrication technologies (Oprea et al., 2009). There are two methods to improve a great humidity sensing material: (a) the creation of a new material and (b) an enhancement in the property of conventional materials (He et al., 2010). It must be taken into consideration that excellent sensor performance is ensured by strong and specific chemical interaction between the sensing material and the target analyte (Oprea et al., 2009). Thus, until now there is no optimum material for the sensing element that could simultaneously fulfill all those requirements (Yuk & Troczynski, 2003), and discovering a novel humidity sensing materials with high efficiency is a crucial task for researchers (Yuan et al., 2011). Recently, various materials such as ceramic, electrolyte, organic polymer materials have been employed as sensing materials (Erol et al., 2011; Yuan et al., 2011).

2.2. Common design of humidity sensor

The popular pattern of a humidity sensor involved an interface in direct contact with the sample, the receptor. Mostly the receptor represents a thin layer placed at the surface of an inert carrier. There are electrical contacts, devices for signal processing and many other types of units, reliant on the sensor types. The transducer, i.e. the most important element for sample diagnosis, can be produced by different means such as thick and thin film. In thick-film technology, various layers are screen-printed on the surface of a carrier. However, in thin-film technology, thin layers are produced by vapor deposition, sputtering or chemical vapor deposition. A combination of thick and thin film technologies can also be observed in sensors fabrication. Examples of multilayer sensors are polycrystalline semiconductor gas sensors, where the sensitive tin dioxide layer is deposited by sputtering on the surface of a conductive layer which fabricated to be a heater, consisting either of platinum (Pt) or gold (Au). The latter can also be generated by sputtering. Another specimen is a gas sensor type where a paste of fine oxide particles is deposited on a ceramic substrate. The paste is fired and sintered in the next manufacturing step. Layers of equal material and in equal order can be produced by thin-film as well as by thick-film techniques. Methods for sensor fabrication have gotten a high degree of perfection and are very significant for microelectronics. The performance of such methods can be showed by seeing modern integrated electronic circuits where millions of transistors are situated on a single silicon chip. Microelectronic structures can be two or three dimensional. They intensely vary with a resolution. With thick films, only rough structures can be obtained. With thin films on silicon wafers, high resolution is achievable and complex three-dimensional structures can be obtained. The latter is fundamental for new technological fields like micromechanics. Chemical sensors can be integrated into such instruments.

Thin films of inorganic materials on a substrate are deposited by sputter deposition, high vacuum deposition and chemical vapor deposition (CVD). Sputter deposition and vapor deposition are similar procedures. They apply different methods for producing the metallic particles in the gas phase. Vapor-deposition methods are thermal processes where the material is heated electrically whereas target is bombarded by high accelerated ion gas in sputtering process. As far sputter deposition functions by means of plasma, there are mostly produced in an argon atmosphere. In CVD, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. Such procedures operate at high vacuum (2×10^{-5} mbar).

Between a heated anode and cathode, a high voltage of 2 to 5 kV is used. The consequential glow discharge generates argon ions which are accelerated by the electric field and shot against the sputtering target on the cathode where they knock out a few atoms at a time. Atomic clusters generated in this way tend to deposit on all surfaces in the chamber. The geometric arrangement ensures that the substrate is deposited sufficiently. Film deposition can be improved by adding small amounts of reactive gases like O_2, N_2 or H_2 (reactive sputtering). Nitride layers, e.g. tantalum nitride, are deposited by sputtering a metallic target in an N_2/Ar atmosphere. Sputtering is capable to create layers of alloys or elements which are not volatile. The deposited films have the same composition as the target material. DC sputtering will not work if the films of insulating materials must be deposited. It can be deposited, however, by RF magnetron sputtering, where a high-frequency field is used between the poles.

2.3. Electrode design

Films on a substrate, either thin films or thick, cannot perform generally as transducer or receptor instantly and need high electrical conductive electrode to transfer the electron. The most common configuration of microelectrodes is interdigitated lead structures, microdisks, and narrow bands on a support.

