

Types and processing of electro-conductive and semiconducting materials for smart textiles

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Abstract: The latest technological advances in new materials and devices enabled textile solutions to wearable systems. These solutions require electro-conductive textile materials as a basic component. This chapter first discusses key terms used in the context of electro-conductive textiles. It then addresses different conductive and semiconductive materials and their production methods that are applied in textiles.

Key words: electronic textiles, conductive and semiconductive yarns, production methods, coating technology.

2.1 Introduction

For a long time, the textile industry has used metallic yarn in weaving and knitting for aesthetic and decorative purposes. The first known conductive fabric was silk organza, which consisted of two types of yarns: a plain silk yarn running in the warp direction and, as the weft, a silk yarn wrapped in thin copper foil. Copper provided a shiny and reflective appearance; the silk core gave tensile strength. These yarns have been woven in India over the last century utilizing other metals such as silver and gold. In the 1920s and 1930s, metallic yarns were also used for ecclesiastical and courtly robes to give them the appearance of ‘golden clothes’. In the 1950s, Lurex[®], made from a thin strip of aluminium, entered the market. It could be added to a number of conventional fibres and yarns to create metallic fabrics, which were very popular at that time (Braddock *et al.*, 1999).

However, let us turn away from the aesthetic and decorative purposes of metallic yarns in clothing and take a look at the functional aspects that metallic filaments and yarns can fulfil. In more technically-oriented areas, conductive materials have been in use for anti-static and shielding purposes for the last 30 years. However, the conductivity needed for these purposes is rather low, which is explained in Section 2.2. With the increasing interest in smart textiles, the demand on highly conductive textile materials has also increased. They are used, for instance, in sensors, as transmission lines or as heating elements.

Besides using metals, such as copper, silver, stainless steel or aluminium, in fibre or filament form or incorporated into yarns, other types of conductive

materials are now used, such as conductive polymers, conductive coatings and inks. In Sections 2.3 and 2.4, a range of conductive and semiconductive textile materials is discussed.

Conductivity can be introduced at different levels in a textile material:

- on a fibre, yarn or fabric level;
- during production; or
- applied as after-treatments.

The different possibilities are further discussed in Section 2.5.

2.2 Electro-conductive and semiconductive materials

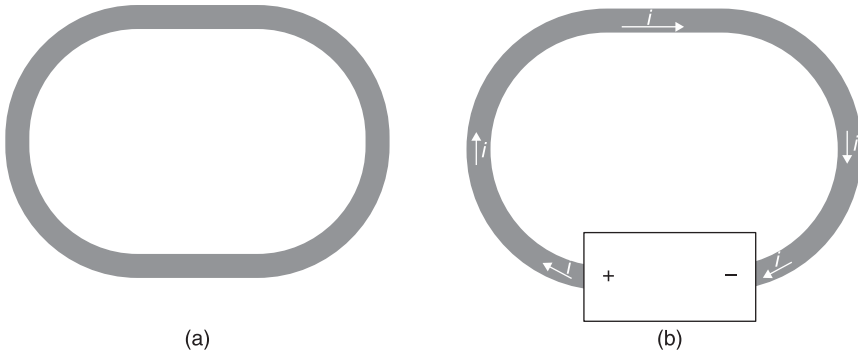
2.2.1 What is electrical conductivity?

This section focuses on terms used to describe electrical properties of materials, such as electrical current, conductivity, resistance and resistivity, starting with the former term. Electrical current means charges in motion through an object. Depending on the matter, this charge is transported either by electrons (in a metal conductor), by ions (in an electrolyte) or by a combination of both, electrons and ions (in a plasma). Here, only electrons as charge carriers in solid conductors, such as metal filaments, are addressed, as they are of the most interest in the context of smart textiles.

To constitute an electrical current, there must be a flow of charge through an object along a potential difference that corresponds to an electrical voltage. Without a potential difference, no current will flow. This phenomenon can be depicted with the help of a copper wire (Fig. 2.1(a)). If we consider a closed-loop copper wire, free electrons will travel through it in all directions. Although electrons are available, no electrical force acts on them, as they are all at the same potential, and thus there is no current. If a battery is inserted into the loop (Fig. 2.1(b)), the conducting loop will no longer be at a single potential. Electrical fields act inside the copper wire, causing the electrons to move and thus establishing a current (Halliday *et al.*, 2001).

Conventional electrical current is defined by the movement of positive charge carriers in an electrical field (called drift movement). However, in metallic solids, such as copper wires, charge carriers are electrons, which are negative and therefore flow in the opposite direction. As illustrated in Fig. 2.1(b), the flow of current is indicated by an arrow associated with the symbol i to indicate the direction of the conventional current flow.

The electrical current that flows through an object is dependent on the material it is made of. For instance, if the same potential difference between the ends of copper wires or glass rods is applied, having the same geometry, different currents result. The object's resistance towards the flow of current through it plays a role.



2.1 (a) A closed loop of copper wire; the wire is at one potential;
 (b) An electrical potential difference is caused between the ends of the copper wire due to a battery to which the ends are connected. The battery produces an electric field within the wire and causes charges (current i) to move around in one direction.

The resistance between any two points of a conductor is determined by applying a potential difference V between those points and measuring the current I that results. The resistance R is:

$$R = \frac{V}{I} \quad [2.1]$$

The resistance is expressed in Ohm (Ω). It can be seen in the formula, that for a given potential difference, the greater the resistance is (to the current), the smaller the current. This formula is often referred to as Ohm's Law. However, it should be noted that resistance can be linear or non-linear. Only linear resistance obeys Ohm's Law, which states that the current is directly proportional to the potential difference between the two ends of the copper wire.

