

**ANTISTATIC APPLICATIONS:
METAL COATED FIBERS
BY MAGNETRON SPUTTERING**

**A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
MASTER OF SCIENCE
in Physics**

**by
Zeynep MERİÇ**

**July, 2011
İZMİR**

We approve the thesis of **Zeynep MERİÇ**

Assoc. Prof. Dr. Lütfi ÖZYÜZER
Supervisor

Assoc. Prof. Dr. Aysun AKŞİT
Committee Member

Assist. Prof. Dr. Yusuf SELAMET
Committee Member

1 July 2011

Prof. Dr. Nejat BULUT
Head of the Department of
Physics

Prof. Dr. Durmuş Ali DEMİR
Dean of the Graduate School of
Engineering and Sciences

ACKNOWLEDGMENTS

First of all I would like to express my deepest gratitude to my thesis advisor, Lütfi Özyüzer who showed me new ways of approaching scientific problems and also special thanks for his encouragement helped during my master thesis education. His suggestions and critical reviews have helped me to understand the aspects described in this work.

I also extend my thanks to my family, my brother Asilkan Meriç, my mother Nurhayat Meriç and my father İbrahim Meriç. They stood by me and my decisions whenever I needed. I can not find better words to explain their support and their patience during my education.

I would like to express my special thanks to Ceylan Taşbaşı and Dilek Eren for all the general support throughout my master education.

Special thanks to my group members Yasemin Demirhan, Hilal Sağlam, Mehmet Ali Olgar, Mutlu Devran Yaman and Hakan Alaboz for their support and also creating a funny and nice atmosphere while studying together. Especially I would like to thank Yasemin Demirhan for her endless patient and support.

I offer sincere thanks to Ministry of Industry of Turkey and Teknoma Company to let us to study this great research. This research was supported by Ministry of Industry of Turkey, project number 00422.STZ.2009-2.

Finally I am grateful to Zebih Çetin. He has made available his support in a number of ways...

ABSTRACT

ANTISTATIC APPLICATIONS: METAL COATED FIBERS BY MAGNETRON SPUTTERING

The utilization of textile materials with nanotechnology is increasing in many industries especially for automobile, medical and health care. These materials have recently been of increasing interest to both the academic and the industrial sectors. Today, a wide range of nanoparticles, nanofilms and nanocomposites with various structures can be applied to the fibers, bringing new properties to the final textile product. For all these technical applications, it is desirable to produce such textile materials with especially designed surface features to meet various needs. Various techniques have been developed to functionalize textile materials. Physical vapor deposition (PVD) has been applied to modify textile materials various functions and solvent-free process. In this study, for this aim we designed a new magnetron sputtering system which is called inverted magnetron sputtering. The surfaces of synthetic fibers, such as PP and PA, whose diameters are in the range between 60-125 μm , coated with electrical conductors. In this study silver is used because of silver has the highest electrical conductivity in metals and additionally it has antibacterial properties. Textile fibers were coated in nanometer thickness and electrical conductivity is aimed to increase. These fibers weaved into fabrics in order to investigate antistatic and antibacterial properties. For characterization optical microscope and SEM images were taken. Besides, XRD, electrical results, mechanical strength tests were done. In order to determine optimum film thickness, by using three different methods coating thicknesses were investigated and results compared. Resistances of Ag on fibers were found and film thickness calculated from bulk Ag resistivity. The thickness was also calculated from deposited mass of silver. The both results were compared with independent thickness measurement on a glass substrate with a surface profilometer. The analysis of data commented surface scattering effect. When these fibers were weaved to become fabric due to these properties, fabrics will take place of technical textiles. Besides, the obtained fabrics have potentials to be used for electromagnetic shielding, radar absorbing materials and infrared camouflage.

ÖZET

ANTİSTATİK UYGULAMALAR: MİKNATISSAL SAÇTIRMA İLE METAL KAPLANAN FİBERLER

Nanoteknoloji ile tekstil malzemelerin kullanımı özellikle otomobil, sağlık ve tıp gibi birçok endüstride artmaktadır. Bu malzemelere ilgi son zamanlarda hem akademik çevrelerce hemde sanayide artan bir ilgiye sahiptir. Bugün tekstil malzemelerine yeni özellikler katmak için nano parçacıklar, nano filmler ve nano kompozitler fiberler içerisine katkılanılmaktadır. Bütün bu uygulamalar için istenilen, çeşitli gereksinimler için tasarımılanan teknik özellikleri içeren fonksiyonel tekstil malzemelerinin üretilmesidir. Tekstil malzemelerini fonksiyonel yapmak için çeşitli teknikler geliştirilmiştir. Yüksek vakumda fiziksel buhar biriktirme (PVD) yöntemi, çevreye zararlı kimyasal kullanmasından dolayı, tekstil malzemelerini modifiye edip fonksiyonel hale getirmek için yeni yeni uygulama alanı bulmaya başlamıştır. Bu çalışmada amacımıza uygun olarak yeni mıknatıssal saçtırma sistemi tasarlanmıştır ki bu sistem silinirik mıknatıssal saçtırma sistemi olarak da adlandırılmaktadır. PP ve PA gibi 60 ile 125 μm arasında değişen çapa sahip sentetik fiberlerin yüzeyleri elektriksel olarak iletken metallerle kaplanmıştır. Ayrıca bu çalışmada kaplama malzemesi olarak gümüş kullanılmıştır çünkü gümüş hem elektriksel olarak en iyi iletken hemde anti bakteriyel özelliğe sahip bir metal. Tekstil fiberleri nanometre kalınlığında iletken ince film ile kaplanarak iletkenliğin artırılmak istenmektedir. Kaplanan bu fiberler antistatik ve antibakteriyel özelliklerin araştırılması için kumaşa dokunmuştur. Karakterizasyon için optik mikroskop ve taramalı elektron mikroskop incelemeleri yapılmıştır. Ayrıca XRD çekilmiş, elektriksel sonuçlar alınmış ve mekanik dayanım testleri yapılmıştır. Optimum film kalınlığının bulunması için üç farklı yöntem kullanılarak elde edilen kaplama kalınlıkları hesaplanmış ve sonuçlar karşılaştırılmıştır. Kaplanan gümüşün öz direncinden yola çıkılarak yapılan direnç hesaplamasından film kalınlığı hesaplanmıştır. Ayrıca kaplanan gümüş kütlelerinden film kalınlığı hesaplanmıştır. Sonuçlar, aynı deney parametreleri ile kaplanan cam örneği yüzeyinden yüzey profilometre kullanılarak bulunan film kalınlığı ile karşılaştırılmıştır. Sonuçlar ince film yüzey saçılması olayı ile açıklanmıştır. Bu fiberler kumaş haline getirildiğinde özellikleri sayesinde teknik tekstillerin yerini alabilecektir. Bunun yanısıra, elde edilecek teknik kumaşların elektromanyetik kalkan, radar dalgası soğurması ve kızılötesi kamuflej amaçlı da kullanım potansiyeli bulunmaktadır.

TABLE OF CONTENTS

LIST OF FIGURES	ix
LIST OF TABLES	xi
CHAPTER 1. INTRODUCTION	1
1.1. Antistatic.....	1
1.1.1. Electrical Charge	2
1.1.2. The Occurance of Static Electricity	3
1.1.3. The Use of Antistatic Textile Products	4
1.1.4. Static Charge Generation and Dissipation	5
1.2. Technical Textiles	5
1.3. Literature Overview	6
CHAPTER 2. THEORY	9
2.1. Antistatic Applications.....	9
2.1.1. Electrostatic Discharge (ESD)	9
2.1.2. Surgery Room Clothes	10
2.1.3. Clean Room Garments	10
2.1.4. Military	11
2.1.5. Electromagnetic (EM) Shielding	11
2.2. Fabrication Methods for Antistatic Fibers	12
2.2.1. Metal Fibers	13
2.2.2. Bicomponent Fibers	14
2.2.3. Melt Compounding Method	15
2.2.4. Chemical Processing	16
2.2.5. Metallization of Fibers	16
2.3. Thin Films	17
2.3.1. Physics of Thin Films	17
2.3.2. Applications of Thin Films	18
2.3.3. Thin Film Processing Methods	18
2.3.3.1. Chemical Vapor Deposition	19
2.3.3.2. Physical Vapor Deposition	21

2.3.3.3. Thermal Evaporation	21
2.3.3.4. Sputtering	22
2.3.4. DC and RF Sputtering	23
2.3.5. Reactive and Magnetron Sputtering	24
2.4. Deposition Materials	27
2.4.1. Silver	27
2.4.2. Silver in Textiles	28
2.4.3. Other Materials	29
2.5. Electrical Modification of Fibers by Thin Film Coating	31
CHAPTER 3. EXPERIMENTAL	32
3.1. Motivation	32
3.2. Material Type	33
3.2.1. History of Polymers	33
3.2.2. Polypropylene (PP).....	34
3.2.3. Polyamide (PA).....	34
3.2.4. Polyester (PET).....	35
3.3. Plasma Cleaning.....	35
3.3.1. What is Plasma?.....	35
3.3.1.1. Low Frequency (LF) Plasma Cleaning	37
3.3.1.2. Radio Frequency (RF) Plasma Cleaning.....	38
3.3.1.3. Comparison of LF and RF Plasma Cleaning	38
3.4. Inverted Cylindrical Magnetron Sputtering System	40
3.5. Conduction Process in Thin Films.....	42
3.6. Scattering Mechanism in Thin Films.....	43
3.7. Electrical Conductivity of Fibers	46
CHAPTER 4. RESULTS AND DISCUSSIONS	47
4.1. Mechanical Strength Results.....	47
4.2. Optical Microscope Studies	50
4.3. Scanning Electron Microscope (SEM) Studies	51
4.4. XRD Result	54
4.5. Electrical Results	54
4.6. Thin Film Thickness Measurements	57
4.6.1. Calculating from Measured Resistance	57

4.6.2. Calculating from Deposited Silver Mass	58
4.6.3. Calculating from Calibration Sample	58
4.7. Optimization of the Film Thickness	59
4.8. Antibacterial Results	59
CHAPTER 5. CONCLUSION	63
REFERENCES	65

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 1.1. The static charge occurring between foot and floor	1
Figure 1.2. The atom	3
Figure 1.3. Antistatic surgery room clothes	6
Figure 1.4. Antistatic foot wear	7
Figure 1.5. Antistatic T-shirt	7
Figure 2.1. Antistatic clean room garments	11
Figure 2.2. Antistatic rain-wear	12
Figure 2.3. Mobile phone case for EM Shielding	12
Figure 2.4. Metal fibers for electromagnetic shielding	13
Figure 2.5. Bicomponent fiber produced at Vektron	14
Figure 2.6. Bicomponent fibers	15
Figure 2.7. The cross section view of fibers after chemical processing	16
Figure 2.8. Three modes of thin film growth	19
Figure 2.9. A schematic view of CVD system	20
Figure 2.10. Simplest view of thermal evaporation system	21
Figure 2.11. Species during sputtering	22
Figure 2.12. Simplest view of sputtering process	23
Figure 2.13. DC sputtering	24
Figure 2.14. RF sputtering	25
Figure 2.15. Schematic representation of reactive sputtering	26
Figure 2.16. DC magnetron sputtering system	26
Figure 2.17. Picture of our planar magnetron sputtering system	27
Figure 2.18. Plasma generated during magnetron sputtering	27
Figure 2.19. Conductive fibers produced by melt compounding (a) and thin film coating (b) methods	31
Figure 3.1. 12, 18, 25, 31 and 37 nm Au coated fabrics	32
Figure 3.2. Optical microscope image of 37 nm Au coated fibers	32
Figure 3.3. Schematic representation of plasma	37
Figure 3.4. LF Plasma Cleaning System	37
Figure 3.5. Our Designed Inverted Magnetron Sputtering System picture	40
Figure 3.6. Schematic view of our Inverted Cylindrical Magnetron Sputtering Sys- tem	41

Figure 3.7. During deposition fibers passing through the target plasma zone	42
Figure 3.8. Diffuse scattering of electrons from film surface in Thomson Model	44
Figure 3.9. Resistivity versus Temperature relation for metals	45
Figure 3.10. Band diagram of textile fibers	46
Figure 4.1. Mechanical strength results of 125 μm diameter polyamide	48
Figure 4.2. Mechanical strength results of 150 μm diameter polyamide	49
Figure 4.3. 85 nm silver coated PP multifilament fibers (36 multifilament, each monofilament 60 μm in diameter)	50
Figure 4.4. Optical microscope image of PP multifilament	50
Figure 4.5. SEM image of silver coated fibers	52
Figure 4.6. SEM image of silver coated fiber surface	52
Figure 4.7. SEM image of silver coated fiber surface	53
Figure 4.8. SEM image of cracks on the fiber surface	53
Figure 4.9. X-ray diffraction results of PA and silver coated PA	54
Figure 4.10. X-ray diffraction results from literature (Jung, 2004)	55
Figure 4.11. Deposition speed versus resistance	57
Figure 4.12. Normalized resistivity versus κ values	60
Figure 4.13. Silver coated fibers woven into fabric	61
Figure 4.14. ASTM-E 2149 Antibacterial Test	61

LIST OF TABLES

<u>Table</u>		<u>Page</u>
Table 1.1.	Threshold voltages of some of electronic circuit elements	2
Table 2.1.	Thin film applications according to their properties	19
Table 2.2.	Properties of silver	28
Table 4.1.	Some of our electrical results	56
Table 4.2.	Comparison of 3 methods	59
Table 4.3.	Antibacterial test results	62

CHAPTER 1

INTRODUCTION

1.1. Antistatic

Materials always try to eliminate static electricity which is caused by triboelectric effect. Triboelectric effect simply known as charge transfer between dissimilar materials. When materials touch each other, electrons can be exchanged between materials. For instance, while neutrally charge person walking on the wool carpet, electrons transfer through the carpet. As a result person become positively charged. In Figure 1.1 the occurring static charge between foot and floor can be seen.

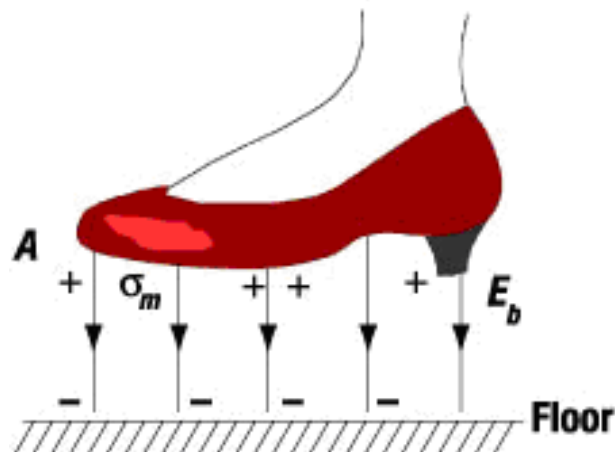


Figure 1.1. The static charge occurring between foot and floor

The human body is as much as a resistance and at the same time it is a capacitor. Walking on the carpet has one of the highest rate that load our body static charge. This static electricity occurs in few seconds and we see this event in our daily lives. After we load static charge if we contact an electronic material, it becomes useless or it can not work properly. According to recent studies, in daily life 25% electronic breakdowns caused by the electrostatic discharge (ESD) events. We will discuss ESD details in the next section. ESD also causes damage 50% materials which run currently. The cost of ESD failures in the world was determined as approximately a total of 25 trillion dollars.

Table 1.1. Threshold voltages of some of electronic circuit elements

MOSFET	100 V
CMOS	250 V
Film resistance	300 V
Schottky Diode	300 V

Induced static electricity in our bodies is harmful for both our health and electronic devices that we are using now. Researches show that static charge does not discharge suddenly, it is seen that discharge is occurring slowly and curvilinear flow through $1\text{ M}\Omega$ resistance. In the Table 1.1 threshold voltages of some electronic circuit elements are given.

Materials we use in electronic laboratories do not cause ESD and also should be able to discharge in appropriate standards. Therefore, in all environments those have electronic materials should use antistatic materials against the static charging events. Conductors have surface resistance between $10^4 - 10^5\Omega$ and they discharge quickly. Insulators are the source of static electricity and have higher than $10^{12}\Omega$ surface resistance. Between these materials has an impedance region and in these region materials have surface resistance between $10^6 - 10^{12}\Omega$ which we call antistatic materials.

1.1.1. Electrical Charge

By walking on the carpet and then bring our finger close to a metal door or something, we can produce a spark. This especially happens in dry weathers. Likewise, when we rub a glass rod and a silk fabric, we can see that they draw each other. These are because each one has an electrical charge.

Objects consist of these electrical charges and electrical charge is an intrinsic characteristic of the fundamental particles. This property comes naturally with those particles wherever they exist. Every object consists of atoms and atoms also consist of particles. As we can see from the figure these particles are electrons, protons, and neutrons. (See Figure 1.2) Each electron has a small negative charge. An atom has equal number of electrons and protons so we can say atoms have no electrical charge. Actually every object has too much amount of electrical charge. But this amount is not seen in other words it

The Atom

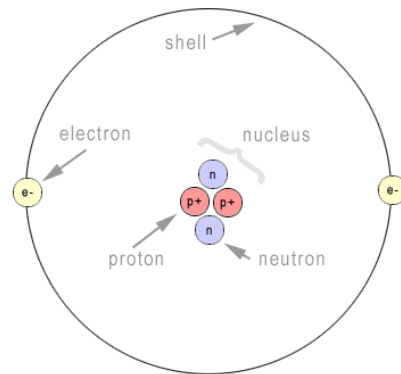


Figure 1.2. The atom

is hidden because object has equal amount of two kinds of charge which are positive and negative charges. In such a balance of charge object known as neutral which means there is no net charge. But if object has imbalance that means there is a net charge that can be positive or negative.