Interdigitated electrodes (IDE) are among the frequently used periodic electrode structures which were utilized for a wide range of applications such as acoustic sensors, biosensors, and chemical sensors (Radke & Alocilja, 2005; Lee et al., 2007; Qi et al., 2008; Tian et al., 2013). Numerous electrode systems with various forms were assessed with the goal to enhance the sensitivity. An electrode that has gained attention is the rectangular IDE (Shim et al., 2013). This form of electrode offers several benefits in addition to other possible configurations, including reduced resistance, high surface to volume ratio, improved signal-to-noise ratio, steady-state signals, small charging currents, low cost production, and also easy to fabricate (Couniot et al., 2013; Settu et al., 2013).

IDE is a device that is made up of two interlocking comb-shaped arrays of metallic electrodes (in the fashion of a zipper) as shown in Figure 2.1. Latest developments in such fields as telecommunications, microelectromechanical systems (MEMS), chemical sensing, nondestructive testing (NDT), and biotechnology involve IDE in very different ways. The IDE is frequently selected as a component for those sensing operation, where electrical signals generated by the sensing material have to be detected via IDEs. In many of these examples, the IDE was fabricated by photolithography in a lift-off process. In some cases, very fine lines in the range of 250-500 nm in width can be manufactured in high density in this manner. The number of fingers can be up to 2000. More often, the width of the digit (finger) is on the order of 3 to 15 μm and the number of fingers is around several hundred for this method. Several different metals had been used for this application, for example, Au, Pt, and Pd-Ag, which were often deposited by sputtering, thermal and e-beam evaporation and its thickness is in the range of 30 to 300 nm. The photolithography process is another method that consists of many steps and requires the use of special equipment.

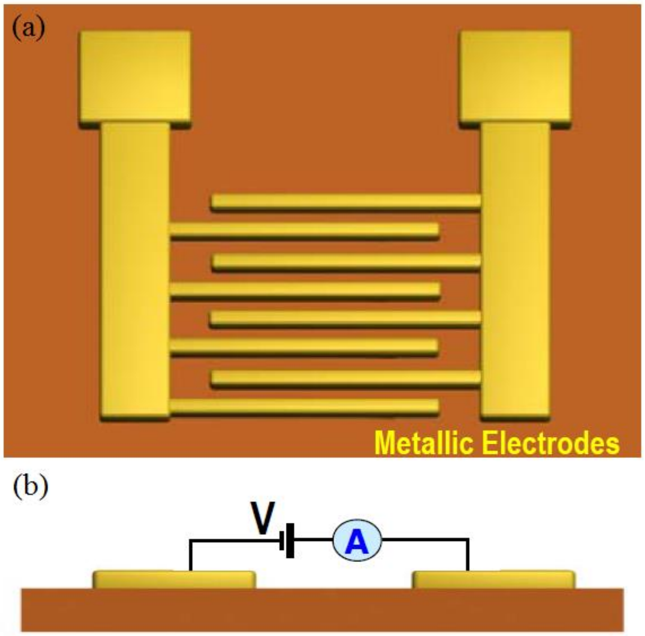

Figure 2.1: IDE (a) top view and (b) cross-section view with an electrical contact (Guo et al., 2016).

Therefore, there are a few efforts in recent years to try to simplify the fabrication process for IDEs. For example, Chou et al. (Chou & Lee, 2014) fabricated silver IDE with a stamp on a glass substrate. By adjusting parameters, the authors were able to fabricate IDEs having length 2.7 cm and width 1.3 cm. Screen printing is another method to fabricate usable IDEs for various sensor applications (Bittencourt et al., 2004; Ivanov et al., 2004b). Bittencourt et al. (Bittencourt et al., 2004) used a screen printing technology to fabricate IDE with gold paste on a ceramic substrate.

The evaporation method is commonly used for a thin layer of IDE deposition. The source material is vaporized in a vacuum. The vacuum permits vapor particles to travel directly to the substrate, where they condense back to a solid state as shown in Figure 2.2. Evaporation is used in microfabrication, and to make macro-scale products such as a thin layer of the transducer.