It is often necessary to take a general view and deal with materials instead of particular objects, because if the dimensions of the object change, the resistance will also change. However, a material's ability to oppose or conduct the flow of electrical current should be definable regardless of its dimension or shape. In this case, the potential difference V across a particular resistor should be regarded as an electrical field \vec{E} at a point in a resistive material. It should not be focused on the current I through the resistor, but on current density \vec{J} at the point in question. Instead of the resistance R of an object, it then needs to be referred to the resistivity ρ of the material:

$$\rho = \frac{E}{J} \quad [2.2]$$

Combining the SI units for E and J , ohm-metre (Ωm) results as unit of ρ :

$$\frac{\text{unit}(E)}{\text{unit}(J)} = \frac{\frac{V}{m}}{\frac{I}{m^2}} = \frac{V}{I} m = \Omega m \quad [2.3]$$

We often speak of the conductivity σ of a material. This is simply the reciprocal of its resistivity, resulting in:

$$\sigma = \frac{1}{\rho} \quad [2.4]$$

If we know the resistivity of a material, such as copper, we can calculate the resistance of a length of copper wire. If the current density is uniform throughout the wire, the electrical field and the current density will be constant for all points within the wire and will have the values:

$$E = \frac{V}{L} \quad \text{and} \quad J = \frac{I}{A} \quad [2.5]$$

where A is the cross-sectional area of the wire (in m^2) and L is its length (in m). The two formulas can be combined to give:

$$\rho = \frac{E}{J} = \frac{\frac{V}{L}}{\frac{I}{A}} \quad [2.6]$$

However, V/I is the resistance R , which allows recasting the formula as:

$$R = \rho \frac{L}{A} \quad \text{or} \quad \rho = R \frac{A}{L} \quad [2.7]$$

However, this formula, also known as the Pouillet formula, can only be applied to a homogenous isotropic material of uniform cross section. We can also give this formula a more ‘textile character’, as the cross-sectional area A of a fibre or yarn can be determined in different ways:

- It is possible to calculate the cross-sectional area applying a geometrical formula, when the dimension of the electro-conductive part in a fibre or yarn is known.
- The calculation can also be based on the linear density of the metallic fibre or yarn used and the electro-conductive material density of this fibre or yarn, respectively. By knowing the linear density of the fibre or yarn expressed in g/10 000 m (dtex), as well as its density ρ_d in $g\ cm^{-3}$, its diameter D can be calculated (Morton and Hearle, 2008) by:

$$D = \sqrt{\frac{400 * dtex}{\pi \rho_D}} \quad [2.8]$$

D is expressed in μm .

Applying the Pouillet formula, the resistivity can then be calculated by:

$$\rho = R \frac{\left[\left(\sqrt{\frac{400 * dtex}{\pi \rho_D}} \right) 10^{-a} \right]^2 \pi}{4} L^{-1} \quad [2.9]$$

expressed in $\Omega \text{ mm}^2 \text{m}^{-1}$.

However, in the case of fibres and yarns, difficulties often appear when the cross-sectional area is included in the formula, as it assumes that the material is homogeneous. Hence, parameters, such as fineness, density and measured resistance per unit length, are considered to be constant along the yarn's axis. Since yarns are composed of several individual fibres or multiple filaments, they are far from homogeneous. This implies that the cross-sectional area A can vary along their length. Consequently, the variances may be too high to result in reliable results.

Against these considerations, the most reliable approach is also the most straightforward, that is to relate the electrical resistance R_y of a fibre or yarn to its length L :

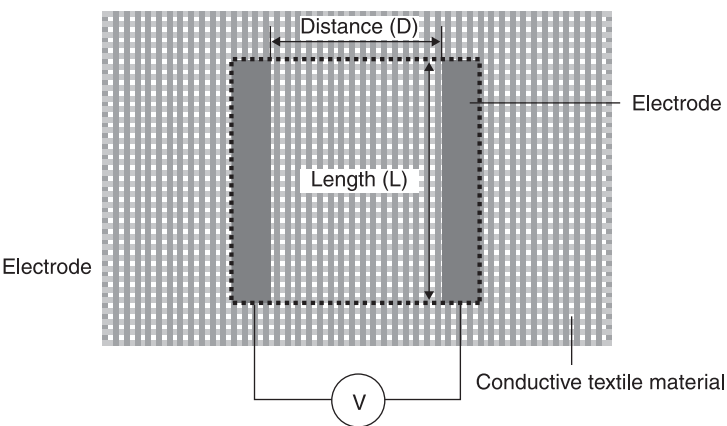
$$R_y = \frac{R}{L} \quad [2.10]$$

where R_y is related to length L and is expressed in $\Omega \text{ cm}^{-1}$.

The same difficulties appear when trying to express the resistivity of a conductive fabric, whether it be woven, knitted, braided, printed or a non-woven. Due to the textile's inhomogeneity and anisotropy, it is difficult to relate the resistance to the volume of the conductive area. Hence, it is often advantageous to express the surface resistivity of the fabric instead of its volume resistivity. The surface resistivity only takes into account the distance (D) between the two measuring electrodes and their contact length (L) with the sample, which are equal (Fig. 2.2). The physical dimensions, such as thickness and diameter of the conductive layer or yarn, are not considered.

The resistivity is therefore the quotient of the potential gradient, in V/m , and the current per unit of electrode length, A/m . Since the four ends of the measuring electrodes define a square, the lengths in the quotient cancel and surface resistivities are reported in ohms, although it is common to see the more descriptive unit of ohms per square (Ω/\square) (IEC, ASTM).

Before turning to the differences between conductors, semiconductors and insulators, a tabular summary of the above discussed quantities, namely voltage, current, resistance, resistivity and conductivity, is presented in Table 2.1.



2.2 Set-up for surface resistivity measurements.

Table 2.1 Overview of quantities used in electronics around electric current

Quantity	Symbol	Unit of measure	Abbreviation
Voltage	V or E	Volt	V
Current	I	Ampère	A
Resistance	R	Ohm	Ω
Resistivity	ρ	Ohm metre	$\Omega\text{ m}$
Conductivity	σ	Siemens per metre	S m^{-1}

2.2.2 What is the difference between conductors, semiconductors and insulators?

The differences between conductors, semiconductors and insulators can be roughly explained when looking at their resistivities (Table 2.2). A conductor is a material that allows an electrical current to pass easily. Hence, it has a low value of resistivity. An insulator is just the opposite of a conductor. It opposes electrical current to flow and thus has a high resistivity. Semiconductors have electrical properties somewhere in the middle, between those of a conductor and an insulator.