1.1.2. The Occurance of Static Electricity

At the beginning of the 20th century first industrial application of electrostatic was done by Frederick Cottrell who produced electrostatic precipitator or electro filter. In this manner he prevented the formation of environmental pollution by keeping the ashes of burning objects.

Carlson, lawyer and physicist, was working a patent office and sometime patent paper's copies were needed then he decided to make copy machine. He used both electrostatic and photoconductivity principles and created working principle of copy machine but nobody believed this would work, unfortunately it would not work. But after years these studies, known as electrostatic, helped Xerox.

In Central-Western America in the 1930s, explosions occur in the grain warehouses. Also increasing the number of explosions in operating rooms and laboratories attributed to the electrostatic. Electrostatic discharge was the source of these explosions.

Static electricity was not the only cause for explosions. Same thing happen printing industry as well as the textile industry. The papers were stuck together and fibers plugged the filters. Static electricity caused the shock when we touch somewhere and car

radios got confused. In order to prevent this, wheels were become conductive by addition of some conductive elements. The production of nylon and Teflon in the 1940-50s, static electricity become a phenomenon that used every day.

In 1960s static electricity has seen in electronic industry. Some believes the MOS-FET are the beginning of the electronic revolutionary. When complex electronic circuits were broken, it is defended that this cause deterioration between the charge and electric field strength. This was not the static electric this was the electrostatic. According to most people electrostatic was new in the electronic industry. They accepted the electrostatic as a new field and gave a name, we known as Electrostatic Discharge (ESD).

1.1.3. The Use of Antistatic Textile Products

Antistatic and conductive bags are used while electronic devices are carrying and when they are stored. There are many types such as protected against moisture and completely conductive. Additionally these types are also very ideal for Electromagnetic field protection.

Packing foams are used in packaging and to hide electronic equipments in them. There are two types producing; antistatic and conductive.

Table coverings also have antistatic and conductive types. These coverings provide protection against chemicals.

Antistatic wrist strap are made from metal or textile. Especially people who are working with electronic devices should use wrist strap in order to ground themselves.

Antistatic heel strap can be used as an alternative to antistatic shoes. It provides employees and visitors to use their own shoes in order to ground static electricity through antistatic heel strap (See Figure 1.4).

Antistatic aprons are electrical conductors when they are produced from carbon absorbed textiles. In this manner, they prevent static electricity produced from clothes. The only thing is they should have one layer and be conductive.

Antistatic seats are used many sectors such as chemical, medical, pharmaceutical, oil and military industry, hospital clean rooms and manufactory which produces electronic devices. Antistatic seats have ESD property. The structure of seats is textile products. They consist of special conductive fibers so static electricity discharges by using conductive fibers.

1.1.4. Static Charge Generation and Dissipation

Static charging is an important problem for our daily lives. We have to overcome this problem because it results in serious consequences. For instance, electronic equipments can be break down. If there is electronic device, static charge could be anywhere. Static discharge in an operating room may lead to explosion. Moreover we have to use antistatic textiles in clean rooms. Because it could prevent electronic equipments to be break down and also we get rid of dirt and dust particles. Dirt and dust particles are usually charged particles so these particles also could cause static charging. When charged particles attract to the fibers and adhere irreversibly, this discolors them.

Everyone has experienced static discharge buildup and discharge effects virtually. Generally static charging occurs with textile fibers including polyester and this happens during textile operations such as weaving. Static charging requires charge motion that is impossible in perfect insulators. Because of being good insulators PA, PP and other hydrophobic fibers do not develop static charge easily. If they do, these charges are mobile.

1.2. Technical Textiles

Technical textile fibers have recently been of increasing interest to both the academic and the industrial sectors. Today, a wide range of nanoparticles, nanofilms and nanocomposites with various structures can be applied to the fibers, bringing new properties to the final textile product (Sen, 2007). So called "Intelligent Textiles" or "Smart Clothes" represent the next generation of fibers, fabrics and readymade products which have an added value regarding the textiles basic functions. In recent years, textile industry benefits from these studies. New fiber types add additional value of textile materials so that basic functions such as protection thought to be refined (Wei, 2008) (Horrocks, 2000).

1.3. Literature Overview

The utilization of textile materials with nanotechnology is increasing in many industries especially for automobile, medical and health care. For all these technical applications, it is desirable to produce such textile materials with specially designed surface features to meet various needs. Various techniques have been developed to functionalize textile materials. Physical vapor deposition (PVD) has been applied to modify textile materials various functions and solvent-free process. High vacuum physical vapor deposition method due to its inherent merits, such as environmental friendly properties, to modify and functionalize textile materials started to find new applications. Sputter coating is one of the most commonly used techniques in PVD, which has been widely used in glass, ceramic and micro-electronic industries. Sputter coating produces very thin metallic or ceramic coatings (nanometer thickness) on to a wide range of substrates, which can be either metallic or non-metallic in different forms.



Figure 1.3. Antistatic surgery room clothes

To be defined a fabric as an antistatic it should show $10^6 - 10^8 \Omega/\text{sqr}$ surface resistance. For this aim, the fibers were coated with thick enough Cr and Ag to provide antistatic properties. Arising from friction or other events, the charge accumulates on the surface of a fabric. It is possible to discharge the static charge by a very thin conductor, These fibers were weaved into fabrics, and antistatic and antibacterial properties of these fabrics were investigated.



Figure 1.4. Antistatic foot wear

Antistatic fabric and work clothes are a type of technical textile which is in need by uniform manufacturers. Hospitals, electronic industry firms, electrostatic-affected-dye houses, military personnel, transport personnel of fuel and gas, pharmaceutical and medical equipment manufacturers, and research laboratories are using antistatic uniforms.



Figure 1.5. Antistatic T-shirt

The surfaces of synthetic fibers (10-100 μm in diameter PA, PP etc. fibers) were coated in high vacuum with electrical conductors such as Ag and Ti metals and electrical conductivity is aimed to increase. When these fibers are weaved to become fabric and due to their antistatic and antibacterial properties, these fabrics will take place of technical textiles which are imported from abroad. To be defined a fabric as an antistatic it should show $10^6 - 10^8 \Omega/\text{sqr}$ surface resistance. Therefore, the fibers were coated with thick enough Ag to provide antistatic properties. Arising from friction or other events, the

charge accumulates on the surface of a fabric. It is possible to discharge the static charge by a very thin conductor, 20 nm or less, on the surface.

In this thesis, the synthetic fibers and yarns were coated with the metal in a high vacuum at high speed (10-100 m/min). The vacuum coating machine were designed and manufactured, and the process parameters were obtained for optimal deposition. These fibers will be weaved into fabrics and antistatic and antibacterial properties of these fabrics will be investigated. Besides, the obtained fabrics have potentials to be used for electromagnetic shielding, radar absorbing materials and infra-red camouflage.

Therefore, to make commercially available coating machine will provide a new patent and can be used in mass production and will provide us knowledge about construction of other types of machineries. This type of yarn production will bring Turkey in the leading position in the world for technical textile manufacturing technology. Moreover, besides exporting as a fabric, it is possible to reach the end-user as a uniform etc (Hasegawa, 2008).

In order to maintain competitiveness of Turkish textile sector, it should be directed to the innovative and advanced technology products. T.R. Ministry of Industry published a Textile Strategy Report in September 2008; as of the end of 2006, Turkey has the world's seventh largest synthetic yarn capacity, at the same time that it has the the largest synthetic capacity in EU and emphasizes the importance of directing technical textiles (Hegemann, 2005).

CHAPTER 2

THEORY

2.1. Antistatic Applications

2.1.1. Electrostatic Discharge (ESD)

Depending on the moisture in the environment while walking on a carpet you can charging. The sudden electric current flows between two materials that have different electrical potentials can be explained by electrostatic discharge (ESD). Main cause of the ESD is static electricity which I mentioned about chapter 1. This occurs while two materials contact and then separating suddenly. In other words this is called triboelectric effect. Another cause of ESD can be said electrostatic induction. This produces when electrically charged material come to near a conductive material isolated from ground. while this is happening net electrostatic charge of the material does not change. The charged material cause the electrical charges on the surface of the other material to redistribute.

Today also the devices that we use getting smaller and smaller by the development of nanotechnology. At some point these devices become charge sensitive. For electronic equipments and the other electronics ESD is a dangerous phenomenon. Static discharge in an operating room may lead to explosion and because of electric discharge electrical equipments can be overloaded and break down. In order to prevent these damages there are a lot of equipments which I mentioned before.

ESD garments allow people to control destructive ESD events. By using this kind of garments we can prevent ESD damages. In this manner the electronic devices, electronic components and high technology materials quality can be improved. The charging should be slowly that is the correct thing. So manufacturers use antistatic garments. To improve performance of these garments they do some tests.

2.1.2. Surgery Room Clothes

Nowadays, functionalized textiles are using in many areas such as surgery room clothes. New added values of these textiles make them usefull for desired applications.

In a surgery room, environment and all other things must be very clean including people. All equipments must be sterilized. As I mentioned before dust particles are also charged particles. These particles may cause harmful effects during the surgery. Patients can be influenced by dirty environment. In surgery room there are electronic equipments which are very sensitive. Electrostatic discharge effects devices and may cause explosions. In Figure 1.3 surgery room clothe can be seen.

Therefore by using antimicrobial textiles, it is possible to prevent patient from any microbial effects. These antimicrobial textiles bring desired properties to the consumer.

2.1.3. Clean Room Garments

Experiments are being done in the clean room environment anymore. In order to prevent any harmful damage caused from electronic equipments or working people, clean room garments are used. With the development of nanotechnology experimental samples become in the range of nanometer and they become very sensitive to charging. By using these textile both electronic equipments in the clean rooms and samples preventing from electronic damages.

In Physics department of Izmir Institute of Technology there is a clean room. Everyone have to wear clean room garments. These garments have surface resistance $10^5\Omega/\text{sqr}$. If we look at fabric of garment, easily conductive coated fibers can be seen which are woven at regular intervals. In Figure 2.1 antistatic clean room garment can be seen.



Figure 2.1. Antistatic clean room garments

2.1.4. Military

Textiles have many advantages such as mechanical, aesthetic and material advantages which make them unique in both industry and society. In military main advantage of these textiles can be talked about integrated electronics into military dressings. What desired is computers which are convenient, durable and comfortable as clothing but this is not truly possible. Most of wearable computing equipments are not truly wearable. To integrate these electronic sensing equipments into textiles and clothing is very useful for military dresses. These technologies let us intervention whenever needed. Soldiers can find easily their partner's position and commanders can give directions to the soldiers. Figure 2.2 shows an antistatic rain-wear which is suitable for military purposes.

2.1.5. Electromagnetic (EM) Shielding

We all know about dangerous sides of electromagnetic radiation on people, plants and animals. Electrically conductive textile materials can be used as shielding to protection against electromagnetic fields. Radiation of different frequencies causes damages on efficiency of electronic equipments. In order to prevent harmful effects of electromagnetic waves, electrically conductive textiles can be used because of their shielding property.

In our daily life it is necessary to protect some special areas or buildings from electromagnetic field sources. For example banks, hospitals or any other data bases should



Figure 2.2. Antistatic rain-wear

be protected from external fields that can allow to connect their information systems.

From Tv and radio to mobile phones, all devices have dangerous effects on human



Figure 2.3. Mobile phone case for EM Shielding

health. When electromagnetic wavelengths get smaller these waves behave like energy distribution called photon. At these energies electromagnetic radiations are X and gamma rays. When these too energetic rays strike on molecules, molecules ionize and this causes defects in the molecule structure that cause harmful biochemical reactions. As a result these reactions effect the cancer formation.

According to Specific Absorption Rate (SAR) value it is accepted that EM radiation which causes the $1^{\circ}C$ increase human body temperature is harmful. In the Figure 2.3 mobile phone case can be seen for protecting human body from dangerous radiation.

2.2. Fabrication Methods for Antistatic Fibers

2.2.1. Metal Fibers

According to different purposes fiber diameter and length can be changed. In order to get antistatic fabric one should weave the conductive fibers at regular intervals into the fabric. On the other hand, metal fibers can be woven simply. In Figure 2.4 for EM shielding metal fibers were woven.



Figure 2.4. Metal fibers for electromagnetic shielding

For this purpose you can use just metal fibers. But we know that metals are heavy so fabric would be heavy also. When these fabric become antistatic clean rooms garment for instance, this also makes your movement difficult. Additional to become heavy metal fibers are also expensive. For these disadvantages metal fibers are not preferred.

2.2.2. Bicomponent Fibers

During the production of these fibers you can add conductive filaments at different ratios. Bicomponent fiber have random conductive parts in it. These fibers decomposable and resolvable. Bicomponent fibers can be decompose their conductive and non conductive parts. But in this technique the produced fibers diameters are not uniform and cross section of fibers does not show homogeneity (Supuren, 2007).

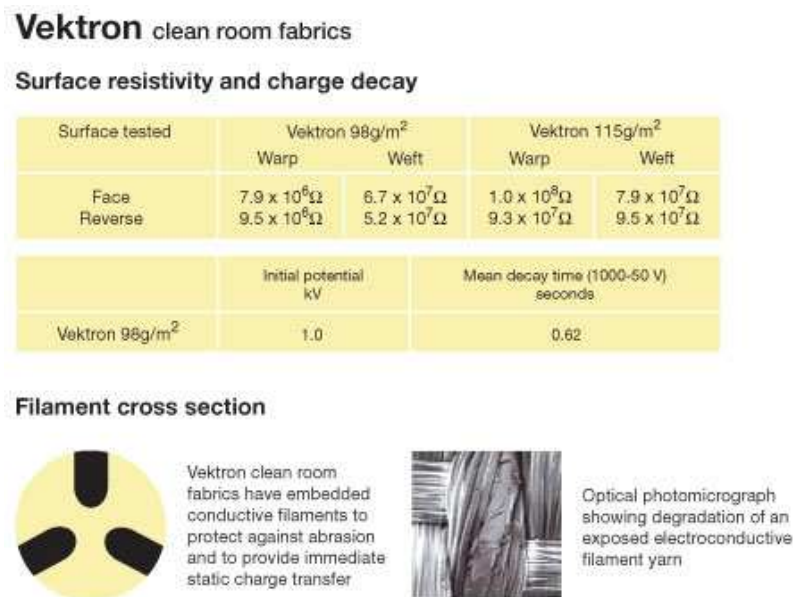


Figure 2.5. Bicomponent fiber produced at Vektron

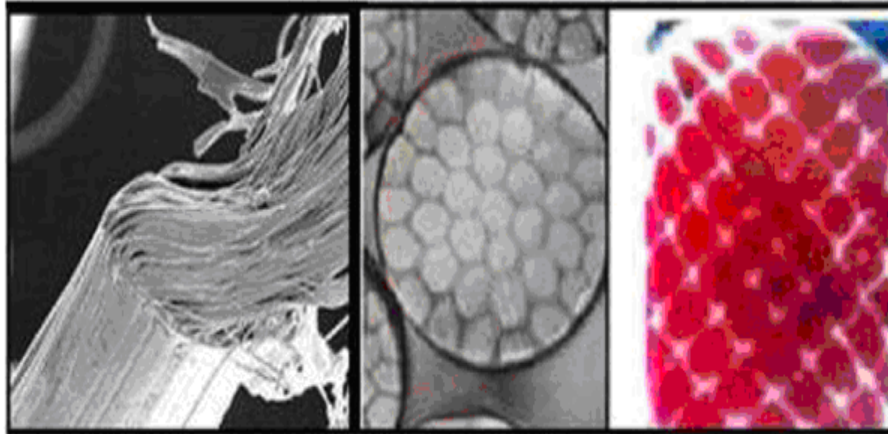


Figure 2.6. Bicomponent fibers

You can see the cross section of a bicomponent fiber in Figure 2.5 which is produced at Vektron. From the figure cross section looks like perfect but in generally getting this homogeneity is difficult.

Our aim is to get the conductivity through the surface of the fiber but in this method conductivity is not continuous on the surface. You can clearly see from cross section of bicomponent fiber there are some uncoated parts that do not have conductive filaments.

2.2.3. Melt Compounding Method

In this technique while the production of the polymer you can add nano particles at different concentrations into polymer solution. These particles would lie in the fiber randomly. If these particles are conductive fiber have conductivity but this would not be continuous because of the random particle distribution.

Melt compounding is a frequently used technique because of its advantages. This method shifts nanocomposite production downstream while giving to the final product many specifications. Also its versatility and compatibility with existing processing infrastructures renders industrially and economically significant. In addition to these advantages the absence of solvents also reduces the costs associated with such solvents and with their disposal environmental impact.

Since our aim is to increase the conductivity of the fibers we have to have conductive part continuously because these random particles are not homogeneous and continuous. The conductive path way should be through the fiber length. So we state that if

we have conductive thin metal film onto fiber this gives us best conductivity through the fiber.

2.2.4. Chemical Processing

In order to get conductive thin film on the fiber surface chemical deposition can be used. This chemical process called as electroless deposition. Electroless deposition consists of 8 steps and at each step you have to use different chemical for different purposes. For example you have to use chromic acid for cleaning at first step. To get thin film you have to use different kind of chemicals which means that you have chemical waste.