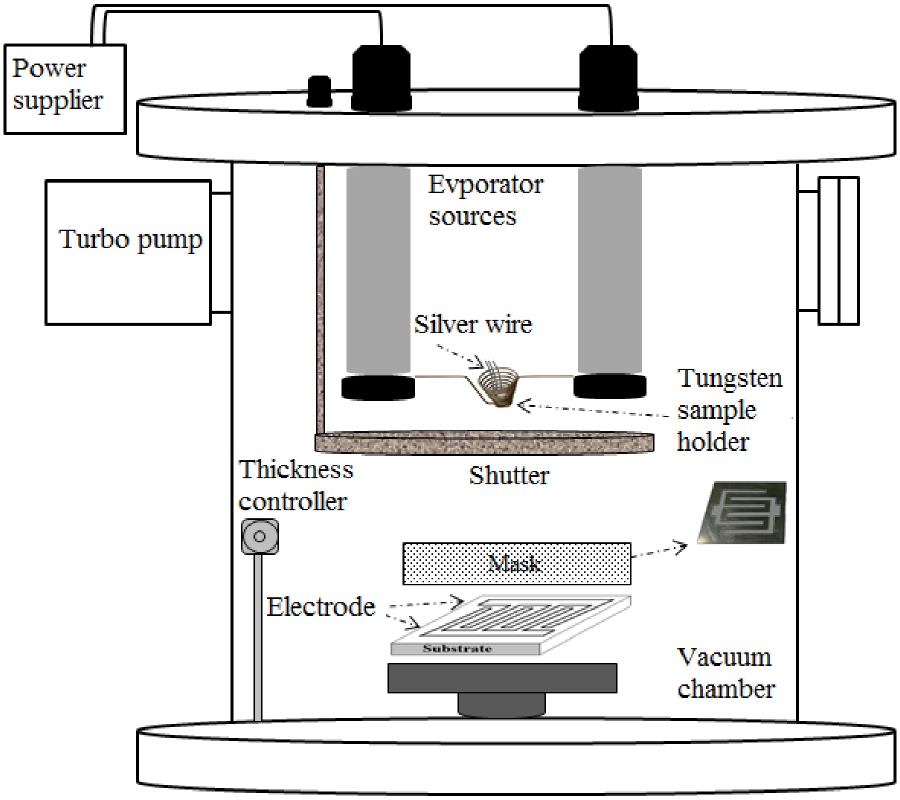

Figure 2.2: Schematic of silver IDE preparation by thermal evaporator.

2.4. Classification of humidity sensors

Based on measurement techniques, the most commonly used units for humidity measurement are RH and absolute humidity (AH) (Dew/Frost point (D/F PT) and parts per million (ppm)). RH is a ratio of the amount of moisture content of air to the maximum (saturated) moisture level that the air can hold at a same given temperature and pressure of the gas. It is stated as a percentage and determined by the expression:

$$\mathrm{RH\%} = \frac{\mathrm{Pv}}{\mathrm{Ps}} \times 100\ \% \tag{2.1}$$

Where Pv is the actual partial pressure of moisture content in air and Ps is the saturated pressure of moist air at the same given temperature (KPa). RH is a function of temperature, and thus it is a relative measurement and it is expressed as a percentage. Dew point is the temperature (above 0 °C) at which the water vapor in a gas condenses to liquid water. Frost point is the temperature (below 0 °C) at which the vapor condenses to ice. D/F PT is a function of the pressure of the gas but is free of temperature and is thus described as AH measurement. ppm represents water vapor content by volume fraction ($\mathrm{ppm_v}$) or, if multiplied by the ratio of the molecular weight of water to that of air, as $\mathrm{ppm_w}$. ppm is also an absolute measurement. Although this measurement unit is more difficult to conceive, it has extensive applications in the industry, especially for trace moisture measurement. Figure 2.3 shows the relationship among of RH, $\mathrm{ppm_v}$, and the D/F PT. RH measurement covers higher humidity range, $\mathrm{ppm_v}$ covers lower humidity range, and D/F PT covers all the humidity range. Therefore, for daily life, RH is constantly used for ease of understanding. For trace moisture measurement, it would better to use $\mathrm{ppm_v}$ or D/F PT, because it tells us the absolute amount of water vapor in a gas or air. According to the measurement units, humidity sensors are separated into two types: RH sensors and AH sensors.