The question arises as to why some materials allow the electrical current to flow easily and some others do not. The question can be answered when looking at the energies of the electrons that are present in a material. In a conductor, such as a copper wire, there are plenty of electrons that, roughly speaking, are only loosely held in place within the molecules and require only a little energy to become free. An electrical field applied across the conductor can supply that

Table 2.2 Different materials and their resistivity

Material	Resistivity ρ (Ω m)
<i>Typical metals</i>	
Silver	$1.62 \cdot 10^{-8}$
Copper	$1.69 \cdot 10^{-8}$
Gold	$2.44 \cdot 10^{-8}$
Aluminium	$2.75 \cdot 10^{-8}$
Nickel	$6.93 \cdot 10^{-8}$
Iron	$9.68 \cdot 10^{-8}$
Platinum	$10.6 \cdot 10^{-8}$
Stainless steel	$72 \cdot 10^{-8}$
<i>Typical semiconductors</i>	
Silicon, pure	$2.5 \cdot 10^3$
Silicon, n-type ¹	$8.7 \cdot 10^{-4}$
Silicon, p-type ²	$2.8 \cdot 10^{-3}$
<i>Typical insulators</i>	
Glass	10^{10} – 10^{14}
Polyamide	10^{16}
Polyester	10^{17}

¹ Pure silicone doped with phosphorus impurities to charge carrier density of 10^{23}m^{-3}

² Pure silicone doped with aluminium impurities to charge carrier density of 10^{23}m^{-3}

energy. The field would not only free these loosely-held electrons but would also propel them along the wire. Thus, the electrons travel together through the material forming an electron drift. Generally speaking, most metals are good electrical conductors (Halliday *et al.*, 2001; Tutorials. 2011a,b).

In an insulator, all or most of the electrons are firmly locked into place within the molecules and significantly greater energy would be required to free them so they could move and participate in an electrical current. Any reasonable electrical field applied to the insulator cannot supply enough energy to move the electrons and hence, no current will flow giving these materials their isolating properties. Insulators play an important role within an electrical circuit as they prevent short circuits. Glass, epoxy glass resins and most polymers, also in textile form, are good insulators.

A semiconductor is like an insulator, except that the energy required to free some electrons is less. It has very few free electrons because its atoms are closely grouped together. However, by adding certain impurities or dopants to the semiconductive structure, charge carriers can be supplied that are very loosely held within the material and thus are easily movable. Charge carriers can be additional electrons or removed electrons, which act like a movable positive charge. Moreover, by controlling the doping of a semiconductor, the density of

charge carriers that can participate in a current can be controlled, and thereby its electrical properties (Halliday *et al.*, 2001).

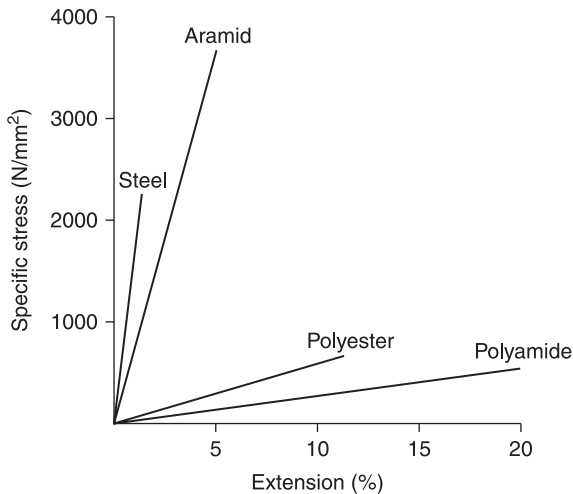
2.3 Electro-conductive materials and their properties

The variety of electro-conductive materials has significantly increased in recent years. The choice of which material to use depends to a large extent on its properties. Next to the material's electro-conductive properties, its chemical characteristics, such as reactivity to humidity, air or fluids, and its mechanical behaviour are relevant parameters during processing and for the performance of the final product.

The chemical characteristics of an electro-conductive material, especially in the case of metals, are best described when talking about corrosion. Corrosion means, in general, oxidation of metals due to an oxidant such as oxygen being present in the surrounding air. Hence, a metal oxide is formed on the surface of a metal. In most cases, the oxide of a metal has worse electro-conductive properties compared to the pure metal. Stainless steel, for instance, is covered with a chromium oxide layer after some time. This protective, non-conductive layer determines the high contact resistance of stainless steel surfaces. On a copper surface, to give another example, a layer of copper(I) and copper(II) oxide can be formed – surface corrosion processes that seriously affects its electro-conductive performance. Silver is an exceptional metal. Although an oxide film is built up over time on the silver's surface, the metal is not compromised in its electro-conductive behaviour, because silver in oxide form possesses the same electro-conductive properties as in its pure metal form. Noble metals, such as gold or palladium, possess a surface that is remarkably resistant to oxidation. Corrosion may also appear in polymers. However, in this context, the term degradation is most likely used.

As aforementioned, the mechanical properties of an electro-conductive material is another important aspect when choosing the right material. It is known that metal filaments compromise good electro-conductive properties with weak mechanical characteristics. They can hardly be stretched or stressed without breakage or at least a change of their electrical resistance. Oppositely, conventional polymeric yarns possess excellent elongation and recovery properties. Typical stress–extension curves are illustrated in Fig. 2.3.

When textiles are combined with electro-conductive materials, it is expected that the elastic behaviour of the conductive material is enhanced. This is important not only for comfort but also for processability. Electro-conductive yarns or metal filaments integrated into textiles need to be stressed during production and to be stretched during use. Thus their fragility will pose a major problem for their application in textiles, and their non-elasticity will decrease their service life. A good compromise can be achieved when combining metal filaments with elastic



2.3 Typical stress–extension curves of steel, aramid, polyester and polyamide.

yarns, that is, a metal filament is wound around an elastic core yarn. While a metal filament is almost inextensible, an elastomeric yarn has a high extensibility. The combined yarn levels out the strength of the metal filament and the extension of the elastic core yarn (Schwarz *et al.*, 2011). The following discussion is subdivided by the origin of conductive materials, starting with classical metals in Section 2.4.1. Carbon and carbon-based materials are addressed in Section 2.4.2. Finally, in Section 2.4.3, we close with conductive polymers.

2.4 Metals

Metals are one of the most important industrial materials. They are usually classified into ferrous materials and non-ferrous metals. Both types are used in the textile world. However, their characteristics most likely define their application area in textiles. This section gives an overview of the most widely applied metals in combination with textiles and their properties.