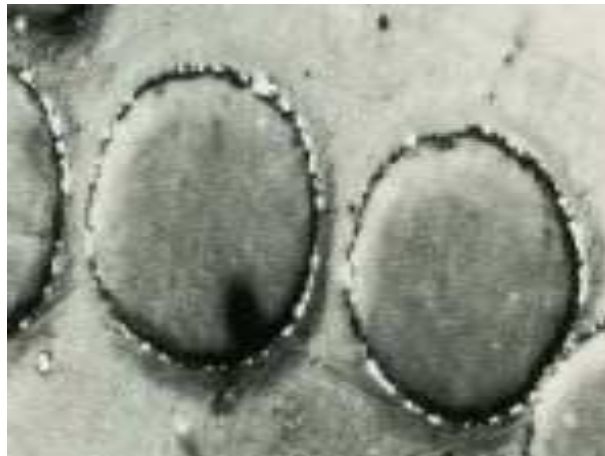


Figure 2.7. The cross section view of fibers after chemical processing

On the other hand, as it is obvious from Figure 2.7, fiber surfaces can be damaged because of chemicals. The cross section view shows that properties of fiber surface can be effected from chemicals.

2.2.5. Metallization of Fibers

Metallised fibers which coated with electrically conductive metals such as Al and Ag. Thin layer of metal gives the fabric some important properties. For examples when metal coated fibers are woven into fabrics, fabric become conductive. Also metal thin film make the fabric reflective for decorative purposes. Additionally, fabrics have reflection

property and does not allow light through. Depending on the metal that deposited also other important advantages can be gained.

In literature there are many studies in order to metallise fibers. Some of them using vacuum coating systems and others using chemicals and any other techniques. For example by using sol-jel technique you can prepare films but films are not uniform and compact. Another disadvantage is bonding force between film and sample is too low to adapt to the durable applications. At this point it is an advantage to use vacuum coating systems which are also chemical waste free and provide good film adhesion. When we look at the literature we can easily see that the most commonly used metals are silver and copper.

2.3. Thin Films

In order to understand what the thin films are all we have to do is understand the structure and find out what is so attractive in thin films for desirable applications.

Generally, a thin layer coated on a substrate by condensation of the species, called thin film. This condensation can be in two ways; physical process or chemical reaction.

In thin films, as a result of growth process, from the properties of the corresponding bulk materials deviations come out because of small thickness, large surface to volume ratio and unique physical structure. Deviations from small thicknesses are optical interference, electronic tunneling through an insulating layer, high resistivity and low temperature coefficient of superconductor, the Josephson effect and planar magnetization. Because of small thickness and microstructure, the high surface to volume ratio may influence gas adsorption, diffusion and catalytic activity.

There are three main steps in thin film deposition. First there should be produced atomic, molecular or ionic species, second these species should be transported through the substrate and finally these species should be condensed to get solid deposit on the substrate.

2.3.1. Physics of Thin Films

There are three main steps in any thin-film deposition process. First producing the species (atomic, molecular, or ionic), then transport these species to the substrate and finally condensation on the substrate.

Creation of a thin-film completed by the end of the nucleation and growth processes. When species impact the substrate, they adsorb there because they lose their velocity component normal to the surface. These adsorbed species start to move over the surface because they are not in thermal equilibrium at first. They are called as clusters or nuclei. Depending on the deposition parameters they try to desorb in time because they are thermodynamically unstable. They start growing in size when they collide with adsorbed species before getting desorbed. This formation step also called nucleation stage. We can clearly say that nucleation barrier have been overcome after reaching critical size.

By the help of surface diffusion of the adsorbed species nucleus may be grown parallel to the surface. On the other hand, by direct impingement of the incident species, may be grown perpendicular to it. These grown nuclei called island.

Then these small islands start to coalesce with each other and the create bigger form of islands called agglomeration. Agglomeration increases with the surface mobility of the adsorbed species, like increasing the substrate temperature.

Finally, by leaving channels and holes of uncovered surface these larger islands grow together. We get completely continuous film.

Depending on mentioned thermodynamic parameters, nucleation and growth stages can be categorized as (a) island type called Volmer-Weber type, (b) layer type called Frank-van der Merwe type and (c) mixed type called Stranski-Krastanov type. (see Figure 2.8)

2.3.2. Applications of Thin Films

It is hard to think a world without computers, mobile phones, compact disc (CD), and digital video disc (DVD) players. Technology developments have renewed day by day. To capture innovations in the technology the first question to ask is "What properties are required for the application?" In order to get desired materials we can functionalize materials by different techniques. Thin film coating is one of them. Thin films are deposited onto substrate to achieve desired properties. Thin film applications is very broad but it is important to know what we need. In general case we can divide typical applications within each category as given in the Table 2.1.

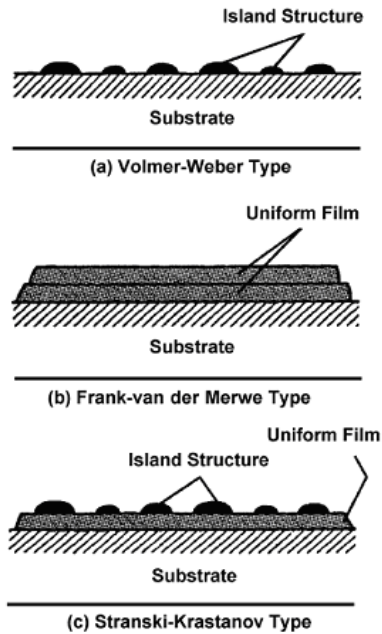


Figure 2.8. Three modes of thin film growth

2.3.3. Thin Film Processing Methods

Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are the most commonly used methods to grow film being deposited onto a substrate. If this growth mechanism occurs without chemical reactions, just by physical means, process called PVD. If process occurs by the help of chemical reaction, process is classified as CVD.

Table 2.1. Thin film applications according to their properties

Optical	Reflective/antireflective coatings, Memory Discs (CDs)
Electrical	Insulation, Conduction, Semiconductor devices
Chemical	Protection against oxidation or corrosion, Gas/liquid sensors
Mechanical	Hardness, Adhesion, Micromechanics
Thermal	Barrier layers, Heat sinks

2.3.3.1. Chemical Vapor Deposition

Chemical vapor deposition (CVD) is based on making use of a gas transport reaction. This method especially in semiconductor device fabrication is very important. Basic principle is a chemical reaction between a volatile compound of the material from which the film is to be made with other suitable gases so as to facilitate the atomic deposition of a nonvolatile solid film on a substrate. It should be emphasize that usually raised temperatures are required because film occurs on the heated substrate. By using this method material which are difficult to evaporate can be deposited.

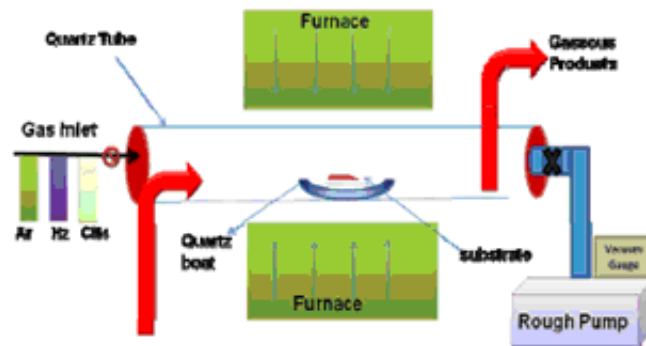


Figure 2.9. A schematic view of CVD system

2.3.3.2. Physical Vapor Deposition

In PVD processes such as evaporation, sublimation or ionic impingement on a target surface occur. Evaporation and sputtering are the two most commonly used PVD methods.

2.3.3.3. Thermal Evaporation

Thermal evaporation is used to deposit materials which have low melting point. Deposition occurs while current passing through a filament or a boat that have evaporated material in it. Generally boat is tungsten or tantalum because they have higher evaporation points. In thermal evaporation, while current passing through the filament or boat, current heat up the boat and evaporated material stick onto the desired surface. This takes place under vacuum conditions.

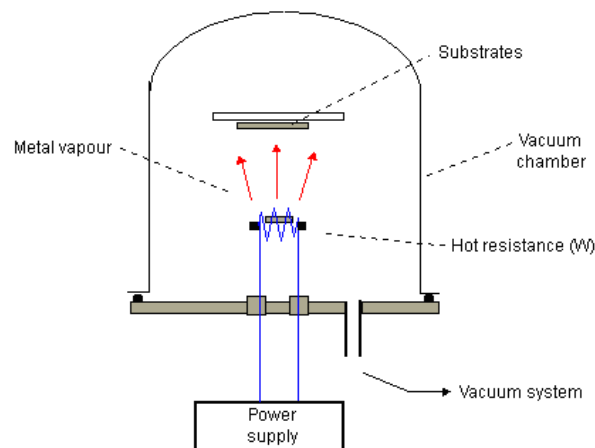


Figure 2.10. Simplest view of thermal evaporation system

2.3.3.4. Sputtering

When materials (solid or liquid material) are heated up to enough temperature, it is possible to obtain atoms escape from surface. In other words, causing erosion of atoms from a surface, called evaporation. If materials bombard with high enough energetic atomic particles (generally ions), with the help of this energy it is easy for individual atoms to gain enough energy with collision in order to escape from the surface. In other words, causing ejection of atoms from a material (surface) is called sputtering. Sputtering occurs whenever enough energetic particle impinging against a surface. The most convenient way is to accelerate ions whose energies suitable for sputtering.

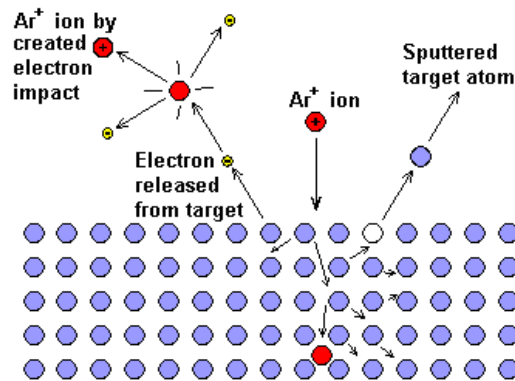


Figure 2.11. Species during sputtering

An extended definition of sputtering is made by Sigmund as "the erosion of material surfaces by particle impact" (Sigmund, 1993). Sigmund clarifies: "Sputtering is a phenomenon on the atomic scale. By this is meant that one can identify an individual sputter event, i.e., the emission of a number of atoms or molecules from a material surface initiated by a single bombarding particle" (Sigmund, 1993). In addition to ions, photons electrons and neutral particles are known to cause sputtering.

The sputtering phenomenon can be summarized in three steps

- Acceleration of ions through the cathode sheath
- Erosion of the target making series of atomic collisions
- Backward ejection of backbounding target atoms

In general, incident particle energies are in the range of hundreds of eV in sputtering process. Ions whose energies are in this range is much easier to arrange compared

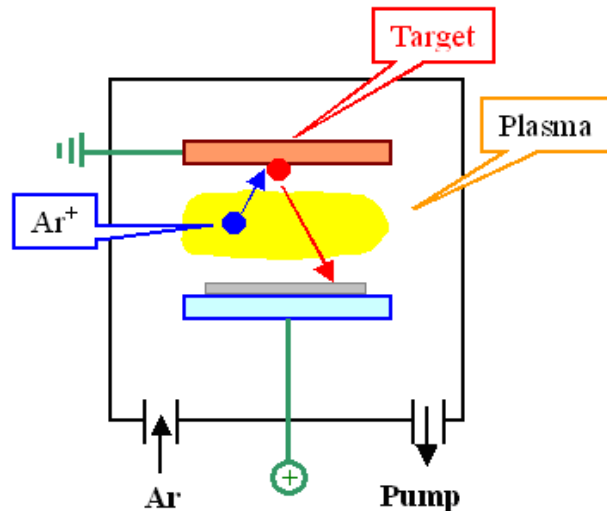


Figure 2.12. Simplest view of sputtering process

to neutral atoms for sputtering. These ions also reply to (respond to) electric fields and potentials. Most commonly used systems in order to generate ions are plasmas and ion beams. In the plasma source, the surface is actually in the plasma to be bombarded. In the ion beam source, plasma separated from the target and ion beam bombarded the surface. This is the main difference of these two ion generating systems.

2.3.4. DC and RF Sputtering

In DC sputtering, power supply is a high-voltage (several kilovolts) DC source. The sputtering target is cathode and substrate is anode. The main advantage of DC sputtering is it provides high deposition rates but we can only use conductive targets. Because if we bombard non-conducting target with positive ions this cause charging of the surface. This also causes a shielding of electrical field and the ion current would die off. Today in all industrial applications, DC sputtering is designed with magnetic plasma confinement by magnetron cathodes, which improves sputtering rate and reduces the electrical resistance of the plasma. I will mention about magnetron sputtering in the next section. When we create plasma by applying power between anode and cathode, electrons from DC supply collide with Argon atoms and ionized them. Then ions are accelerated across the target and bombard the target surface, cause sputtering of the target material and deposit material on the surface of the substrate. These ions also produce a small amount of electrons, called secondary electrons. These secondary electrons cause further ionization

of the Ar gas so plasma is sustained.

For metal targets DC sputtering is most widely used in order to get conductive coating. To obtain non-conducting coatings, DC reactive process is used with a metallic target and in this case we introduce some gases which are reactive and so coating material is produced by chemical reaction between target material and this reactive gases. I will mention about reactive sputtering in forthcoming section. RF sputtering is similar to DC

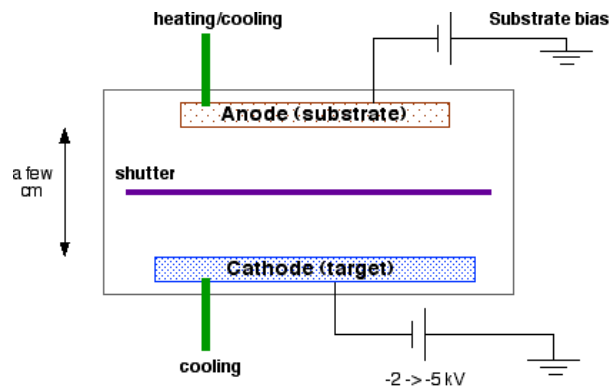


Figure 2.13. DC sputtering

sputtering but the only thing is we used RF power source instead of DC power supply. Furthermore RF sputtering is one step ahead because it provides higher deposition rates although it needs lower voltages and lower sputtering gas pressures. In RF sputtering same atomistic processes occur as in DC sputtering. In RF sputtering, source is a high voltage, typically 13.56 MHz, RF source although in experiments run from 60 Hz to 80 MHz or more.

Actually rf diode is different than the dc diode in operation. Here cathode and anode are electrically reversed. Inside the plasma chamber at every surface, with the changing driving frequency also the sign of the electrical field changing. This has a significant advantage which is prevent charging on an insulating surface so reduces arcing, because it provides equal amount of ions, then electrons, then ions, and so on. By this way insulators or metals can be sputtered in reactive environment. So RF sputtering works well with insulating targets.

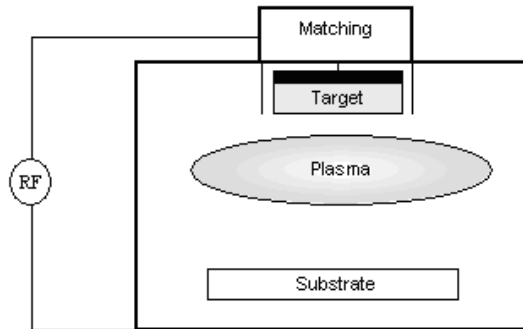


Figure 2.14. RF sputtering

2.3.5. Reactive and Magnetron Sputtering

In reactive sputtering, a target material is sputtered in order to produce a compound by the help of a reactive gas, usually with the inert working gas (Ar). This type of sputtering is used to produce functional coatings for desirable applications. The key parameter is to obtain the best coating rate and film stoichiometry which are important functions of the reactive gas partial pressure and also control this pressure. Most commonly reactively sputtered compounds are oxides (oxygen), nitrides (nitrogen, ammonia), carbides (methane, acetylene, propane) and sulfides, respectively. For example, if titanium is the metal and nitrogen is the reactive gas, then the deposited thin films are in the form of Ti_xN_y where x and y represent the composition of titanium and nitrogen in the film respectively. Most experiments performed to obtain aluminum oxide, silicon dioxide, titanium nitride, aluminum nitride and silicon nitride. Pressure is the key point because at low partial pressures film compositions are not ideal and at high partial pressures target can be effected badly with the reactive gas. Magnetron sputtering is presently the

most widely used commercially practiced sputtering method, 95% of all sputtering applications. The fundamental reason for magnetron sputtering's success is its high deposition rates (e.g., up to $1 \mu\text{m} / \text{min}$ for Al) Magnetron sputtering can be used DC or RF mode. Same procedure happening in magnetron sputtering. The inner magnet and the outer magnet have opposite poles so we can obtain a magnetic field parallel to the surface of the target an perpendicular to the electric field which is applied between target and substrate. For magnetic targets we do not need magnets. By the help of magnets, magnetic field created and this field help the electrons can be trapped in the target surface region, resulting much more ionization in this region.