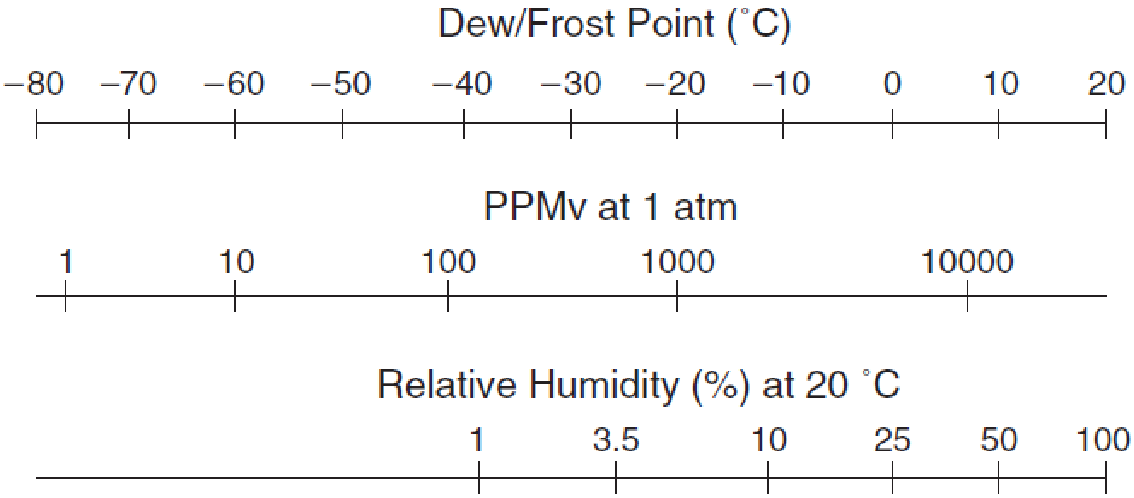

Figure 2.3: Correlation among humidity units: RH, Dew/Frost point (D/F PT), and parts per million by volume fraction (ppm_v) (Alwis et al., 2013).

In the common of humidity measurement applications, RH measurements are more desirable than AH attributed to generally simpler, inexpensive and are widely applied in applications such as indoor air quality and human comfort issues (Kulwicki, 1991). Consequently, in research laboratories and public applications, RH is universally applied to simplify the design process and further use as a secondary sensor. AH is more often utilized for traceable purposes (trace moisture measurement) as primary sensors.

As most of the commercially accessible humidity sensors in use are based on RH measurement. These can be grouped according to their operating principle and based on their sensing material. In the 1986s the different sensing elements were categorized into three main groups of electrolytes, porous ceramics and organic polymers confirming to the Yamazoe and Shimizu classification (Yamazoe & Shimizu, 1986). Around ten years later, according to Traversa‘s classification, commercially developed humidity sensors were based on the electrolytic, organic polymer films and porous ceramics as shown in Figure 2.4 (Traversa, 1995).

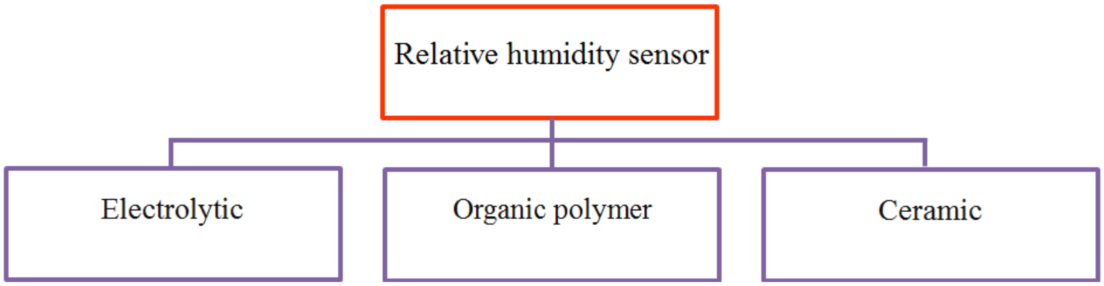

Figure 2.4: Classification of RH sensor according to sensing element.