2.4.1 Ferrous materials – stainless steel

In general, steel has a moderate electrical conductivity compared to other metals and is most often used for antistatic purposes in carpets and protective clothing. Stainless steels are high-alloy steels and have good corrosion resistance because they contain relatively large amounts of chromium (at least 10%) (Design, 2011). Nonetheless, as mentioned above, when exposed to air and humidity, stainless steels are covered with a thin layer of chromium oxide, which reduces their

surface conductivity. Another issue to consider is that nickel is also present in stainless steel, causing a risk of allergenic reactions when applied on the human skin. Furthermore, the electrical contact resistance of stainless steel has to be critically assessed. When, for instance, being woven into a structure, interlacing stainless steel filaments exhibit a very high contact resistance, which does not allow the current to spread uniformly on the structure. Consequently, local hot spots and burns, when being applied on the skin, are very likely to appear (Banaszczyk *et al.*, 2009). Stainless steels are available as pure filaments, yarns and blended with polymeric fibres (Bekaert, 2011). As they are very heavy (generally 66% heavier than aluminium), stiff, and have a rough and abrasive surface handle, they may cause damage during processing, such as weaving and knitting. Examples of typical stainless steel yarns are depicted in Fig. 2.4.

2.4.2 Non-ferrous metals – copper, silver, gold, aluminum, nickel

Copper (Cu)

Copper possesses excellent electrical and thermal conductivity. It oxidizes in air, or more precisely with atmospheric oxygen, forming a copper oxide layer on its surface. This oxide layer prevents a further bulk corrosion and it is therefore often reported that copper has a good resistivity to corrosion (Association, 2011). However, its oxide layer is badly conducting, with the application of copper where surface conductivity is very important. On the contrary, in applications requiring materials with good electro-conductivity where inertness¹ is not so crucial, copper is a good choice. This includes textile transmission lines and textile heating elements. Furthermore, researchers have demonstrated the good antimicrobial properties of copper, which is a very important characteristic for touch surfaces such as textiles (Grzybowski and Trafny, 1999; Michels, 2006; Gould *et al.*, 2009). Disregarding its application as



(a)



(b)

2.4 Stainless steel yarn forms: (a) stainless steel staple yarn twisted around a core yarn; (b) stainless multifilament yarn.

electro-conductive components, it can also be used as an antimicrobial agent, for instance in healthcare environments.

Due to its malleability and formability, copper is extruded in wire forms having a diameter of a few micrometres, which is compatible with use in textiles (Fig. 2.5(a)). Copper is also applied as a thin layer onto textile surfaces (Gimpel *et al.*, 2003; Scheibner *et al.*, 2003; Westbroek *et al.*, 2006; Wei *et al.*, 2008a, *Fibres*, 2011; Schwarz *et al.*, 2012) (Fig. 2.5(b)).

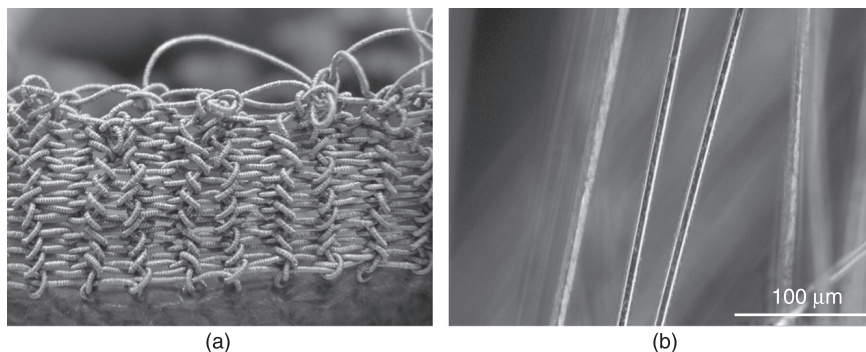
Silver (Ag)

Silver can be regarded as a direct competitor to copper, as it also offers very high electrical and thermal conductivity among all metals (even higher than copper) and the lowest contact resistance, possesses antimicrobial properties and oxidizes when exposed to air. In contrast to copper, silver oxide is as conductive as pure silver and hence it is often applied in textiles to shape electrodes having direct contact to the human body and the environment (Cömert *et al.*, 2008). Due to its ability to protect against bacterial and fungal infection, its application in textiles has been extensively studied during the last 25 years (Tweden *et al.*, 1997; Pollini *et al.*, 2009; Landsdown, 2010; Filipowska *et al.*, 2011).

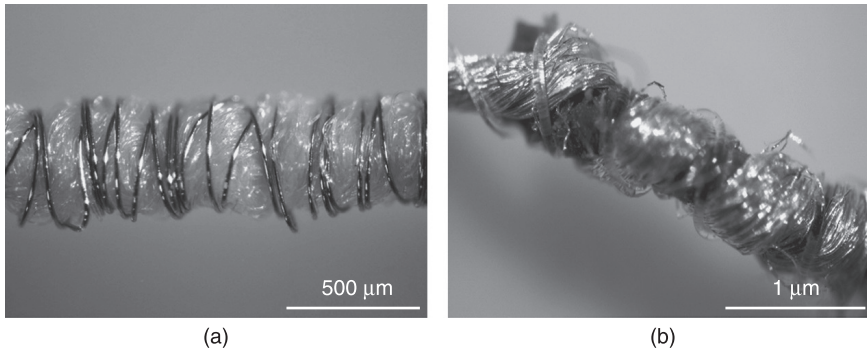
Silver is also very malleable and ductile and is therefore available in thin wire form that can be incorporated into textiles (Fig. 2.6(a)). Also, it is applied as coating (Fig. 2.6(b)) or printing onto textile structures (Jiang *et al.*, 2005, 2010; Scholz *et al.*, 2005; Statex – Ericson *et al.*, 2004; Swicofil 2011; Kazani *et al.*, 2012).

Gold (Au)

In history, gold has been predominately used to advertise affluence and wealth due to its rarity and permanence. Today, researchers and scientists take advantage



2.5 Textile-compatible copper: (a) copper wires are twisted around elastic yarns and knitted; (b) copper-coated para-aramid yarn.