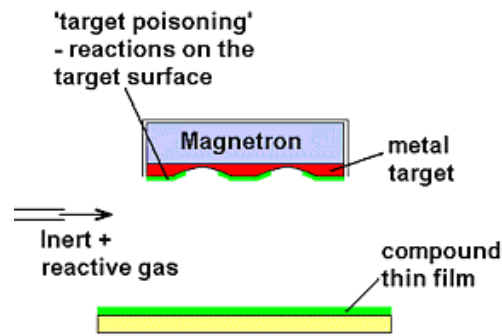


Figure 2.15. Schematic representation of reactive sputtering

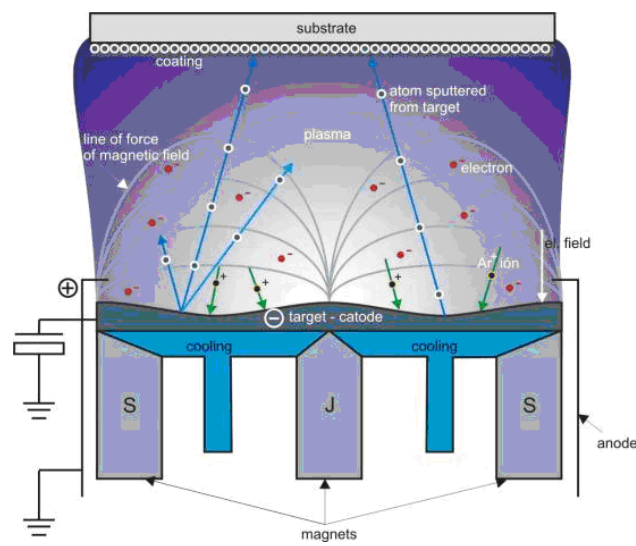


Figure 2.16. DC magnetron sputtering system

There are different configurations of magnetron sputtering but the most popular one is planar. In planar magnetron sputtering only planar surfaces can be coated. On the other hand our aim is to coat the cylindrical fiber surface so for this aim cylindrical magnetron sputtering system was designed and details will be given in next chapter.



Figure 2.17. Picture of our planar magnetron sputtering system



Figure 2.18. Plasma generated during magnetron sputtering

2.4. Deposition Materials

2.4.1. Silver

In this thesis our aim is to make fibers conductive. Fibers are insulators but when we deposit conductive thin films on the surface of the fibers we have conductive fibers. For this aim, we focused on silver thin films. Because silver has highest electrical conductivity in all elements and also it has highest thermal conductivity of any metal but studying cold will reduce this conductivity. In addition to these electrical properties, silver is very important for textile products because it shows antibacterial property.

Hegemann et al. reported why they prefer silver in their study. There are many reasons but first one is high electrical conductivity. Besides, antibacterial property, ductility, lower price and harmless for human skin are reasons (Hegemann, 2009).

Additionally, metallic thin films such as Ag, Cu and Al, all have FCC structure and show (111) planes which is intended because of having highest packing density. That means higher adatom mobility (higher film density higher adatom mobility).

Table 2.2. Properties of silver

Bulk resistivity ($\mu\Omega.cm$) at $20^{\circ}C$	1, 59
Mean free path of electron (nm)	52
Thermal conductivity (W/cm.K)	4, 25
Melting point ($^{\circ}C$)	961

Silver is a transition metal and its atomic number is 47. As we mentioned before silver has FCC structure. Also it has lowest contact resistance. Besides silver is employed in the electrical industry: printed circuits are made by using silver paints, and computer keyboards are using silver electrical contacts. Silver's catalytic properties make it ideal for use as a catalyst in oxidation reactions. Other applications are in dentistry and in high-capacity zinc long-life batteries. Also in many applications such as optical materials and wound dressings, silver demonstrates good optical, electrical and biocompatibility properties as well (Bosetti, 2002) (Mohebbi, 2002).

In general silver has three types:

- more than 99.9% pure silver
- silver alloy that has 90% silver and 10% copper
- powder in several forms such as amorphous powder, silver powder.

2.4.2. Silver in Textiles

In addition to what I mentioned in previous section when we look at the literature we can clearly say that silver is most commonly used inorganic coating for textile products. Silver makes bond with molecules and then block cellular metabolism after that kill the micro-organisms. Silver's antimicrobial activity is known to be efficient against nearly 650 trends of bacteria. For that reason silver is preferred metal for textile products.

Scholz et al., studied silver, copper, platinum, platinum/rhodium and gold layers on textile substrates and compared them according to their bonding strength and anti-microbial effectiveness. They also emphasize silver has antibacterial property and also exhibit low toxicity towards mammalian cells (Scholz, 2005).

Wang et al., deposited silver thin films by using RF magnetron sputtering. They conclude the relation between sputtering parameters and antibacterial properties. While sputtering power and Ar pressure did not show an important change on antibacterial properties, deposition time showed (Wang, 2008).

Silver is friendly for human skin because it is non-toxic so it can be used in many areas all of which make contact with human skin like nonwoven materials in order to minimize the bacteria amount of air or water filters, medical clothing, woven textile fabrics (Moza, 2005).

In recent years, also in most of the studies silver used because it shows good optical, electrical and biocompatibility properties. It has been used in many applications ranging from optical materials to decorative purposes.

Silver colloids are nano sized particles of silver. Colloids have antibacterial effect on textile products and polymers. Additionally colloids are valuable for study because of being treated textile fabrics.

2.4.3. Other Materials

Copper, aluminum, titanium dioxide, tin-doped indium oxide, zinc oxide, aluminum-doped zinc oxide are another coating materials for textile products.

Copper was sputtered to deposit functional nanostructures on the surfaces of PP spunbonded nonwovens. 10, 50 and 100 nm coating thicknesses investigated. Results show both surface characteristics and electrical properties improved. Cu coating alter the surface characteristics of fiber surface and also when coating thickness is increased, resistivity reduced obviously. The best resistivity result was seen 100 nm thickness. Improving the surface properties by sputter coating, fibers provide conductive surface for desired applications (Wei, 2008).

Wei et al., studied also RF magnetron sputtered titanium dioxide on polyamide 6 surface. Because TiO₂ has unique dielectric and optical properties. In this study AFM showed difference in the morphology of the fibers before and after the coating. Additionally *TiO₂* surface wettability investigated. Before UV sputtered fibers present water droplets on their surfaces. After UV radiation coated fibers showed water film on their

surface instead of water droplets. This clearly shows the effect of UV radiation on the wettability of the sputtered layers (Wei, 2006).

One of the studies was functionalised polyethylene terephthalate (PET) with aluminium by using sputter coating. Both optical and electrical properties were investigated. Spunbonded nonwoven PET fibers coated 50 nm and 200 nm and electrical results showed 200 nm coated fibers have lower resistance but it is difficult to see difference by looking SEM images. This study also showed the Al sputter alter the surface of the fibers (Deng, 2007).

In another study ITO and AZO magnetron sputtered PP fibers were compared. Tin-doped indium oxide and aluminum-doped zinc oxide are used in order to deposit transparent nanostructures on the fiber surfaces. They compared the results under the same sputtering conditions and found that ITO was more compact structure on the fiber surface. On the other hand, in the same thicknesses, AZO provided better UV shielding effect compared to ITO. But in the same thickness ITO showed lower electrical resistance (Wei, 2009).

Zinc oxide (ZnO) is an alternative to ITO transparent and conductive material. Deng et. al., studied ZnO in order to find new approach to textile materials. In their study nonwoven PET surfaces coated with ZnO by magnetron sputtering technique. They indicated the relation between changing parameters like sputtering time, sputtering power, sputtering pressure. while sputtering power is increased, increased the size of ZnO nano-clusters. Increasing power means more particles being knocked off the target so larger clusters can be seen. The ZnO nano-clusters change their shape by changing sputtering pressure (Deng, 2007).

2.5. Electrical Modification of Fibers by Thin Film Coating

So far, in many studies many techniques were used in order to make textile fibers conductive. But for all these technique there is a disadvgne which is conductivity is not continuously occuring. For instance, melt compounding method conductive particles have random distrubution in the fiber formation. So the conductive particles are not homogeneously occuring. On the other hand if we coat fiber surface we can get continous homogeneous conductivity on the surface of the fiber. In this thesis fort his aim we designed inverted cylindrical magnetron sputtering system which provides to deposit desired metal on the surface of the fiber continuously.

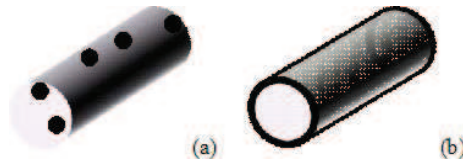


Figure 2.19. Conductive fibers produced by melt compounding (a) and thin film coating (b) methods

CHAPTER 3

EXPERIMENTAL

3.1. Motivation

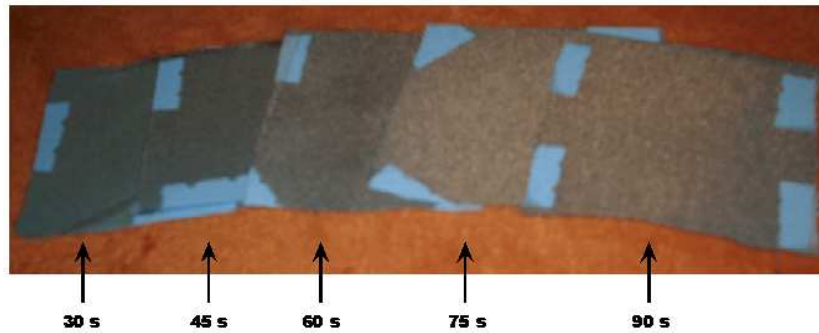


Figure 3.1. 12, 18, 25, 31 and 37 nm Au coated fabrics

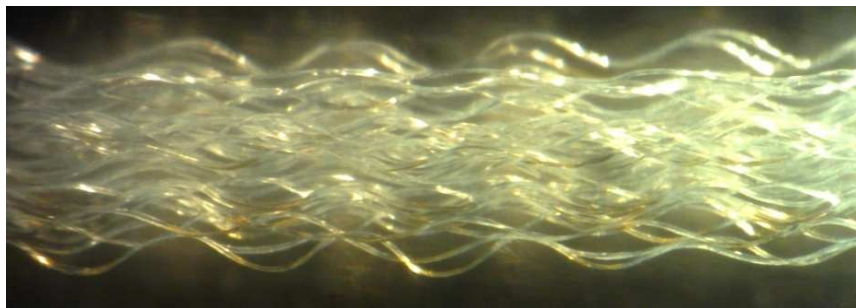


Figure 3.2. Optical microscope image of 37 nm Au coated fibers

In our first study we just cut the fabrics and coated with different thicknesses. When we look at optical microscope image of coated fibers we did not see any change in the conductivity because of the interrupted paths on the fibers. So we decided to coat not whole fabric just fibers and then we see if these electrically coated fibers are woven into fabrics at regular intervals we can get antistatic fabric.

Because of no change in surface resistance of coated fabrics, not whole fabric, fibers were decided to coat only. For this aim PP fibers were coated with Cr and Ag.

Results show electrical resistance values are improved. Besides electrical investigation, also antibacterial test was done and bacteria reduction is increased with the increasing thickness (Ozyuzer, 2010).

The major goal of this study is to get homogenous deposition on cylindrical surface of the fibers. For this aim we designed inverted cylindrical magnetron sputtering system. Before coating fibers were cleaned by using RF plasma cleaning system and then the fibers were coated with the desired metals in a high vacuum at high speeds (5-10 m/min).

The vacuum coating machine designed, manufactured and the process parameters obtained for optimal deposition. After coating fibers become conductive and we investigated their antistatic and antibacterial properties.

Therefore, to make commercially available coating machine provided a new patent and can be used in mass production. This type of yarn production will bring Turkey in the leading position in the world for technical textile manufacturing technology.

3.2. Material Type

3.2.1. History of Polymers

Plastic materials divided into two groups; thermoplastics and thermosets. While thermoplastics are composed of linear polymer molecules, thermosets are crosslinked polymers. Because of that, thermoplastics melt, thermosets do not melt. The structure of the polymer, processing method, conditions and additives determine the properties of a polymer material.

Some polymer materials have only small amount of additives and almost pure, whereas others consist of predominantly non polymeric constituents. Additionally, in order to prevent the polymer from oxidizing, some polymers have only a small content of antioxidant, as in polyethylene.

In this study, as a substrate we used Polypropylene (PP), Polyamide (PA) and Polyethylene terephthalate (PET) which are synthetic fibers in the family of chemical fibers.

During last 70-80 years polymer science and technology has developed and the commercial introduction of new polymers has proceeded through three time stages giving rise to three generations of polymers.

The first generation includes polystyrene, polyvinylchloride, low density polyethylene, glass-fibre reinforced polyesters, aliphatic polyamides which was introduced before 1950.

During 1950-1965 the second generation was introduced which includes a number of engineering plastics, for instance; high-density polyethylene, isotactic polypropylene, epoxy resins and aromatic polyesters.

Since 1965 the third generation was introduced. This generation polymers have more complex chemical structure which are described by very high chemical and thermal stability and high strength.

In addition to this new polymers development, existing polymers such as polyethylene have paid important improvement. As examples of the more recently introduced materials, we can mention crosslinked polyethylene and new fracturetough thermoplastic polyethylenes.

3.2.2. Polypropylene (PP)

Polypropylene (PP) has the highest melting point in the family of olefin fibers. Its melting point is $160^{\circ}C$. It is a thermoplastic polymer. Polypropylene has excellent chemical resistance and it has the lowest density. The most important property of polypropylene is versatility.

In nonwovens the basic polymer is PP because of its hydrophilic property.

Beside all these excellent properties, poor dyeability and texturizability limited polypropylene's applications in conventional textile industry.

3.2.3. Polyamide (PA)

Nylon nanofibers were used as substrates for thin film deposition and the coated nanofibers were used to understand the nanoscale properties of these films.

Nylon is in the family of synthetic fibers. It is semi-crystalline polymer. There are two common types of nylon; first one is nylon 6 (polycaprolactam, a cyclic nylon intermediate) and second is nylon 66 (polyhexamethylene adipamide). Because of its mechanical and thermal properties, it is an important thermoplastic in engineering studies.

Why nylon is important in the textile industry can be explained with its versatility. It is also environmentally friendly because it produces from oil waste products.

Additionally, it can be washed easily and dried quickly.

For our study most important property of nylon is its good adhesion of the silver thin film. Best adhesion on fiber surface is obtained with smooth coatings (Hegemann, 2009).

Nylon is widely used in apparel, interiors (especially carpets), also in industrial uses because of its high strength. It holds its shape since it neither shrinks nor stretches.

There is a difference between nylon 6 and nylon 66 and also this is a disadvantage. The thing is nylon 6 has much lower melting point than nylon 66. This is disadvantage because garments made by using nylon 6, must be ironed with considerable care. Another disadvantage is it is uncomfortable fiber for the skin.

3.2.4. Polyester (PET)

Polyester is the most commonly used synthetic fiber. Because of its performance it is highly engineerable. By combining its performance and relative comfort we can say it is the most versatile fiber.

Melting point of polyester is 260°C . When polyester is heated in air up to 150°C , we can clearly see the change of its colour. When we reach to 180°C , polyester loose 50% of its endurance.

Polyester is used in apparel but as fabrics which are woven from polyester. Especially knitwear, fiberfill, nonwovens where durability more important than absorbency.

3.3. Plasma Cleaning

3.3.1. What is Plasma?

The most general definition of plasma is another state of matter except from solids, liquids and gases. Plasma has equal amount of positive and negative charges so plasma is known as neutral. These particles are ionized. Plasma does not have a definite shape or definite volume. Also plasma is electrically conductive. Particles in plasma such as ionized atom sor molecules, photons, free electrons and residual neutral species are so energetic that when they strike a substrate they can modify it. The schematic representation is given in Figure 3.3. This property can be used in order to functionalize surfaces or

clean the contamination. Because when these particles are strike to the surface contaminations leave the surface. In this situation, plasma, mixture of these particles, become a chemically active environment.

Why do we prefer plasma treatment is because it is dry and environmentally friendly technique. After plasma treatment process there is no chemical waste behind. In order to get desired functionality all we need is only chemicals for a few minutes. More plasma cleaning time can change the bulk characteristics of the material so just for functionalize the surface plasma treatment time is an important parameter. For this aim we also did the mechanical strength test before and after the plasma cleaning depending on plasma time.

In addition to time, operating pressure and density are important factors to determine the cleaning effectiveness. In plasma, particles' mean free path is determined by the operating pressure. While operating pressure decreases, mean free path increases so more particles strike. As a result plasma penetrates into small size scale features. I mentioned plasma density which is also important parameter. Higher plasma density means faster particles which strike and remove the contaminations from the surface.

Plasma cleaning system is working on low pressure. At 50 kHz frequency and 200 W power we can create plasma in low pressure plasma cleaning system. We used air in our system and Rotary vane pump to reach 10^{-2} torr pressure during cleaning. It is important that depending on plasma cleaning time fiber's mechanical properties must remain the same as before cleaning. Fiber's mechanical properties mustn't change. So we change the cleaning time and by changing the time we investigate the mechanical strength properties of fibers before and after plasma cleaning. Long cleaning time cause the unwanted modification of fiber surface and because of this fiber's mechanical properties also can change.

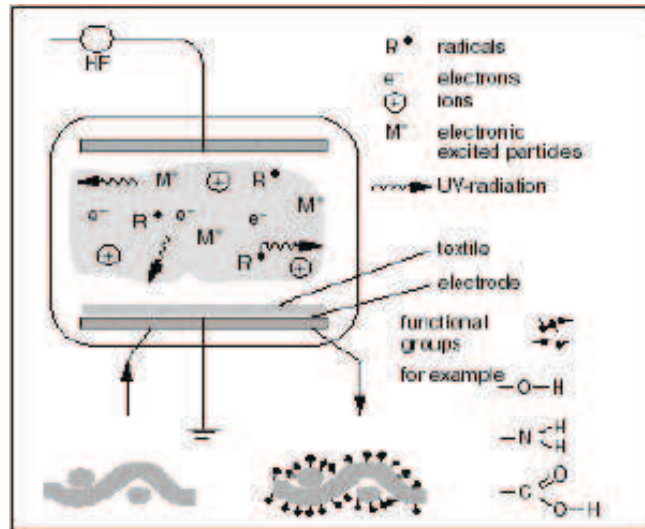


Figure 3.3. Schematic representation of plasma

3.3.1.1. Low Frequency (LF) Plasma Cleaning

When a gas absorbs electrical energy, its temperature increases causing the ions to vibrate faster. In an inert gas, such as argon, the excited ions can bombard a surface and remove a small amount of material. In the case of an active gas, such as oxygen, ion bombardment as well as chemical reactions occur. As a result, organic compounds and residues volatilize and are removed. There are many parameters that affect the plasma and as a result effect the surface chemistry of polymer fibers.