However, ceramic humidity sensors have revealed some superior benefits in comparison to others from the viewpoints of their physical and thermal stability, mechanical strength, and their resistance to chemical attack, which depicts them to be the most potential materials for electrochemical humidity sensor applications (Traversa, 1995; Farahani et al., 2014).

2.5. Technique for production ceramic humidity sensor

The ceramic humidity sensor elements have been produced in different forms such as single crystals (Ponpon et al., 2002), porous solid bodies, thick and thin films. The bulk humidity sensors in the form of disks (Wang et al., 2005b; Rezlescu et al., 2006; Su & Huang, 2007), and pellets (Bayhan & Kavasoğlu, 2006; Vijaya et al., 2007a; Vijaya et al., 2007b), rectangular bars (Wang & Virkar, 2004; Zhang et al., 2011a), plates (Chou et al., 1999; Faia & Furtado, 2013) which were synthesized by the solid state reactions have obtained different applications, meanwhile, their manufacture and quality control is well proven. Nevertheless, miniaturization and integration in electronic circuits' favors film form (Niranjan et al., 2001). For example utilized sensing elements based on a single layer of films allow creating micro humidity sensors (Chen et al., 2009b; Liang et al., 2012).

The advantage of porosity in bulk sensors is the accessibility of large surface area for the functioning of activities. This can be achieved in the thin film sensing materials. For example, it was found that sensing nano crystalline materials involving of spray deposited tin oxide film with an over layer of nano size zirconia film deposited by liquid-liquid interface reaction method had the benefit of the large surface area like bulk, in the thin film form (Niranjan et al., 2001). Thick films have microstructural properties comparable to those of sintered bodies but can decrease the sizes of the sensing devices, which can be utilized in hybrid circuits. Thick-film technology allows easy and trustable developing with low-cost of fabrication (Traversa, 1995). Screen-printing (Qi et al., 2008; Wang et al., 2009a; Liu et al., 2010) is a traditional thick-film technology. But the thick-film sensor elements are also can be produced by using spin coating (Faia et al., 2009; Wang et al., 2010a; Zhang et al., 2010) and sol-gel method (Mistry et al., 2005), as well as tape casting (Saha et al., 2005).

The main disadvantages of a thick film humidity sensor are high pressure/temperature, time-consuming preparation process, and a lack in surface porosity that led to decline in sensor performance (Li et al., 2010; Li, 2016). There are several methods for the deposition of thin films such as chemical solution deposition (Ying et al., 2000; Yadav et al., 2010), spray pyrolysis (Niranjan et al., 2001; Tischner et al., 2008; Wang et al., 2010b), atomic layer deposition (Taschuk et al., 2012), spin coating (Qu et al., 2000; Yuk & Troczynski, 2003), hydrothermal-electrochemical technique (Agarwal & Sharma, 2002), and electrochemical anodisation (Hoa et al., 2000). Selection of the suitable methods of sensitive film deposition can significantly influence ceramic sensor efficiency. Film thickness also is another important parameter that has an influence on sensing properties.

The sensitivity of sensor reduces with an increment of the film thickness due to grain size effect (Rothschild & Komem, 2004). Because of small grain size, the film with low thickness has large grain boundary density. Such grain boundary modulation provides more chemisorption of gas and humidity molecule which affect the sensor performance.

2.6. Operating principles of ceramic humidity sensors

Ceramic sensors are extensively used in industry and research laboratories. The unique structures of ceramic materials comprising grains, grain boundaries, surface areas and controlled porous microstructures, makes them suitable candidates for sensor applications. The common materials utilized as sensing elements in ceramic humidity sensors mostly is metal oxides. The ability of these materials to sense humidity in an environment is affected by their fundamental physical and chemical properties. The sensing mechanism of ceramic humidity sensors is due to water adsorption on the ceramic surface. Humidity sensors use the variation of electrical or mechanical parameters owing to bulk and surface modifications of the sensing elements with water adsorption. To screen the humidity by means of devices with ceramic sensing elements there are utilized various physical operation principles: electrochemical, optic, thermal conductivity and mass-sensitive (Figure 2.5). The same classification can be considered for other sensing element such as electrolytic and organic polymer as shown in Figure 2.5 (Chen & Lu, 2005; Tripathy et al., 2014).