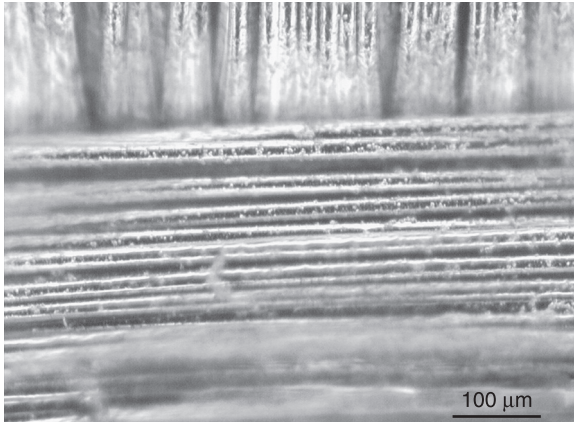
2.6 Textile compatible silver: (a) silver wires twisted around a rubber core yarn; (b) silver-coated Zylon® yarn.

of gold's outstanding chemical and physical properties, as it offers corrosion resistance, very good thermal and electrical conductivity (only silver and copper are better electrical conductors, but are not corrosion resistant). It has high ductility and excellent wear resistance (Corti and Holliday, 2004). Above that, it has a good bio-compatibility and therefore it is applied in versatile areas in medicine, as its surface cannot be changed via oxidation or other influences (Holliday, 2007). Furthermore, it does not cause allergenic reactions of the skin and the electrical properties do not change under the influence of body liquids such as sweat or urine (Council, 2011). Thus, gold is an ideal, but expensive, material to use as a sensing material measuring body parameters, such as heart rate or sweat rate.

In combination with textiles, gold foils, cut into thin strips, were used 90 years ago to decorate robes to give them a precious appearance. Up to today, it is still used as a colorant in textiles (Johnston and Kelly, 2011). Besides these decorative purposes, gold is also applied on yarns in the form of a thin film to produce highly electro-conductive yarns and fabrics (Fig. 2.7). Various methods have already been explored, such as electroless deposition (Pinto *et al.*, 2003; Matsuo *et al.*, 2007; Banaszczyk *et al.*, 2009; Schwarz *et al.*, 2010a), electroplating (Gimpel *et al.*, 2003; Cammarata *et al.*, 2011) and magnetron sputtering (Scholz *et al.*, 2005).

Aluminium (Al)

Aluminium is a very light, ductile and soft metal used particularly in applications where weight is a decisive factor, such as the automotive and airplane industry. Even applied as a very thin film, it is impervious to vapour and light, reflecting approximately 92% of visible light. It is therefore often used in the food and packaging industry. Beyond that, aluminium is also known for its good



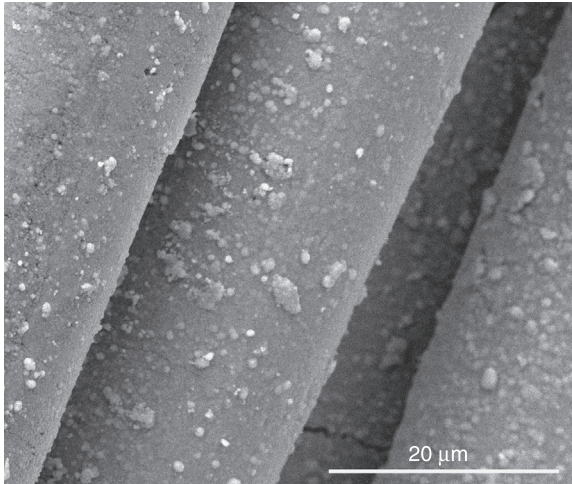
2.7 Gold-coated woven fabric through electroless deposition.

thermal- and electro-conductivity, having 60% the conductivity of copper (Ostermann, 2007). As with copper and silver, a thin layer of aluminium oxide forms on its surface when exposed to air. Forming a passive layer, the oxide protects aluminium from further corrosion. However, the oxide has very poor electro-conductivity, impairing the surface conductivity of the metal. When used close to the body, like many other textiles, it should be also taken into account that its corrosion resistance is often greatly reduced when many aqueous salts are present (e.g. sweat). Thin aluminium mono- and multi-filaments having diameters of at least $8\mu\text{m}$ can be found on the market (Draht, 2011; Imattec 2011). Also, research has been conducted on printing with aluminium-based pastes on textiles (Yip *et al.*, 2009b) and coating textiles with thin layers of aluminium through flame spraying (Voyer *et al.*, 2008).

Nickel (Ni)

When people hear the word nickel, probably they first think about the allergenic reaction it can cause on the skin when used in jewellery. Hence, the amount of nickel that is allowed in products, which come into contact with human skin, is regulated by the European Union (Commission). Nickel belongs to the group of heavy metals and its chemical properties are similar to those of iron. At room temperature it is resistant to air, water and most chemicals. Like iron, it is ferromagnetic at room temperature. Due to its ductility it can be easily extruded in wire form. It is often applied as a coating to protect against corrosion and wear.

In combination with textiles, nickel is predominantly applied for electromagnetic shielding (Jiang and Guo, 2011, Perumalraj and Dasaradan, 2011). It is mostly applied as a thin layer on textile surface through electroless deposition (Pinto



2.8 Nickel-coated polyester fibres through electroless deposition.

et al., 2003; Yuen *et al.*, 2007; Gan *et al.*, 2008; Jiang *et al.*, 2008; Association, 2011) and electroplating (Morin, 1982). An example of a nickel-coated yarn is illustrated in Fig. 2.8. Furthermore, the nickel titanium alloy, also known as *Nitinol*, has gained interest in the textile world due to its shape memory effect. In wire form, Nitinol is processed in textile stents (Riepe *et al.*, 2002; Berreklouw *et al.*, 2007) and in fashion items (Berzowska and Coelho, 2005; Vili, 2007).

2.5 Carbon: carbon black (CB), graphite and carbon nanotubes (CNT)

Carbon materials are well-known for their structural applications in lightweight composites in aerospace and automotive applications. Recently, they have been increasingly investigated for electrical applications, including electromagnetic reflection, heating and sensing. Carbon materials are typically built up in layers. As they only conduct in the in-plane direction, their electrical properties depend greatly on the degree of preferred orientation of the carbon layers. This degree can be influenced during production by applying heat treatments and aligning carbon units, such as carbon fibres in a composite structure. Hence, carbon can exhibit a range of electrical conductivity, which when compared to metals, is still rather low. Carbon is usually obtained by the pyrolysis of hydrocarbon gases and oils. Depending on their production parameters, different forms of carbon called allotropes exist. Next to amorphous carbon (carbon black), other allotropes of carbon are graphite and fullerene, such as carbon nanotubes.

2.5.1 Carbon black (CB)

In amorphous carbon, the arrangement of carbon atoms is non-crystalline and irregular. It is the main constituent of carbon black (CB), a typical filler material for polymers and polymeric fibres, as it provides electro-conductivity. There is a wide variety of CB products. Differences include particle size and particle size distribution, specific surface area, surface structure, amount of agglomeration, moisture content, and minor contaminants, such as metals, sulphur, oxygen and hydrogen (Peters, 1998). Compared to graphite and carbon nanotubes, CB is the least electro-conductive carbon material as it is amorphous.