Figure 3.4. LF Plasma Cleaning System

Low frequency (LF) plasma operates around 40-50 kHz. By using low frequency plasma, one can get more energy per square inch. The efficiency of a plasma system is

the ratio of the energy used in producing the plasma vs. the energy dissipated in losses such as heat. A low frequency plasma system acts like a perfect capacitor with infinite capacitive impedance, or zero current drain when in standby mode. Current applied across the capacitive pair (electrodes) causes the gas to ionize, and the impedance is bridged causing current flow (plasma) between the electrodes.

In addition to these advantages also LF plasma system provides better uniformity which means system has no shadowing so plasma reaches everywhere through the sample.

3.3.1.2. Radio Frequency (RF) Plasma Cleaning

RF plasma operates between 1 kHz and 10^3 MHz with a most common value of 13.56 MHz. This plasma cleaning system actually loses high amount of energy through heat loss. Energy loss with a 13.56 MHz system is up to 850 times greater than with a 40 kHz system. So comparing with the LF plasma system RF plasma system has some limitations.

3.3.1.3. Comparison of LF and RF Plasma Cleaning

Depending on the the role of the plasma treatment (cleaning, etching, functionalization, etc.) the driving frequency of the plasma can be significant or not. The kinds of things that vary from low to high frequencies are:

1) The relative amount of power dissipated in the bulk plasma vs. the sheaths – in low-frequency plasmas the ions are typically accelerated by very strong cathode sheath fields and deposit a lot of energy in the cathode. While the ion bombardment produces secondary electrons which sustain the plasma, the RF plasmas tend to be more efficient at producing ionization (i.e. plasma density) for a given power than their low-frequency counterparts.

2a) The cathode sheath fields tend to be higher for the lower frequency plasmas at a given power. Therefore, plasma chemistry in the cathode sheath can be very different for the high and low frequencies. In the high fields encountered in the low-frequency plasma cathode sheaths, the electrons can attain very high energies, and electron impact processes that might not be as probable for the high-frequency plasmas can be very effective in the low-frequency plasmas. For example, the nitrogen molecule is very difficult to split (it takes about 10 eV, compared to 5 eV needed to dissociate oxygen molecules). Plasmas

with higher electron temperatures (higher than the typical 0.5 - 2 eV range encountered for common glow discharges) or with a significant population of energetic electrons (as encountered in low-frequency plasmas, produced by secondary electron emission from the cathode) may produce significantly more dissociated nitrogen. The point is that the neutral as well as ion chemistry of the plasma can be significantly affected by choice of frequency.

2b) Because the cathode sheath fields can be significantly higher for the lower-frequency plasmas, the issue of whether the sample is placed at floating potential or in the cathode sheath near the cathode (or on the cathode) can have a significant effect (good or bad, depending on whether ion bombardment is helpful or not).

3) Pressure range of operation: typically the RF plasmas will run at lower pressures than their low-frequency counterparts. While the low-frequency discharges generally rely on secondary emission of electrons from the cathode to sustain them, the RF plasmas can benefit from "stochastic heating" of electrons as they effectively "bounce" off the moving sheaths at the electrodes and again become available for ionizing neutrals in the bulk. In order to get lower frequency plasmas to run at lower pressures, typically magnetic fields are used, as in sputter magnetrons, where the electrons produce significant ionization near the target surface as they follow circuitous paths in response to the magnetic field. In such cases, the cathode material is so heavily bombarded by the ions that it is emitted from the target surface at sufficient rates to produce coatings on samples placed facing the cathode and located within a few cm thereof.

For the one-line version, it's:

Low frequency is going to be more effective at cleaning and roughing up the surface for better film adhesion. In the early days of plasma processing, there was a great deal of experimentation with different frequencies of electrical fields, ranging from dc up to microwaves, and even lasers. The chip-making world found out really quickly that more ion energy was not a good thing, especially on nearly built devices, so the world settled on the FCC industrial frequency of 13.56 MHz and its harmonics. Plasmas at this frequency tended to be a good tradeoff between intensity and minimal damage, and were useful for many etch and deposition processes. There's nothing magic about this frequency, as for all practical purposes, dc is anything up to 1MHz, and rf is anything more than that. In terms of getting plasma density, as Jeremy said, the higher in frequency you go, the more you can get. I was once on a nutty project to make microwave excited domestic light bulbs for this reason, and microwave (1-5 GHz) plasmas are used in some chip-making processes, together with species of magnetic confinement. The nice feature is that the

field source is external to the vacuum, so there are more available parameters and no unpleasant sputtering of electrodes. For cleaning a polymer substrate, though, all you need is a big LF hammer.

Practically, LF at 300-450 kHz is used for stress control (compressive - tensile) when depositing oxides and nitrides. LF, at similar frequencies, is used for "eliminating" issues related to build up on the walls as high aspect ratio features are etched during Bosch /MEMS etching Note that both processes also require 13.56 MHz RF(or higher) or a combination in the form of pulses with a certain duty cycle

3.4. Inverted Cylindrical Magnetron Sputtering System

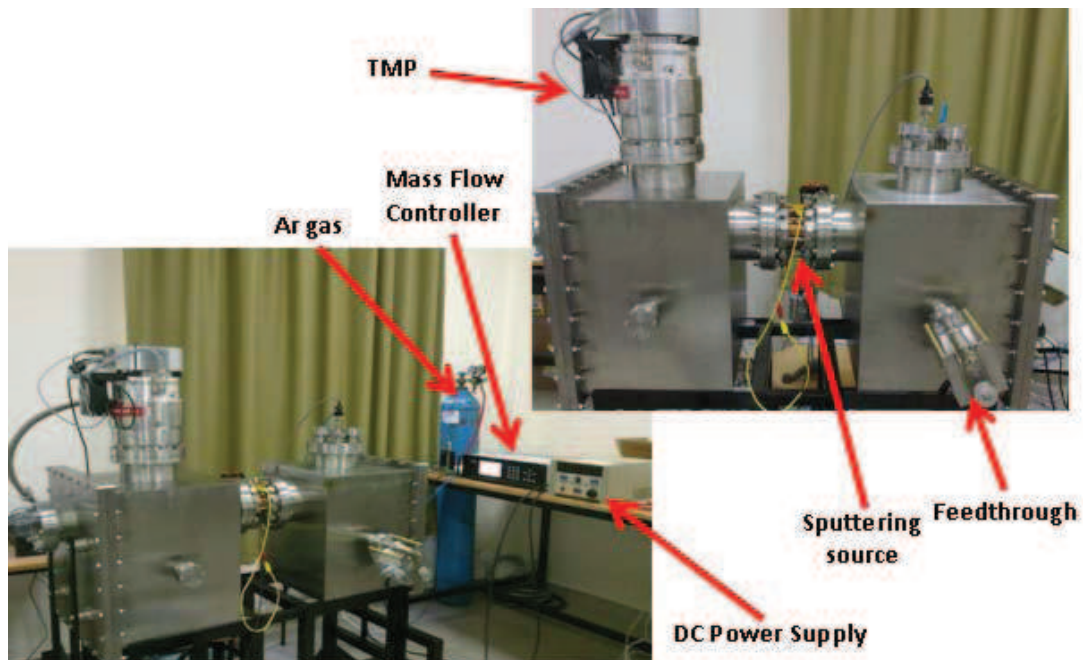


Figure 3.5. Our Designed Inverted Magnetron Sputtering System picture

The schematic representation of our fiber coating coating system is shown in figure. In order to optimize coating parameters for our system we study on different parameters for pressure, magnetic field and applied power. All growth parameters are given in table. Depending on these parameters we investigate thin film thickness. table

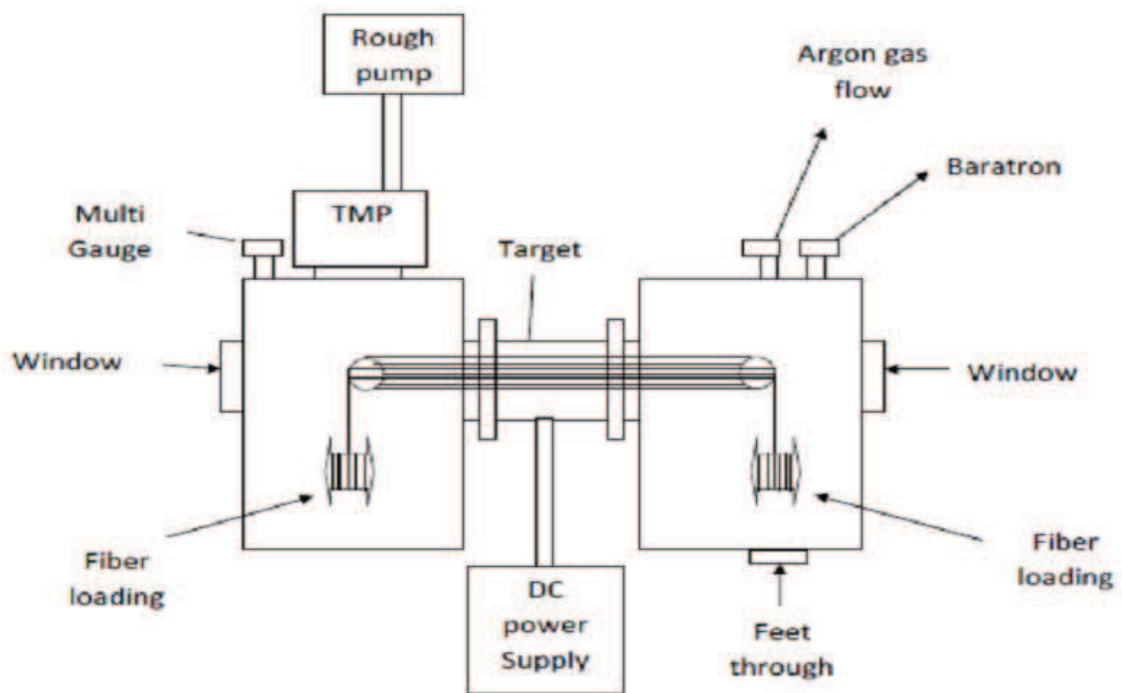


Figure 3.6. Schematic view of our Inverted Cylindrical Magnetron Sputtering System

Fibers placed into the system and both fibers and microscope glass attached onto the fiber coated with Ag. By using Surface Profilometer thin film thicknesses were found. In order to clean the fiber surface we tried different techniques. We compared two techniques here. First we cleaned fibers in ultrasonic cleaner by the help of ethanol second we used low frequency plasma cleaning system, finally we conclude LF plasma is more successful way for cleaning.

In this study, we want to get homogeneous and continuous conductive thin film onto polymer fiber surface. For this aim we used inverted cylindrical magnetron sputtering system as shown in figure. This system designed for 3-dimensional continuous thin film coating. Cylindrical magnetron sputtering system has 3 parts. The first one is substrate loading part, second is metal coating cylindrical target area and finally sample unloading part.

We evacuate system pressure until 10^{-6} torr which is base pressure for this system. We used Rough pump and Turbo Molecular pump, respectively. In this system fiber passing through a cylindrical target with feet through mechanism.

There is a silver target between two vacuum chamber. Fiber substrate passing through the plasma by the help of apparatus that have 16 rollers because of that fiber passing through plasma 15 times. Around the target we have 32 magnets that condense plasma within this area. At the end of the deposition, coated fibers remove from second vacuum chamber.

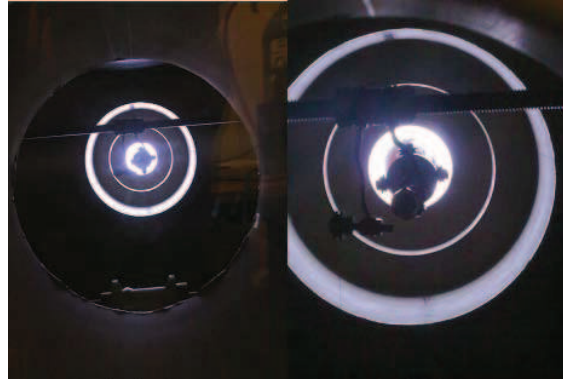


Figure 3.7. During deposition fibers passing through the target plasma zone

3.5. Conduction Process in Thin Films

Since in this thesis silver thin films studied, now let us have a look at conduction mechanisms of metals. All metals are good electrical conductors because in metals there are free electrons and these electrons are responsible for conduction. These electrons are also called conduction electrons. The conduction electrons in a metal are non-localized which means they are not tied to any particle atom and they are free to move randomly in metals. They are free to move but also there are factors that effect their movement such as vibrating atoms, crystal defects and impurities. Actually all atoms vibrate but they vibrate more when they are heated. Additionally in metals free electrons carry the heat energy faster then the atomic vibrations and transfer it by colliding with other electrons of heat energy.

I mentioned about growth mechanisms of thin films in chapter 2. Depending on the effects of the growing stage, whether thin film is perfect or not. In thin film there might be impurities and defects. At this point in order to investigate electrical conduction of metals first I try to state Matthiessen's rule. This rule is for bulk materials and thin metal films. Because Matthiessen's rule rely on two assumptions; first one is impurity and

phonon scattering are independent, second one is the relaxation time is isotropic. This rule states that resistivity of metal is summation of thermal, impurity and defect resistivities, respectively. Electron collisions with vibrating atoms which are also called phonons, impurity atoms and defects cause electrons to scatter elastically or inelastically.

$$\rho = \rho_{Th} + \rho_I + \rho_D \quad (3.1)$$

3.6. Scattering Mechanism in Thin Films

We newly designed cylindrical magnetron sputtering system so while changing the system parameters we meet some problems and also we have to understand these problems. For this system the problem has physical meaning we are facing with electron scattering.

At room temperature and above temperatures, electron conduction process is controlled by collisions with lattice vibrations or scattering. When we look at the literature, studies indicate that resistivity of metal thin films is influenced not only by isotropic electron scattering and surface scatterings but also influenced by grain-boundary scattering. Fuch-Sondheimer theory deal with isotropic and surface scattering. On the other hand, Mayadas and Shatzkes considered grain-boundary scattering in addition to isotropic and surface scatterings.

When the film thickness approaches the mean free path of conduction electrons, surface roughness and grain size affect the electron conduction in thin metal films. This subject has been a topic of research for over six decades. When the mean free path of film thickness smaller than the coating thickness, electrons can scatter and get higher resistivity than bulk resistivity. Because of scattering the conductivity is negatively influenced. In metals, free electrons are negative charge carriers flowing from negative pole to positive pole. Electron scattering occurs as a result of thin film defects, impurities and thermal events.

While temperature increases, electron collisions are also linearly increased as result phonons displaced their equilibrium lattice positions are the source of thermal or phonon contribution. This is called positive temperature coefficient of resistivity which is reverse of metallic behaviour.

At room temperature mean free path of silver is 52 nm. As we mentioned before, when film thickness smaller than the EMFP, electrons scatter and we get higher resistivity

than bulk. This also affects conductivity.

There have been different scattering mechanisms which were trying to explain conduction electrons scattering. Fuchs (Fuchs, 1937) and then Sondheimer (Sondheimer, 1952) stated that while decreasing thin film thickness, resistivity of thin films increased. Fuchs model was focusing on the diffuse and elastic scattering of electrons at surfaces but did not include surface roughness.

Namba realized that in electron scattering, surface roughness was also important because surface roughness induced by grain boundaries (Namba, 1970).

The question is this what is exactly happening to electron when it cannot complete its mean free path because of collisions with the film surface. The electrons then scatter either specular (elastically) or diffuse (inelastically) scattering. Elastic collisions of electrons at the film surface think like photon reflects from a mirror. As a result there is no contribution or change in the resistivity. But the other case, I mean in diffuse scattering, the electron mean free path is ended by impinging on the film surface. After this kind of surface collision, scattering angle is random (as I tried to explain in Thomson model) and electron trajectory is independent of the impingement direction. So resistivity rises because less electrons flow through the reference plane effecting current flow.

Thompson finds out a way to see this effect in terms of classical physics.

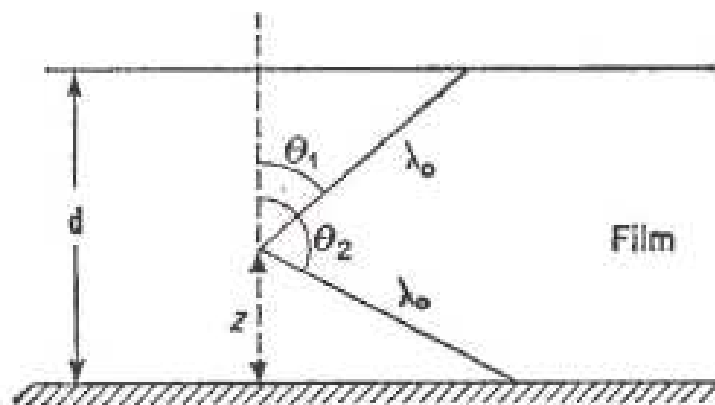


Figure 3.8. Diffuse scattering of electrons from film surface in Thomson Model

Thompson model suggest that, for an electron, a distance z from the thin film surface moving in a direction making an angle θ , mean free path is variable depending on θ and is given by;

$$\lambda = \begin{cases} \frac{d-z}{\cos \theta}, & 0 \leq \theta \leq \theta_1 \\ \lambda_0, & \theta_1 \leq \theta \leq \theta_2 \\ -\frac{z}{\cos \theta}, & \theta_2 \leq \theta \leq \pi \end{cases} \quad (3.2)$$

So, when the film thickness d is smaller this affects λ and cause thin film resistivity increased.