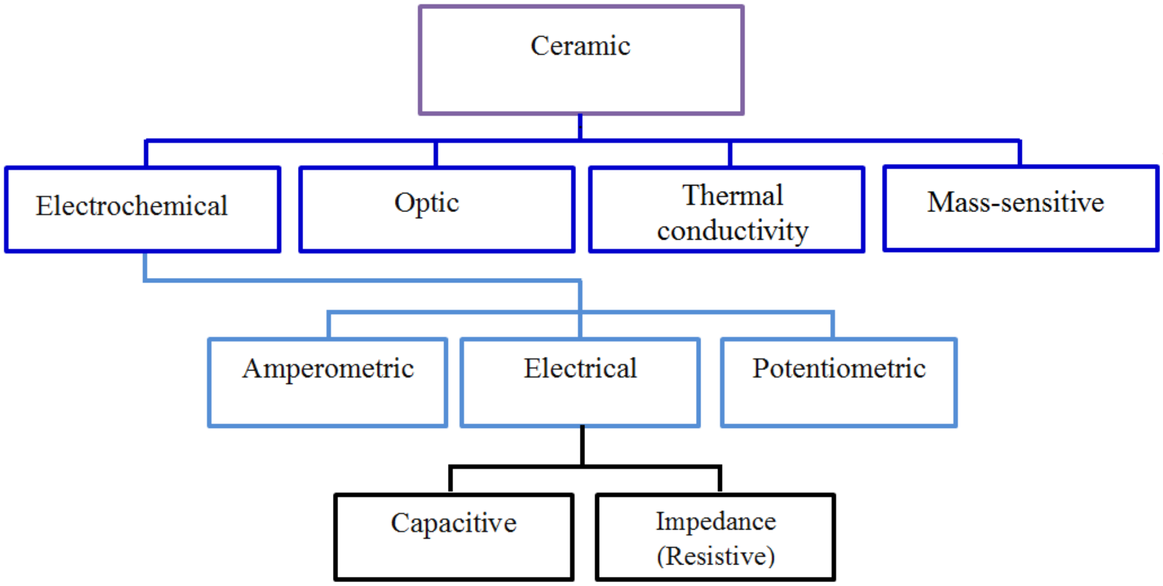

Figure 2.5: Classification of ceramic humidity sensors based on operation (Chen & Lu, 2005; Tripathy et al., 2014).

2.6.1. Electrochemical humidity sensor

Currently, a variety of electrochemical humidity sensors are being used extensively in many stationary and portable applications for personal safety. The most popular electrochemical humidity sensors known as electrical, amperometric, and potentiometric humidity sensor.

2.6.1(a) Electrical humidity sensor

Electronic humidity sensors can be generally distinct into two types: one employs resistive sensing principle, whereas other uses capacitive effects.

2.6.1(a) (i) Resistive humidity sensor

Resistive-type humidity sensors mostly consist of noble metal electrodes either deposited on a ceramic or glass substrate (Figure 2.6) (Geng et al., 2012; Liang et al., 2012; Zhang et al., 2012; Rahim et al., 2018) by thick film printing techniques (Traversa et al., 2000; Park & Gong, 2017) or thin film deposition (Kunte et al., 2008; Ismail et al., 2016). The majority of resistive sensors design structure including IDE (Mamishev et al., 2004; Clifford et al., 2018) configuration to enhance the contact area. The resistivity between the electrodes changes when the sensing layer absorbs water and this change can be assessed with the help of a simple electric circuit.