In textiles, CB is either applied as filler material in polymers or as a layer. For the former, CB particles have been dispersed into different polymer solutions (Flandin *et al.*, 2001; Mallette *et al.*, 2001; Huang, 2002; Heiser *et al.*, 2004; Hwang *et al.*, 2007b). Subsequent extrusion (Hitchcock *et al.*, 1999; Jimenez *et al.*, 2009) or electrospinning (Kim and Yang, 2003; Pedicini and Farris, 2004; Hwang *et al.*, 2007b; Tiwari *et al.*, 2008; Schiffman *et al.*, 2011) produces fibres and fibre webs with electrical properties depending on loading of CB in the polymer solution and the percolation threshold², which is reported to be in the range of 2 to 12 vol.% (Hwang *et al.*, 2007b). Normally, the electrical resistance ranges between 10^5 and 10^7 Ohm/cm. The same effect can be achieved by applying CB coatings or films onto textile structures (Jin *et al.*, 2005; Koncar *et al.*, 2009; Xue *et al.*, 2011). In order to improve their electro-conductive properties, additional metallic particles or thin metallic layers are applied in or on CB containing fibrous and textile substrates (Chakravarthi *et al.*, 2011; Jalali *et al.*, 2011). Due to their high electrical resistance, CB-filled polymer composites are most often applied for antistatic, shielding and heating purposes (Koncar *et al.*, 2009). Their suitability as sensors and electrodes has also been explored (Chung, 2004; Xue *et al.*, 2011).

2.5.2 Graphite

Diamond,³ graphite and fullerene are crystalline forms of carbon, in which each atom bonds with its neighbour forming a regular, repeating pattern. Graphite is the most common crystalline allotrope, with a layered, planar structure. In each layer, also referred to as graphene, each carbon atom forms three links with its neighbours, forming hexagonal rings. As carbon atoms have four electrons to share, each carbon atom can still bond to another carbon atom of another layer holding the material together (Sparrow, 1999).

The so-called flexible graphite is a textile-compatible form of graphite, as it is a flexible sheet made by compressing a collection of graphite flakes without a binder. Due to its microstructure involving graphite layers that are preferentially parallel to the surface of the sheet, flexible graphite has a good electrical and thermal conductivity in the plane of the sheet. It is particularly explored for shielding purposes and as a heating element (Chung, 2004).

2.5.3 Carbon nanotubes (CNT)

Another allotrope is fullerene, which has the form either of a hollow sphere, ellipsoid or cylinder. Fullerenes are similar in structure to graphite, but they may also contain pentagonal (or sometimes heptagonal) rings (Thostenson *et al.*, 2001). Typical fullerenes are carbon nanotubes, which are widely applied in composites. A carbon nanotube is produced by rolling a sheet at a specific angle. The combination of the rolling angle and radius specifies the nanotube properties, for example, whether the individual nanotube is a metal or semiconductor. Both, single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) exist (Chou *et al.*, 2010).

Carbon nanotubes are applied in three different forms in textiles:

1. carbon nanotube fibres;
2. filler material in polymeric fibres and filaments;
3. surface layers on textile structures.

Carbon nanotube fibres

The development of continuous fibres based on carbon nanotubes has recently gained a lot of interest. The most applied technologies include the spinning of carbon nanotubes from solutions (Bhattacharyya *et al.*, 2003) and gels (Li *et al.*, 2004; Koziol *et al.*, 2007; Chae *et al.*, 2007, 2009), as well as the dry spinning from multi-walled nanotubes grown on a substrate (Jiang *et al.*, 2002; Zhang *et al.*, 2007). These technologies are explained in more detail in Section 2.5. Carbon nanotubes are known for their high axial strength and stiffness. Fibres with a greater strength than para-aramid fibres can be produced, depending on the production technologies and process parameters (Koziol *et al.*, 2007; Chou *et al.*, 2010).

Carbon nanotubes as filler material in polymeric fibres and filaments

Carbon nanotubes are used as fillers in polymeric solutions to extrude or spin fibres and filaments. Researchers have explored, for example, the melt spinning of carbon nanotube loaded polypropylene (PP) (Kearns and Shambaugh, 2002; Bhattacharyya *et al.*, 2003), poly(methyl methacrylate) (PMMA) (Haggenmueller *et al.*, 2000), polycarbonate (PC) (Sennett *et al.*, 2003; Potschke *et al.*, 2005; Thomas *et al.*, 2006), polyimide (PI) (Siochi *et al.*, 2004), polyamide (PA) (Sandler *et al.*, 2004), poly(ethylene terephthalate) (PET) (Luo *et al.*, 2006), polyurethane (Chen *et al.*, 2006), and shape memory polyurethane (Hu and Meng, 2008). Furthermore, some attempts were made to produce carbon nanotube loaded fibres through twin-screw extrusion with polyethylene and polyurethane (Chen *et al.*, 2006).

The electro-conductive properties of such fibres depend on a range of factors, including the purity of the nanotubes, the homogeneity of the dispersion in the

polymeric host matrix, its loading and the aspect ratio between length and diameter for the connectivity between single nanotubes (Chung, 2004, Chou *et al.*, 2010). However, the achievable electro-conductivity of these yarns is limited when comparing them to carbon nanotube fibres.

Carbon nanotubes as surface layers on textile structures

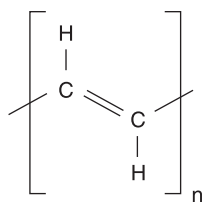
Different technologies are employed to create carbon nanotube layers on textile materials. Chemical vapour deposition, for instance, was used to grow carbon nanotubes on woven fabrics (Baughman *et al.*, 2004; Veedu *et al.*, 2006; Zhang *et al.*, 2007). Another method that was applied in research is dye-printing of carbon nanotubes on polyester yarns (Zhang *et al.*, 2007; Fugetsu *et al.*, 2009). The achieved electrical resistance of the yarn by the latter method is $8 \times 10^5 \Omega/\text{cm}$.