However, the additions from ρ_I and ρ_D are temperature independent. Resistivity vs. temperature relation for metals is given in Figure 3.9. Because there is no dependent of temperature of defects, at low temperatures this is nearly constant. Defects are related to the film structure. Because of depending number of phonons, resistivity that results from phonon-electron interaction at low temperature is zero and at high temperature it is proportional to temperature.

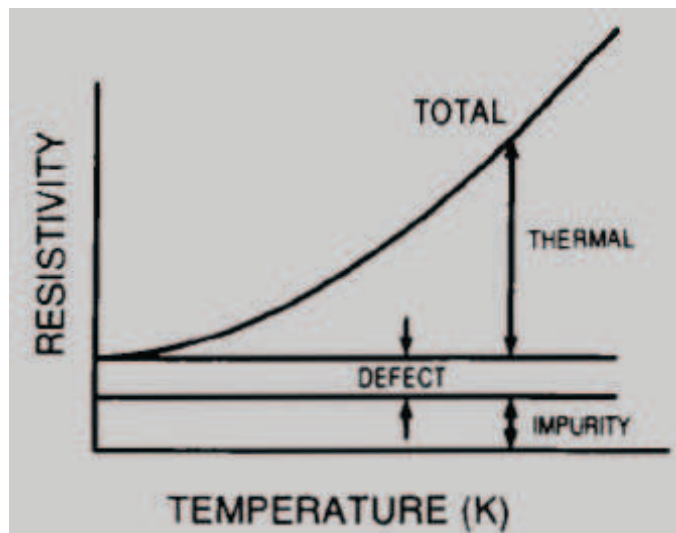


Figure 3.9. Resistivity versus Temperature relation for metals

3.7. Electrical Conductivity of Fibers

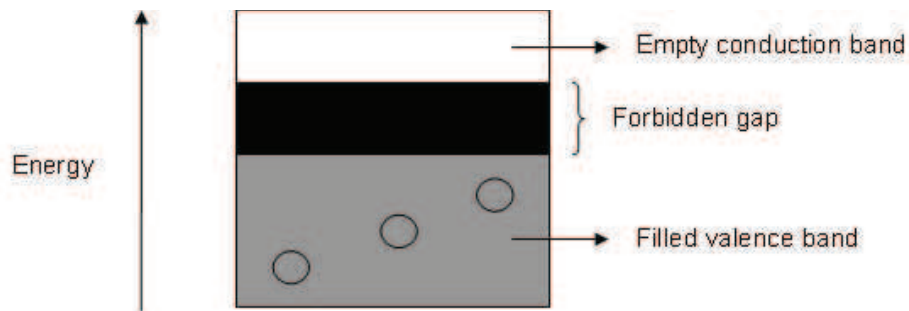


Figure 3.10. Band diagram of textile fibers

Textile fibers have large band gap for this reason like most polymers, textile fibers are electrical insulators. There is no electron free to move, all electrons are shared in the covalent bonds or bound to the nuclear cores.

As shown in Figure 3.10, there are no free electrons in textile fibers. We need large activation kT in order to promote electrons from the valance band to the conduction band.

In general all we know mobile electrons provide electrical conductivity but in textile fibers, ionic species such as impurities, residues from nature, provide because textile fibers do not have mobile electrons since they are insulators. Fibers can be effected from impurity ions which are positively charged and moving through bulk structure. Moreover, when fiber surface is treated with a thin conductive covering or wet with adsorbed moisture, it is possible to be become conductive for textile fibers. In order to get rid of static charge problems, the best way is to coat fibers. This thesis is based on this idea.

CHAPTER 4

RESULTS AND DISCUSSIONS

In this thesis we designed new sputtering system which is called inverted cylindrical magnetron sputtering (ICMS) system. Silver thin films were grown by ICMS, onto textile fibers such as PP and PA. The optical and electrical properties were studied. Besides, mechanical and antibacterial tests were done. In order to determine optimum film thickness, 3 different methods were studied and results were compared. In this part of thesis I will explain all results in detail.

4.1. Mechanical Strength Results

We know that fibers might have oil or contaminants on the surface. This can occur during fabrication of fibers or after the fabrication intentionally. So, to get rid of this contaminants plasma cleaning is dry and environmentally friendly technology. The important thing is to find best cleaning time because fiber properties can be changed and damaged.

In order to investigate the strength properties of fibers before and after plasma cleaning, we made strength tests. In short, we tested strength of fibers at LF and RF plasma cleaning and also different plasma cleaning times.

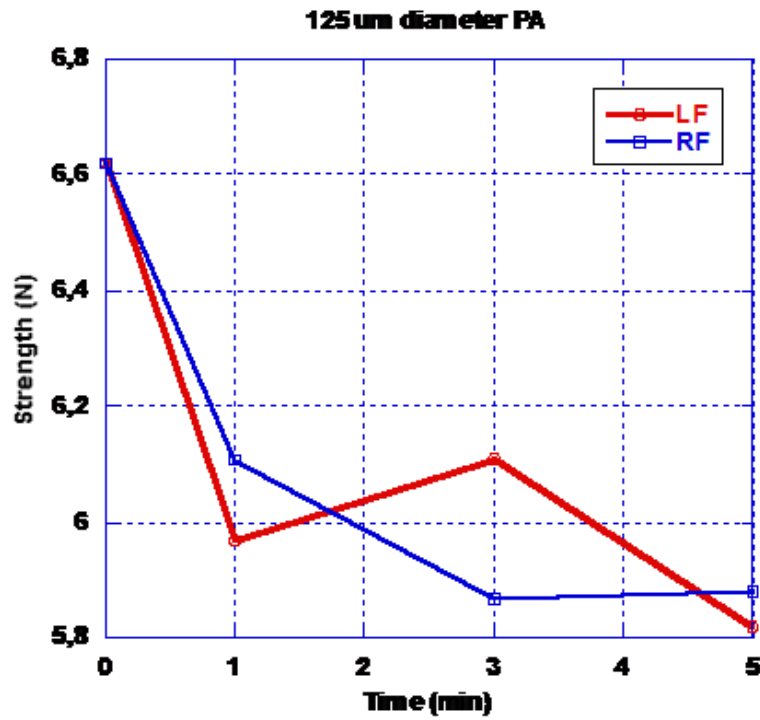


Figure 4.1. Mechanical strength results of 125 μm diameter polyamide

These mechanical strength tests were done at 9 Eylul University Textile Engineering department. We used two different polyamids, 125 μm and 150 μm in diameters. The results are given in Figure 4.1 and 4.2, respectively. For simplicity to compare LF and RF plasma cleaning we draw both in the same graph for different diameter fibers. We compared two plasma cleaning system with two different substrate.

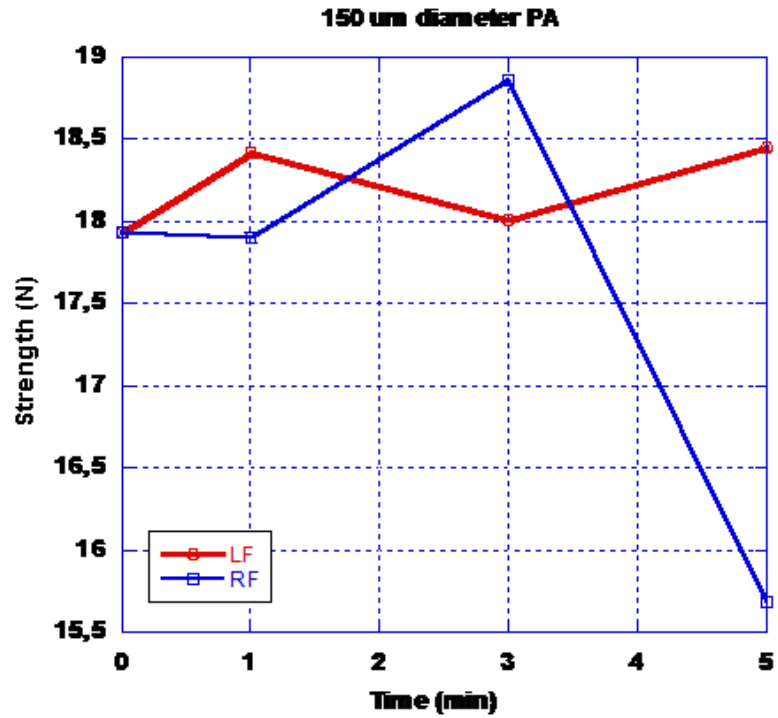


Figure 4.2. Mechanical strength results of 150 μm diameter polyamide

It is obviously seen from the Figure 4.2 that at the end of 150 μm diameter polyamide plasma cleaning there is no important change of fiber strength but in Figure 4.1, 125 μm diameter polyamide lost its strength after 1 min plasma cleaning. As a result of mechanical strength tests we conclude 1 min plasma cleaning is enough for protect the fiber properties.

4.2. Optical Microscope Studies

Figure 4.3 and 4.4 show PP fibers that coated with 85 nm silver by using planar magnetron sputtering system. PP fiber has 36 multifilaments and each monofilament diameter is $60\ \mu\text{m}$. At different magnifications fibers's optical microscope images can be seen in Figure 4.3 and 4.4.



Figure 4.3. 85 nm silver coated PP multifilament fibers (36 multifilament, each monofilament $60\ \mu\text{m}$ in diameter)

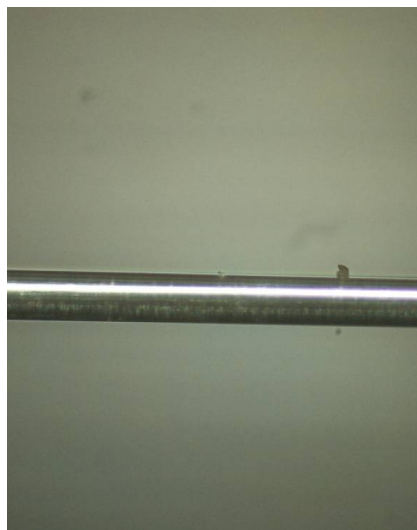


Figure 4.4. Optical microscope image of PP multifilament

As we can clearly see from the images, because of the good adhesion of Ag thin film on fiber surface, there is no roughness or cracks on the surface of the thin film. This also shows that coating thickness is has its optimum value.

4.3. Scanning Electron Microscope (SEM) Studies

By using Scanning Electron Microscope, which is in Physics department at Izmir Institute of Technology, we examined the coated fiber surface. Silver thin film coated fibers were cutted into pieces about 2 cm length and they pasted onto universal sample holder with silver epoxy. In order to prevent charging effect silver epoxy was used. After loading the sample into SEM, we clearly saw that Ag film covers all surface and as a result of this there is no roughness seen in Figure 4.5, 4.6 and 4.7. As I mentioned before this also depends on the thin film thickness. Due to the optimum film thickness there is no crack occuring on the film surface.

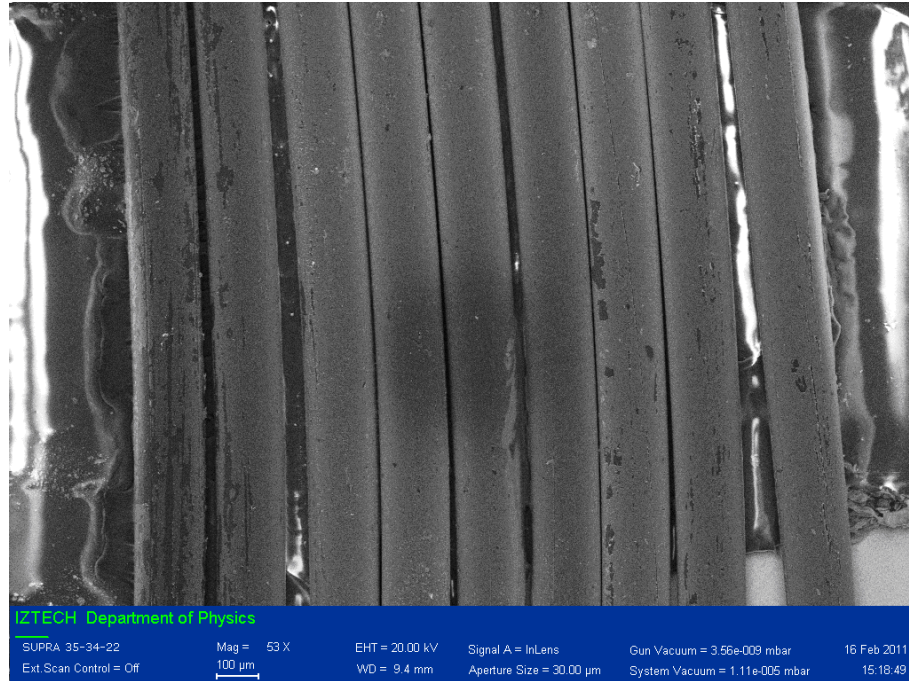


Figure 4.5. SEM image of silver coated fibers

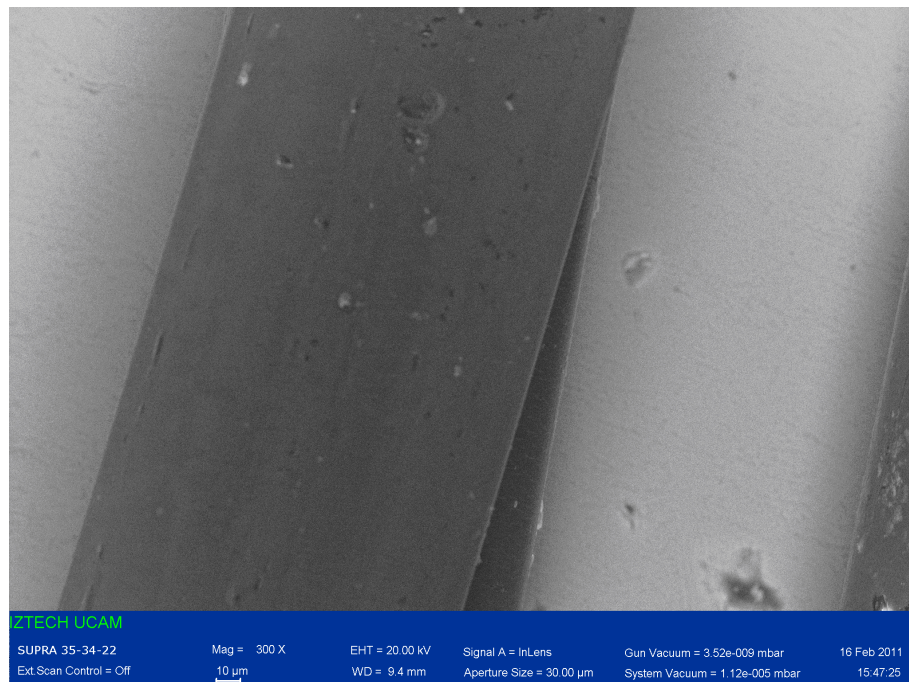


Figure 4.6. SEM image of silver coated fiber surface

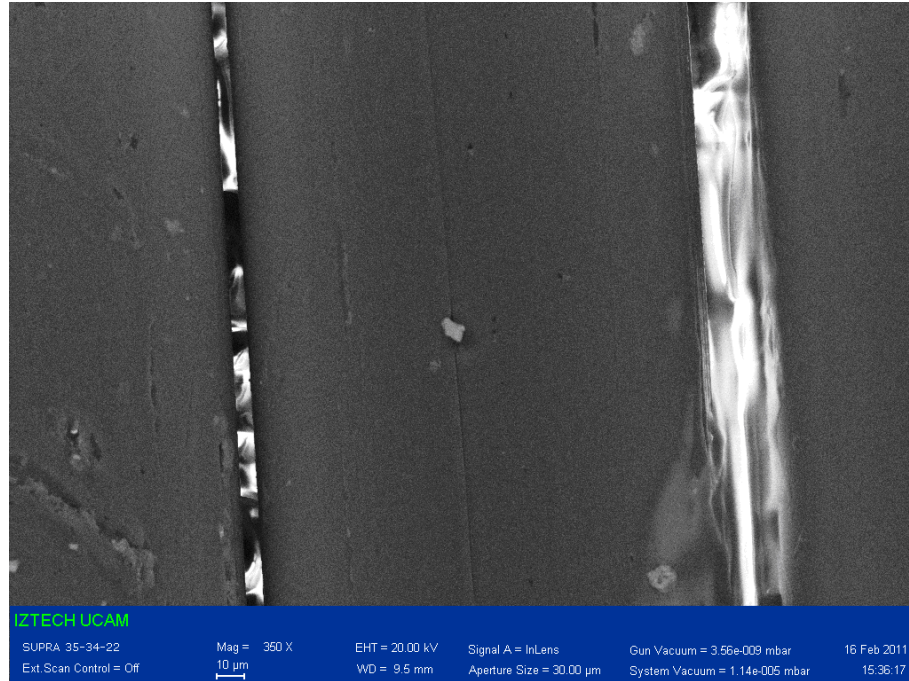


Figure 4.7. SEM image of silver coated fiber surface

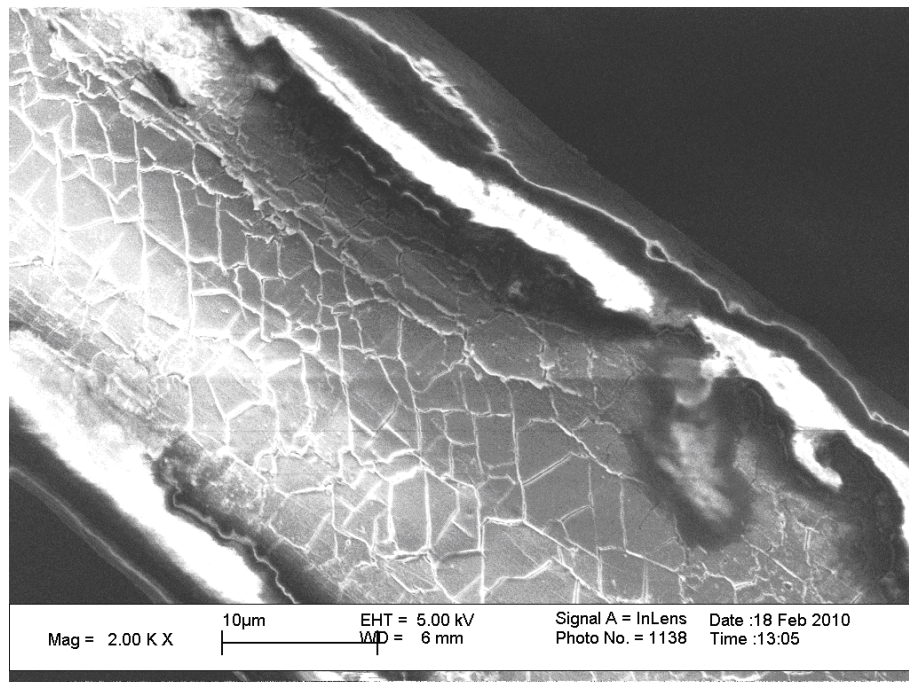


Figure 4.8. SEM image of cracks on the fiber surface

In Figure 4.8, 180 nm silver thin film coated polypropylene fiber can be seen. We obviously compare the thicknesses in figure and conclude that 180 nm is not optimum coating for fibers. Depending on the thin film thickness we can see from Figure 4.8 there are cracks on the surface of thin film.