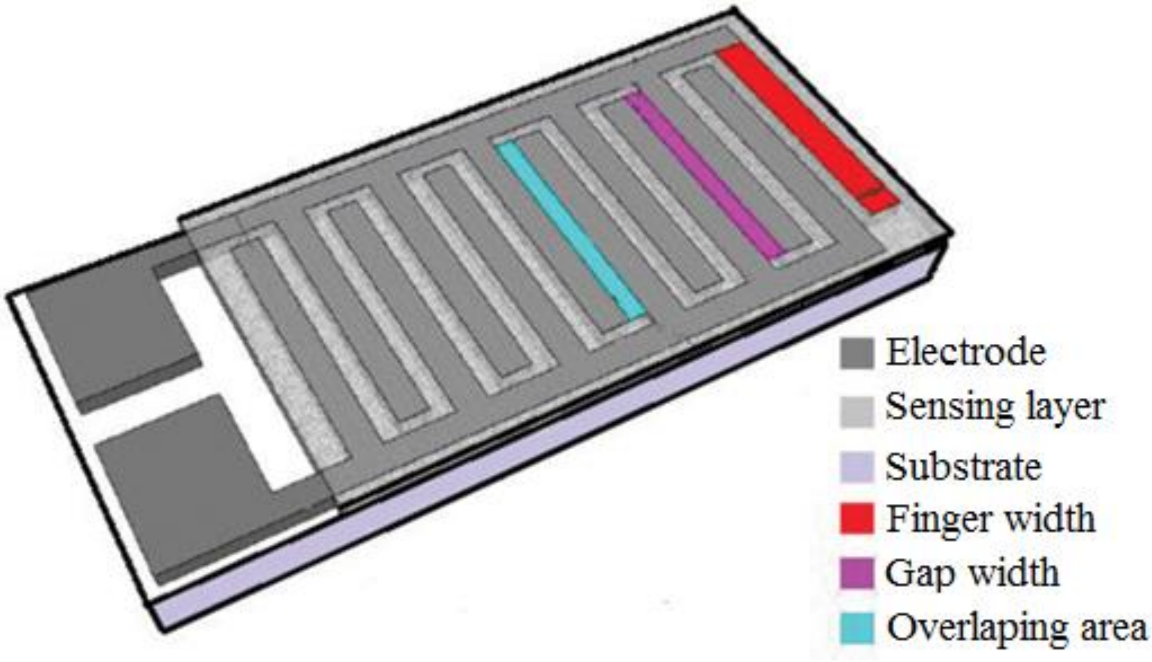

Figure 2.6: Cross-section of the resistive-type humidity sensor (Enhessari & Salehabadi, 2016).

The platform substrate can be deposited either with electrolytic conductive polymers (Moneyron et al., 1991; Kim et al., 2012) or doped ceramic sensing films (Wang et al., 2009b; Anbia et al., 2012). In some cases, the film-based sensors are produced by using both printing techniques e.g., screen or inkjet printing, and deposition techniques, e.g., chemical vapour deposition (CVD) methods such as spin coating and dip coating, or vacuum physical vapour deposition (PVD) techniques such as thermal evaporation and cold sputtering (Tai et al., 2005). Among them, electrochemical deposition is frequently functioning when deposition of a minuscule area with prepared polymers is mandatory. Nevertheless, there are rare works in which various deposition methods such as spray techniques (Racheva et al., 1994) or combination of spray pyrolysis with the other methods were used (Niranjan et al., 2001).

The advantage of resistive-type humidity sensors is the distance between the sensor and signal circuit can be large (suitable for remote operations), low cost, small size, and highly interchangeable as there are no calibration standards which make it suitable for use in industrial, domestic or residential and commercial applications. From another side, resistive-type humidity sensors are sensitive to chemical vapors and other contaminants, the output readings may shift if used with water soluble products.

Resistive-type humidity sensors measure the change of the humidity and translate it into a change in electrical resistance. Normally, the change of resistance to humidity follows an inverse relationship. As a principle, upon adsorption of water vapor, its molecules are dissociated to ionic functional hydroxyl groups and this result in a decrement of film electrical resistance. Furthermore, the response times of resistive sensors usually range from 10 to 30 s for a 63% change of the humidity level (Sakai et al., 1996). A preliminary thin film resistive-type humidity sensor with a high precision of (1%), referred to as “Hument” was established by the Nakaasa Instrument Co. Ltd. in 1978 (Yamazoe & Shimizu, 1986) and it has entered the market.