2.6 Intrinsically conductive polymers (ICP)

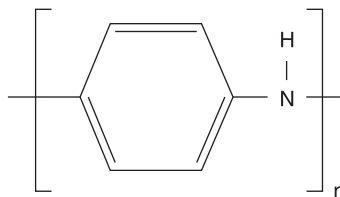
Most polymers are insulating and so are not used in electrical, antistatic or electromagnetic shielding applications. However, in the second half of the last century a new group of polymers was discovered, known as intrinsically or inherently conducting polymers (ICP) or electroactive polymers (EAP), with the intrinsic ability to conduct electricity. A polymer can only conduct electrical charges if it has a conjugated structure, meaning that the chain of carbon–carbon bonds consists of alternating single (σ) and double (π) bonds. By doping, which is a process by which the polymer is either oxidized or reduced to create charge carriers, charge carriers can move along the carbon chain, exhibiting a conductive behaviour. The conductivity of such conjugated polymers is reported to be as high as 10^5 S/cm , which is close to that of copper with 10^6 S/cm (Ramakrishnan, 1997). These polymers include, among others, polyacetylene, polypyrrole (PPy), poly-3,4-ethylenedioxythiophene (PEDOT) and polyaniline (PANI) (Fig. 2.9).

The electrical conductivity of the polymers can be varied by the amount of dopant that is added. Hence, the polymers can be tuned to have semiconductive properties as well as metallic conduction. Furthermore, they have the advantage, due to their nature, that they are lightweight and flexible. However, they are not resistant to high temperatures (e.g. 135°C maximum for PANi) and they become instable over time, because of a low resistance to humidity, oxygen and temperature.

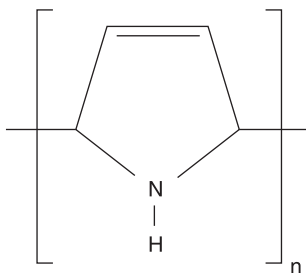
In combination with textiles, PPy and PANi are the main polymers of choice and are usually applied as thin layers (Fig 2.10). Different textile materials have been used to produce, for instance, PPy-coated textiles obtained by chemical reaction, such as polyester (Kuhn *et al.*, 1995; Sparavigna *et al.*, 2008), polyamide (Wu *et al.*, 2005; Ferrero *et al.*, 2006), cotton (Bhat *et al.*, 2006) and wool (Kaynak



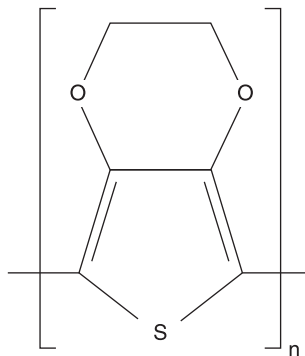
Polyacetylene



Polyaniline (PANi)

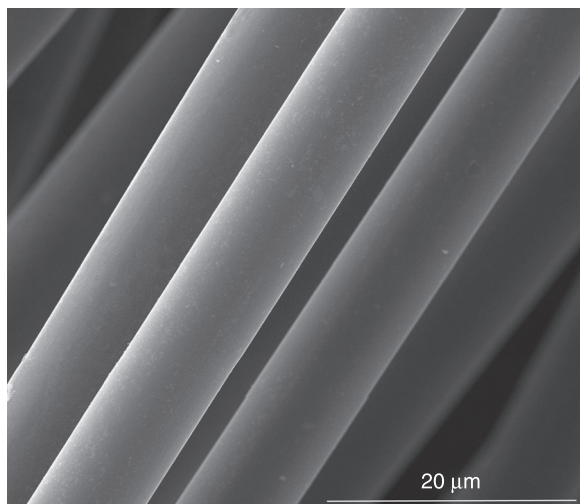


Polypyrrole (PPy)



Polyethylene dioxythiophene (PEDOT)

2.9 Structures of selected conductive polymers.



2.10 Polypyrrole-coated para-aramid fibres.

et al., 2002). Different methods are followed in chemical polymerization. While often a two-step polymerization is the method of choice (Lee and Hong, 2000; Wu *et al.*, 2005; Bhat *et al.*, 2006; Ferrero *et al.*, 2006), *in situ* polymerization (Reynolds *et al.*, 1998; Lee and Hong, 2000) and emulsion polymerization (Yanumet *et al.*, 2004) are also applied. PANi has been applied as a coating on polyester and polyamide fabrics via *in situ* polymerization (Oh *et al.*, 1999; Kim *et al.*, 2004). Moreover, two-step polymerization of aniline on fabrics is commonly used as well (Oh *et al.*, 2001).

Furthermore, conducting polymers are also inkjet- and screen-printed onto textiles (Calvert *et al.*, 2007, 2008, Hu *et al.*, 2011). Other possible techniques include the extrusion of conducting polymer filaments (Wang *et al.*, 2000) and the electrospinning of conducting polymer nanofibres (Henrich, 1996; Huang, 2002; Dai *et al.*, 2005; Pinto *et al.*, 2011). The application of conducting polymers in textiles ranges from sensors (Hwang *et al.*, 2007b) and dielectric layers in fibrous transistors (Krucinska *et al.*, 2011) to electromagnetic shielding (Kaynak *et al.*, 2006) and heating devices (Bhat *et al.*, 2006).

2.7 Semiconductive materials and their properties

Section 2.2 briefly outlined that a semiconductor has an intermediate electrical conductivity between that of a conductor and an insulator. The ability to conduct electrical conductivity can be selectively controlled by introducing impurities, called dopants, into the material. In general, a distinction is made between dopants that act as electron donors and electron acceptors. The former group of dopants contributes extra electrons and is therefore called *n*-type (*n* stands for negative). The latter dopant group withdraws electrons from the material, leaving a 'hole', and is referred to as *p*-type (*p* stands for positive). The addition of dopant is minuscule with a concentration of the order of 1 part in a 100 million (HyperPhysics, Hub, 2011).

In general, a distinction is made between inorganic and organic semiconductors. Inorganic ones typically comprise silicon, carbon, metal oxides and compound semiconductors (Rogers *et al.*, 2008). Their electrical performance is usually high and they have an excellent stability. However, their processing, for instance as thin films, requires temperatures that exceed the glass transition temperature and/or thermal decomposition temperatures of polymeric materials. Attempts are currently made to overcome the high processing temperatures of silicon and hence to tailor it for thin film applications. Organic semiconductors, on the contrary, can be processed by low temperature deposition or printing techniques. The research efforts to improve their electrical performance are promising but the results obtained are still lower than those achievable with inorganic semiconductors (Sun and Rogers, 2007). The following sections summarize the most commonly applicable semiconductors for textile structures.