We can conclude from all SEM images, inverted cylindrical magnetron sputtering system provides continuous and homogeneous thin film coating onto fiber surface. Actual success appears after coated fibers woven into fabrics and perform washing test.

4.4. XRD Result

In order to understand coated material, X-ray diffraction analysis was studied. Figure 4.9 shows XRD pattern of bare PA and silver coated PA. XRD diffraction patterns show both polypropylene and silver peaks. Both curves show PA peaks around 20-25 2θ . We obtained (111) and (200) peaks clearly in silver coated fiber. The crystallization detected in (111) and (200) planes. Black one shows silver coated PA6 and red one is just PA6. The highest peaks are polypropylene peaks. In order to compare results we analyze both just PP fibers and silver coated PP fibers. We can compare also from paper of Yeon S. Jung in Figure 4.10 (2004). We have same peaks as indicated at this study.

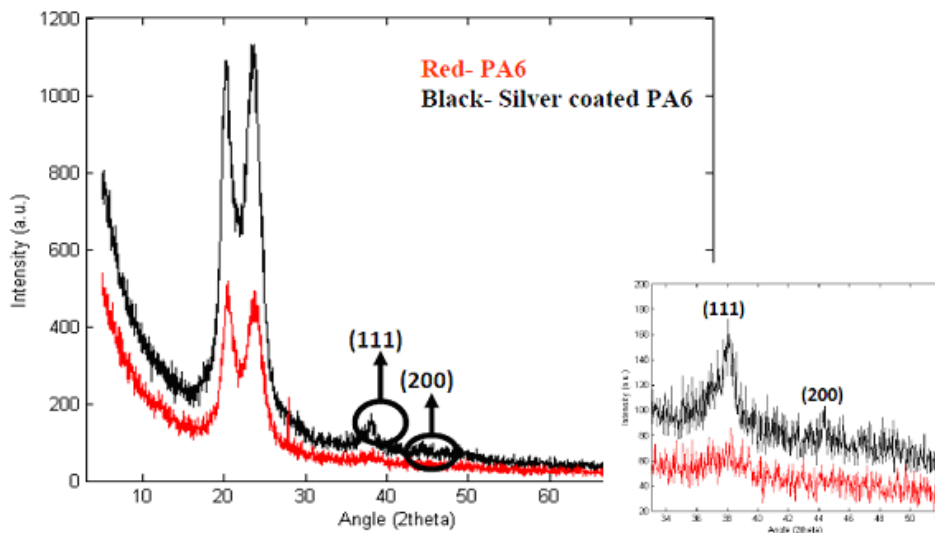


Figure 4.9. X-ray diffraction results of PA and silver coated PA

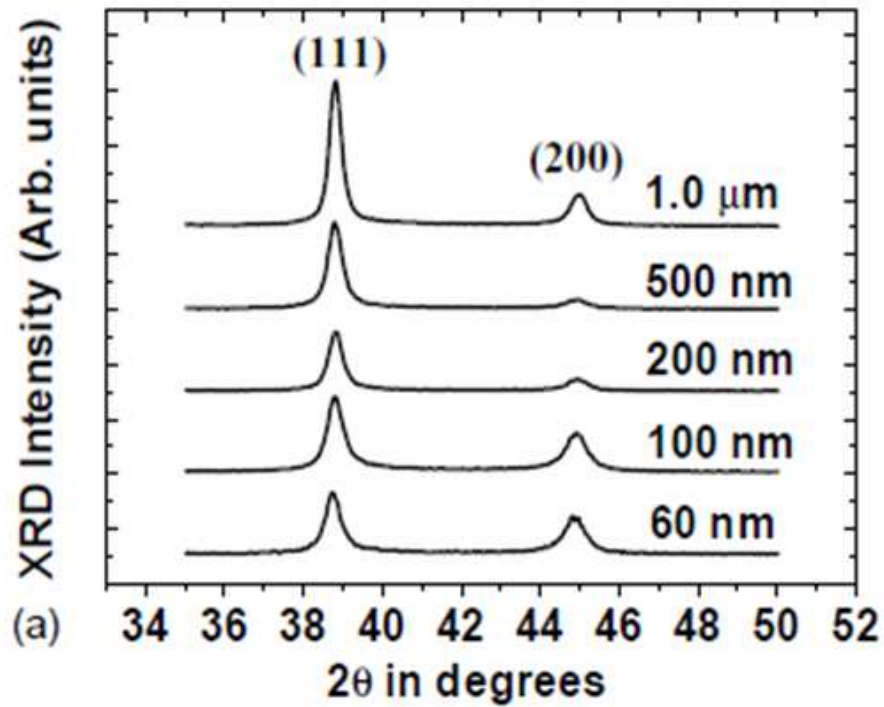


Figure 4.10. X-ray diffraction results from literature (Jung, 2004)

4.5. Electrical Results

By using inverted cylindrical magnetron sputtering system, we coated various textile fibers in different diameters. In order to test our system, we deposited silver film onto 400 μm diameter PP for single pass. Then we decreased the fiber diameters, 300, 200, 150, 125 μm and recently 85 μm , respectively. In Table 4.1, some of the results were given focusing on the PA fiber.

Table 4.1. Some of our electrical results

Fiber	Diameter	passes through the plasma	Gas flow	Feed through speed	Resistance (Ω/cm)
PA6	125 μm	7 times	60 sccm	8 m / min	21
PA6	125 μm	7 times	60 sccm	6.8 m / min	24
PA6	125 μm	7 times	60 sccm	5.1 m / min	20
PA6	125 μm	7 times	60 sccm	6.8 m / min	17
PA6	125 μm	7 times	60 sccm	8 m / min	20
PA6	85 μm	15 times	120 sccm	11 m / min	25
PA6	85 μm	15 times	120 sccm	18.4 m / min	26
PA6	85 μm	15 times	120 sccm	40 m / min	75
PA6	85 μm	15 times	120 sccm	25 m / min	50
PA6	85 μm	15 times	120 sccm	19 m / min	46

If we analyze the Table 4.1, we can clearly see the change of resistance depends on the fiber speed that effects deposited film thickness. If fibers pass through the plasma more times, film thickness is thicker and this effects the resistance values. This difference can be seen at 7 times and 15 times passes. Depending on the deposition speed we can control the thickness. All parameters are depending on each other. Main aim of this thesis is to get the conductive fibers and from table, the improvement of the resistance values can be seen obviously.

If we plot deposition speed versus resistance, with the increasing speed, resistance increasing as expected. In Figure 4.11 this dependence is clearly seen.

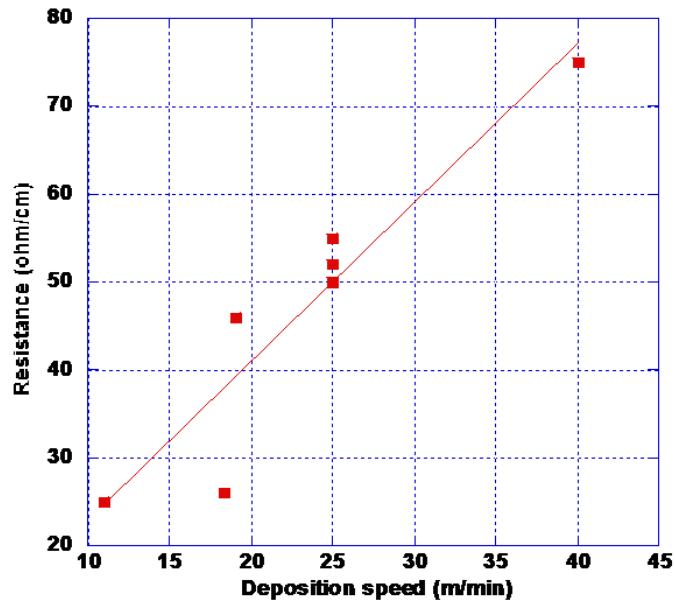


Figure 4.11. Deposition speed versus resistance

4.6. Thin Film Thickness Measurements

In planar magnetron sputtering system the film thickness can be measured by using Quartz Crystal thickness monitor. But in our case, cathode is cylindrical, that's why we cannot locate quartz crystal. On the other hand, if sample was planar, simply thickness could be found by using surface profilometer. We investigated film thicknesses in three different methods and compare the results of thicknesses. In order to compare results, in three methods same fiber was used. Firstly, fiber were cleaned by using LF plasma cleaning. PA fibers were passing through plasma 7 times. After deposition, Ag coated fibers used to determine film thicknesses. In this part, I will explain 3 methods that we used to find film thicknesses.

4.6.1. Calculating from Measured Resistance

First calculation is done starting from resistivity of silver. By using ohmmeter we studied resistance of 1 cm long silver coated fiber as a result we get average resistance

value. For our system measured resistance is $20\Omega/\text{cm}$ for 10 m/min feet through and 250 W applying sputtering power. At room temperature elemental silver resistivity is $\rho = 1.59 \cdot 10^{-6} \Omega \text{cm}$. When we put these values into resistance equation $R = \rho \cdot L/A$ and we find coated silver area. Here we take $L=1$ cm since we measured 1 cm long fiber resistance. Unknown parameter is coated silver's cross section. When we put parameters into equation we get exactly the volume of thin, cylindrical, hollow deposited structure on the fiber surface. Based on this idea we equal calculated area to $2\pi r t$ and as a result we get thickness t . This is 20.2 nm. We have to keep in mind that this result is actually 7 times coated fiber because we have remember fiber is passing through plasma 7 times during deposition. So we have to think result one of seven in 20.2 nm. This result suggest that, when film thickness so small like here, we have to focus on electron scattering from thin film surface.

4.6.2. Calculating from Deposited Silver Mass

Second way to calculate film thickness is derived from deposited silver mass. First we measure the weight of 10 meters fiber after plasma cleaning. After deposition we again measure the weight of this 10 meters fiber and subtract before deposition and mass difference put into density equation. As known pure silver density, we also get the volume of coated silver. As we have thought in first way, film thickness is so small, the volume actually give us coating area. This is second way to find film thickness and by this way we get 242 nm thickness. Again here, it should be remembered that thickness will be one of seven in 242 nm.

4.6.3. Calculating from Calibration Sample

We repeat deposition exactly under the same conditions while coating the fibers. At this time we placed microscope glass as a sample and glass passed through plasma just once. Copper wire was set to pass through plasma once and with feet through 10 m/min. Then we reomove microscope glass from vacuum chamber in order to find film thickness by using profilometer.

With the help of tip that profilometer has we can scan the film step and measure the thickness. As you can see from figure silver thin film thickness is 15 nm. When we deposit 7 times we get 105 nm.

Between calculating from mass and from glass surface there is a 1,5 times difference, while calculating from resistance give 5 and 12 times difference. Because the resistivity value is important for antistatic clothes, we focused on the cause of this difference.

Table 4.2. Comparison of 3 methods

Method	Film Thicknesses (nm)
1	20.2
2	242
3	105.0

The results are given in Table 4.2 and they are not consistent, especially estimation of thickness from measured resistance is very low, so we have to consider surface scattering effect which I mentioned about in chapter 3. Second result is overestimated, that's why we have to look at first and third method both. If we assume third one is correct, first result should be 5 times bigger. With this assumption thickness is around 100 nm. In Figure 4.12, we draw resistivity versus κ value. Here κ is thin film thickness divided by bulk electron mean free path. That means κ is 2, because thickness 100 nm and bulk mean free path 52 nm. For κ equals to 2, this value corresponds to 5 times bigger resistivity. So, if we multiply first method's result by 5, we can get correct results, as indicated in third result.

4.7. Optimization of the Film Thickness

From SEM image we see the cracks if thin film is not optimum so in order to analyse film thickness we draw normalized resistivity versus κ value (See Figure 4.12). As I mentioned before, κ is thin film thickness divided by bulk electron mean free path. Point (3,3) gives us min thickness and optimum resistivity which is optimum value. From that point if we take κ value as 3, we know the mean free path of bulk silver which is 52 nm, so result gives us the optimum value. According to this assumption optimum coating thickness should be around 150 nm.

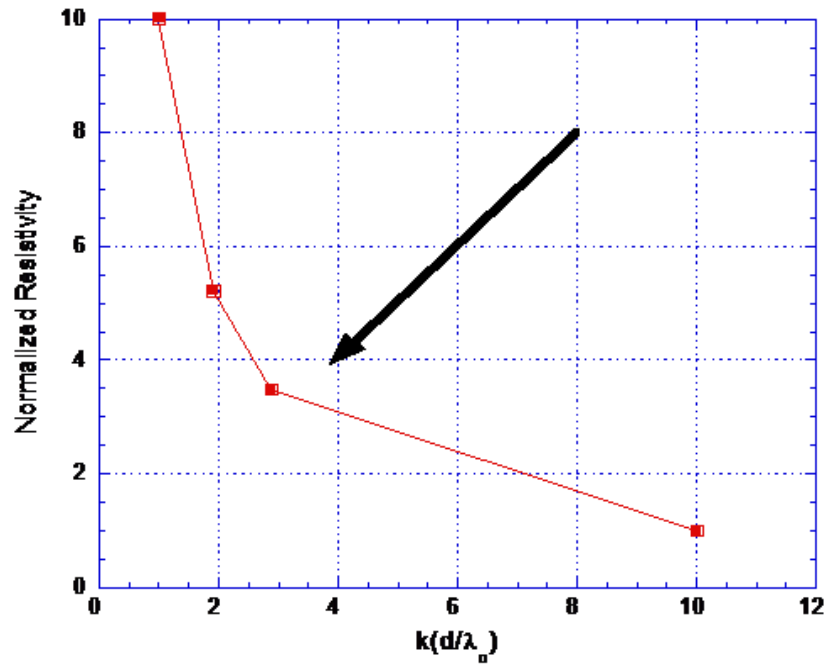


Figure 4.12. Normalized resistivity versus κ values

4.8. Antibacterial Results

After having conductive fibers, future study will be fabric. At this time, we did it by hand. I mentioned about silver antibacterial property. In order to investigate antibacterial property, silver coated fibers were woven into fabrics by hand (See Figure 4.13). Antibacterial test was done according to ASTM E 2149 test was done by Iztech Molecular Biology and Genetics department. Fabrics wait in the e-coli bacteria for 24 hours. In Figure 4.14, counted bacteria can be seen easily. Details are given in Table 4.3.

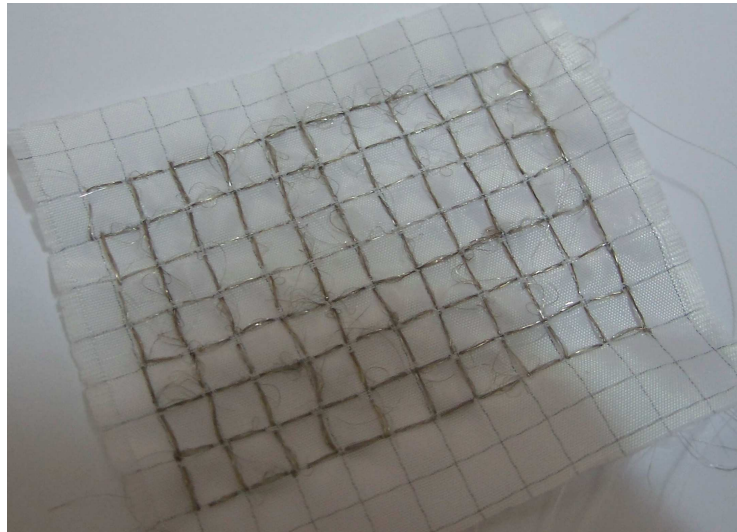


Figure 4.13. Silver coated fibers woven into fabric

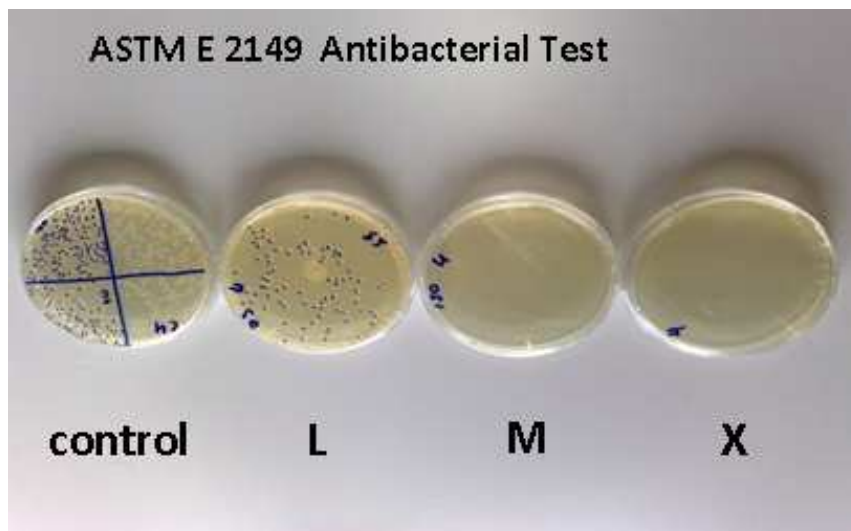


Figure 4.14. ASTM-E 2149 Antibacterial Test

According to standard, fabrics are waited E-coli bacteria environment for 24 hours and then bacteria number is counted. In order to find the reduction, there is a control sample. Before and after the test bacteria reduction is counted and percentage is calculated. From Table 4.3, it is obviously seen that while thickness increases, bacteria reduction percentage gets higher value.

Table 4.3. Antibacterial test results

Coating	Bacteria Reduction Percentage
0 nm	0
75 nm	75
120 nm	99.9

CHAPTER 5

CONCLUSION

Today, a wide range of nanoparticles, nanofilms and nanocomposites with various structures can be applied to the fibers, bringing new properties to the final textile product. For all these technical applications, it is desirable to produce such textile materials with especially designed surface features to meet various needs. Various techniques have been developed to functionalize textile materials.

In this thesis work first, we designed a new magnetron sputtering system which is in accordance with our goal. In our laboratory we have different kind of sputtering systems. We can coat planar surfaces easily by using our planar magnetron sputtering system (see Figure 2.17). But in my thesis my aim is to coat cylindrical fiber surfaces for this purpose we designed new system.

Within this thesis content, in chapter 1 and 2 we explained the general idea of motivation and physics part of thesis which includes thin film coating. Then we gave detailed explanation for the experimental design and what we did in chapter 3. Moreover, in chapter 4 we concluded results in detailed.

Firstly, we examined our inverted cylindrical magnetron sputtering system parameters. In order to find optimum system parameters experiments were done many times and each time changing one parameter or else. After getting the optimum parameters for system, different samples in different diameters were studied. Recently we focused on the polyamide fibers because these fibers can be obtained easily as a monofilament. Furthermore, thin metallic films can wet well on PA fibers. The optical images show that thin film and fiber are compatible. This comes from also cleaning procedure. Before deposition, fibers were cleaned by LF plasma cleaning system. Cleaned polymer fiber surface become oil and the other contaminations free. In this study we focused on silver thin film because of silver's good properties. Firstly silver is one of the highest electrical conductive metal and secondly it has additional antibacterial property. We can conclude also optimum thin film thickness is at around 150 nm. At this thickness there is no cracks on the thin film surface.

To sum up so far what I did in this study, inverted cylindrical magnetron sputtering (ICMS) designed, optimum sputtering parameters were determined, deposition speed reached 40 m/min and this can be increased, surface of coated fibers were investigated,

surface resistance values were found, coating thicknesses were investigated, optimum coating thickness was determined. Silver is a precious metal so we want to deposit the minimum thickness with optimum conductance. But with this optimum thickness we want to have the best antistatic and antibacterial results. Also surface wettability is important because the thicker coating gives the best wettability. Our limitation in this study is surface scattering.

In order to find film thicknesses we used 3 different methods. The film thicknesses results (See Table 4.2) are not consistent, especially estimation of thickness from measured resistance is very low, so we have to consider surface scattering effect. Second result is overestimated. If we assume third one is correct, first result should be 5 times bigger. With this assumption thickness is around 100 nm. If we look at Figure 4.12, for κ equals to 2, this value corresponds to 5 times bigger resistivity. So, if we multiply first method's result by 5, we can get correct results, as indicated in third result. To find optimum thickness, we focus a point where we have minimum coating thickness and optimum resistivity value. At this point, when we look at Figure 4.12, this point is (3,3) and if we calculate thickness from κ value, we get around 150 nm. According to our assumption, optimum thickness is 150 nm for our samples by using ICMS system.

As a result of this thesis work we have a new system which can deposit thin film onto cylindrical fiber surfaces. The results of this thesis, system can be used to coat different thin films onto different fiber surfaces. System can coat 1000 m long fiber now but this can be increased so investigation continues. After getting long enough deposited fibers, these will be woven into fabrics and depending on purpose we can use these antistatic fabrics as in chapter 1 mentioned about applications areas.

REFERENCES

- Amberg, M., J. Geerk, M. Keller, and A. Fischer. Design, Characterization and Operation of An Inverted Cylindrical Magnetron for Metal Deposition, *Plasma Devices and Operation* **12**, No. 3, 175-186 (2004).
- Amberg, M., K. Grieder, P. Barbadoro, M. Heuberger and D. Hegemann. Electromechanical Behaviour of Nanoscale Silver Coatings on PET Fibers, *Plasma Processes and Polymers* **5**, 874-880 (2008).
- Amberg, M., E. Körner, D. Hegemann, and M. Heuberger. Nanoscale Silver Coatings on Polymer Fibers, *NSTI-Nanotech 2010* **1**, 588-591 (2010).
- Bosetti, M., A. Masse, E. Tobin and M. Cannas. Silver coated materials for External Fixation Devices: In vitro Biocompatibility and Genotoxicity, *Biomaterials* **23**, No. 3, 887-892 (2002).
- Chopra L. K. and I. Kaur, 1983. *Thin Film Device Applications*. Plenum Press.
- Demir, A. and F. Oruc. Polimer Esasli Nanoliflerin uretimi, www.tad.com.tr/makale.aspx?id=126, (2007).
- Deng, B., X. Yan, Q. Wei and W. Gao. AFM Characterization of Nonwoven Material Functionalized by ZnO Sputter Coating, *Materials Characterization* **58**, 854-858 (2007).
- Deng, B., Q. Wei, W. Gao, and X. Yan. Surface functionalization of nonwovens by aluminum sputter coating , *Fibres and Textiles in Eastern Europe* **15**, No. 4(63), 90-92 (2007).
- Freund, L. B. and S. Suresh. 2003. *Thin Film Materials, Stress, Defect Formation and Surface Evolution*. Cambridge University Press.
- Fuchs, K., *The Conductivity of Thin Metallic Films According to The Electron Theory of Metals*, 100-108 (1937).
- Gedde, U. W., 1995. *Polymer Physics*. Chapman and Hall.
- Glocker, D. A. and S. I. Shah, 1995. *Handbook of Thin Film Process Technology*. IOP Publishing Ltd.
- Hasegawa, Y., M. Shikida, D. Ogura, Y. Suzuki and K. Sato, and J. Micromech. Fabrication of a wearable fabric tactile sensor produced by artificial hollow fiber, *Journal of Micromechanics and Microengineering* **18**, 085014 (2008).

- Hegemann, D., C.Oehr and A.Fischer. Design of Functional Coatings, *Journal of Vacuum Science and Technology* **23**, No. 1, 5-11 (2005).
- Hegemann, D., M.Mokbul Hossain and D.J.Balazs. Nanostructured Plasma Coatings to Obtain Multifunctional Textile Surfaces, *Progress in Organic Coatings* **58**, 237-240 (2007).
- Hegemann, D., M. Amberg, A. Ritter, and M. Heuberger. Recent Developments in Ag Metallised Textiles Using Plasma Sputtering, *Materials Technology* **24**, No. 1, 41-45 (2009).
- Horrocks, A. R., and S. C. Anand. 2000. *Handbook of Technical Textiles*. Woodhead Publishing Series in Textiles No. 12.
- Mayer, J. H., ESD Garments Cover Up, *Test and Measurement World From the ESD advertising supplement* , (2002).
- Journet, C. and P. Bernier. Production of Carbon nanotubes, *Applied Physics A* **67**, 1-9 (1998).
- Jung Y. S., 2004. Study on Texture Evolution and Properties of Silver Thin Films Prepared by Sputtering Deposition, *Applied Surface Science* **221**, 281-287 (2004).
- Keller, M., A. Ritter, P. Reimann, V. Thommen, A. Fischer and D. Hegemann. Comparative Study of Plasma-induced and Wet-chemical Cleaning of Fibers, *Surface Coatings and Technology* **200**, 1045-1050 (2005).
- Koprowska, J., J. Ziaja and J. Janukiewicz. Plasma Metallization Textiles s Shields for Electromagnetic Fields, 2008 IEEE, *Electromagnetic Compatibility - EMC Europe, 2008 International Symposium on* , 1-4 (2008).
- Lieberman M. A. and A. J. Lichtenberg, 1994. *Principles of Plasma Discharges and Materials Processing*. John Wiley and Sons.
- Mahan, J. E., 2000. *Physical Vapor Deposition of Thin Films*. John Wiley and Sons.
- Martin, P.M.. *Physics of Thin Films: Size Effects and Surface Scattering* , *Vacuum Technology and Coating*, October 2010, 6-11 (2010).
- Meoli, D., and T. May-Plumlee. Interactive Electronic Textile Development: A review of Technologies, *Journal of Textile and Apparel, Technology and Management* **2**, Issue 2, 1-12 (2002).
- Mohebbi, M., R. Fedosejevs, V. Gopal and J. A. Harrington, Silver coated Hollow-glass Waveguide for applications at 800 nm, *Applied Optics* **41**, No. 33, 7031-7035 (2002).

- Moza, S., Tomaszewska, M. and Morawski, A.W.. Decomposition of nonionic surfactant in a labyrinth flow photoreactor with immobilized TiO₂ bed, *Applied Catalysis B* **59**, 155-160 (2005).
- Namba Y., 1970. Resistivity and Temperature Coefficient of Thin Metal Films with Rough Surface, *Japanese Journal of Applied Physics* **9**, 1326 (1970).
- Ohring, Milton, 1992. *The Materials Science of Thin Films*. Academic Press.
- Ozyuzer, L., Z. Meric, Y. Selamet, B. Kutlu and A. Cireli. Antistatic and Antibacterial Properties of Metal Coated Polypropylene Fibers by Magnetron Sputtering, *The Journal Of Textiles and Engineers* **78**, 1-5 (2010).
- Palamutcu, S. and N. Dag. Functional Textiles I: Electromagnetic Shielding, Purposed Textile Surfaces, *Electronic Journal of Textile Technologies* **3**, No. 1, 87-101 (2009).
- Palamutcu, S., R. Keskin, N. Devrent, M. Sengul and B. Hascelik. Functional Textiles II: Antimicrobial Textiles, *Electronic Journal of Textile Technologies* **3**, No. 3, 95-108 (2009).
- Post, E.R., M. Orth, P.R. Russo, and N. Gershenfeld. E-broidery: Design and Fabrication of Textile-based Computing IBM *Systems Journal* **39**, No. 3, 840-860 (2000).
- Prater W. L., E. L. Allen, W. -Y. Lee, M. F. Toney, A. Kellock, J. S. Daniels, J. A. Hedstrom and T. Harrell, 2004. Microstructural Comparisons of Ultra -thin Cu Films Deposited by Ion-beam and dc-magnetron Sputtering, *Journal of Applied Physics* , (2004).
- Rosnagel Krishna, 2002. *Handbook of Thin Film Deposition Processes and Techniques: Principles, Methods, Equipment and Applications*. Noyes Publications.
- Schilt, A.. *Innovative Plasma Technology for Textile Treatment*, TNO Security and Safety. www.tno.nl
- Scholz, J., G. Nocke, F. Hollstein, and A. Weissbach. Investigations on fabrics coated with precious metals using the magnetron sputter technique with regard to their anti-microbial properties, *Surface Coatings and Technology* **192**, 1 (2005).
- Sen, A. K., 2007. *Coated Textiles*. CRC Press.
- Shanmugasundaram, O. L.. *Application of Plasma Technology in Textile Industry-An Overview*. www.fibre2fashion.com
- Shishoo, R.. 2007. *Plasma Technologies for Textiles*. CRC Press.

- Sigmund P., 1993 Fundamental Process in Sputtering Atoms and Molecules, *Matematisk-fysiske Meddelelser* **43**, (1993).
- Smith, D. L.. 1995. Thin-film deposition: principles and practise. McGraw-Hill press.
- Sondheimer, E.H.. The Mean Free Path of Electrons in Metals , *Advances in Physics* **1**, No. 1, 1-42 (1952).
- Stuart, R. V. 1982. Vacuum Technology, Thin Films, and Sputtering. Academic Press.
- Supuren, G., Z.E. Kanat, A. Cay, T. Kirci, T. Gülümser and I. Tarakcıoglu Nanolifler (Bolum1), *Tekstil ve Konfeksiyon* **17**, No. 1, 15-17 (2007).
- Wagendristel A. and Y. Wang, 1994. An Introduction to Physics and Technology of Thin Films. World Scientific Publishing Company.
- Wang, H., J. Wang, J. Hong, Q. Wei, W. Gao and Z. Zhu. Preparation and Characterization of Silver Nanocomposite Textile, *Journal of Coating Technology Research* **4**, No. 1, 101-106 (2007).
- Wang, H.B., Q. F. Wei, J. Y. Wang, J. H. Hong and X. Y. Zhao. Sputter Deposition of Nanostructured Antibacterial Silver on Polypropylene Non-wovens, *Surface Engineering* **24**, No. 1, 70-74 (2008).
- Wang, R. X., X. M. Tao, Y. Wang, G. F. Wang and S. M. Shang. Microstructures and Electrical Conductance of Silver Nanocrystalline Thin Films on Flexible Polymer Substrates, *Surface and Coatings Technology* **204**, 1206-1210 (2010).
- Warkusz, F.. Size Effects in Metallic Films , *Electrocomponent Science and Technology* **5**, 99-105 (1978).
- Warner, Steven B., 1995. Fiber Science. Prentice-Hall Press.
- Wei, Q.F.. Surface Characterization of Plasma-treated Polypropylene Fibers, *Materials Characterization* **52**, 231-235 (2004).
- Wei, Q., Q. Xu, Y. Cai and Y. Wang. Evolution of the Interfacial Bonding Between Fibrous Substrate and Sputter Coated Copper, *Surface Coatings and Technology* **202**, 4673-4680 (2008).
- Wei, Q., L. Yu, N. Wu and S. Hong. Preparation and Characterization of Copper Nanocomposite Textiles, *Journal of Industrial Textiles* **37**, No. 3, 275-283 (2008).
- Wei, Q.F., H. Ye, D. Y. Hou, H. B. Wang, and W. D. Gao. Surface Functionalization of Polymer Nanofibers by Silver Sputter Coating, *Journal of Applied Polymer Science* **99**, 2384-2388 (2005).

- Wei, Q., F. L. Huang, D. Y. Hou and Y. Y. Wang. Surface Functionalisation of Polymer Nanofibers by Sputter Coating of Titanium Dioxide , *Applied surface science* **252**, 7874-7877 (2006).
- Wei, Q., Y. Wang, Q. Yang, and L. Yu. Functionalization of Textile Materials by Plasma Enhanced Modification, *Journal of Industrial Textiles* **36**, No. 4, 301-309 (2007).
- Wei, Q., L. Yu, D. Hou and F. Huang. Surface Characterization and Properties of Functionalized Nonwoven, *Journal of Applied Polymer Science* **107**, 132-137 (2008).
- Wei, Q., X. Xiao, D. Hou, H. Ye and F. Huang. Characterization of Nonwoven Material Functionalized by Sputter Coating of Copper , *Surface and Coating Technology* **202**, 2535-2539 (2008).
- Wei, Q., D. Shao, B. Deng and Y. Xu. Comparative Studies of Polypropylene Nonwoven Sputtered with ITO and AZO , *Journal of Applied Polymer Science* **114**, 1813-1819 (2009).
- Wei, Q. , D. Tao, B. Deng and F. Huang. Comparative Studies of Silver Nanocomposite Fibers, *Journal of Industrial Textiles* **38**, No. 4, 309-316 (2009).
- Yousefi H. R., M. Ghoranneviss, A. R. Tehrani and S. Khamseh, Investigation of Glow Discharge Plasma for Surface Modification of Polypropylene, *Surface and Interface Analysis* **35**, 1015-1017 (2003).
- Ziaja, J., J. Koprowska and J. Janukiewicz. Using Plasma Metallization for Manufacture of Textile Screens Against Electromagnetic Fields, *Fibres and Textiles in Eastern Europe* **16**, No. 5(70), 64-66 (2008).