2.7.1 Silicon

Common semiconducting materials are crystalline solids, such as silicon. In pure form it has such a high resistivity that it is an insulator. However, its resistivity can be greatly reduced by doping, which is achieved by adding impurities, such as phosphorous (to create an *n*-type semiconductor) or aluminium and boron (to create a *p*-type semiconductor), to a melt and subsequently allowing the melt to solidify into the crystal. Silicon exists with various levels of crystallinity, from amorphous (a-Si:H) to nanocrystalline (nc-Si), microcrystalline (μ c-Si) and polycrystalline (pc-Si). Currently, low temperature processes, such as radiofrequency plasma-enhanced chemical vapour deposition (RF-PECVD) and hot-wire chemical vapour deposition (HW-CVD), are explored for all silicon types (Conde *et al.*, 2001; Wertheimer *et al.*, 2006; Sun and Rogers, 2007; Jeong *et al.*, 2010). In textiles, plasma-enhanced chemical vapour deposition has been applied to deposit amorphous silicon on Kapton fibres (Bonderover *et al.*, 2003).

2.7.2 Carbon

In general, carbon can be used as *n*-type and *p*-type semiconductor. A single graphite sheet, for instance, exhibits typically a semiconductive behaviour. Furthermore, as reported in the previous section, carbon nanotubes can be tuned to either possess conductive or semiconductive properties by imparting small differences in their diameter and chirality, such as the sheet direction in which the graphite sheet is rolled to form a nanotube cylinder (Baughman *et al.*, 2002).

The most common method to obtain semiconductive carbon-based textiles is to extrude composite fibres using carbon as filler material. Semiconductive properties can be achieved by the right amount of carbon filler content, the orientation of the carbon filler in the matrix and the contact resistance of neighbouring carbon components (Chou *et al.*, 2010). CB, to give one example, has been used as filler material in a thermoplastic resin to extrude or spin semiconductive fibres (Hwang *et al.*, 2007a, SmartFiber, Thostenson *et al.*, 2001). Above that, carbon nanotubes are applied as a coating on polyester fibres (Kuraray, 2011).

2.7.3 Metal oxides

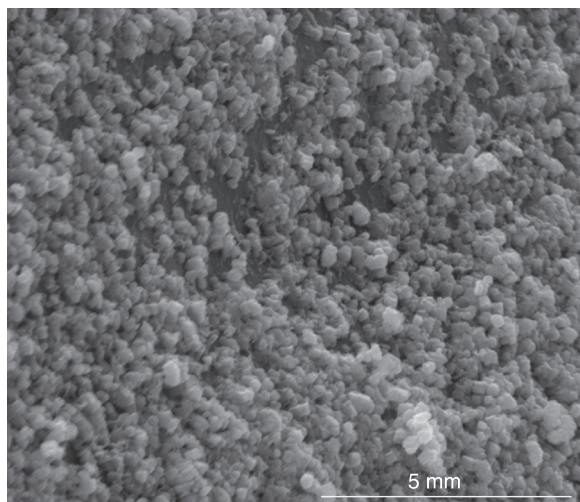
Oxides of transition metals provide another class of inorganic semiconductors. These oxides, such as zinc oxide (ZnO), aluminium-doped zinc oxide (AZO) or tin-doped indium oxide (TIO), are ubiquitous in electronics and can be easily combined with textiles as they show in general a good compatibility with plastic substrates (Carcia and McLean). Especially zinc-oxide has drawn considerable attention as it offers a high chemical stability, electrical conductivity and optical transparency in the visible range (Wei *et al.*, 2009a). Usually dopants are used in a metal oxide to modify or improve its properties. Hence, AZO is an *n*-type semiconductor exhibiting a wide range of conductivities and conductivity changes

under different environmental conditions allowing to sense gases (Suchea *et al.*, 2007). Like undoped zinc oxide, it is attractive due to low cost and non-toxicity (Wei *et al.*, 2009a). Indium doped metal oxides, on the contrary, are associated with high cost and limited availability. However, they are still one of the most widely used oxides due to their optical transparency, convenient processability and electrical properties (Henrich, 1996).

In general, metal oxides can be applied as thin films either by sputtering or solution processes onto textiles (Fig. 2.11). Magnetron sputtering of zinc, aluminium-doped zinc oxide and TIOs, for instance, is explored by different research groups on various textile substrates, such as polyester non-wovens (Wei *et al.*, 2007), PP non-wovens (Wei *et al.*, 2008c, 2009b) and polyamide nanofibres (Wei *et al.*, 2010). Solution processes include sol-gel coating of nanofibres with ZnO (Wei *et al.*, 2008b) and pulsed electrodeposition on polyamide filaments (Schlettwein *et al.*, 2009).

2.7.4 Polymeric and short organic semiconductors

Polymeric and short organic (oligomeric) semiconductors are an attractive alternative to inorganic semiconductors, especially when applied in textiles, due to their good mechanical flexibility, low-temperature processability and inherent compatibility with other polymers (Rogers *et al.*, 2008). In order to exhibit semiconductive properties, organic semiconductors require a highly conjugated π -system. Π -conjugated organic oligomers and polymers can function either as *p*-type or *n*-type semiconductor in which, respectively, the majority of carriers are holes or electrons. As a consequence, *n*-type materials are characterized by a high

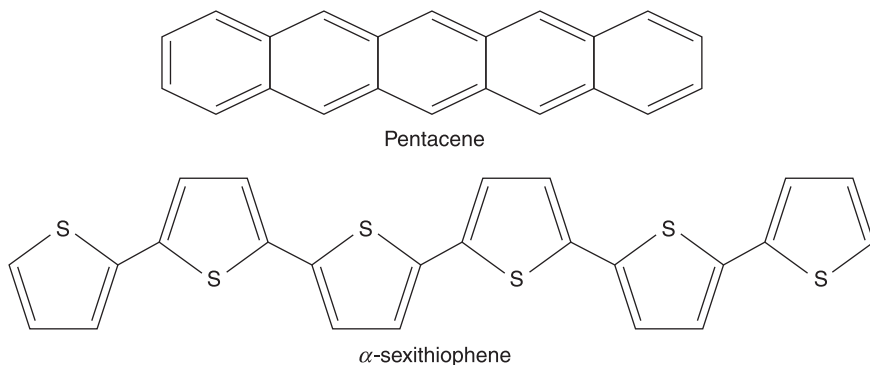


2.11 ZnO-coated fibre surface through electroless deposition.

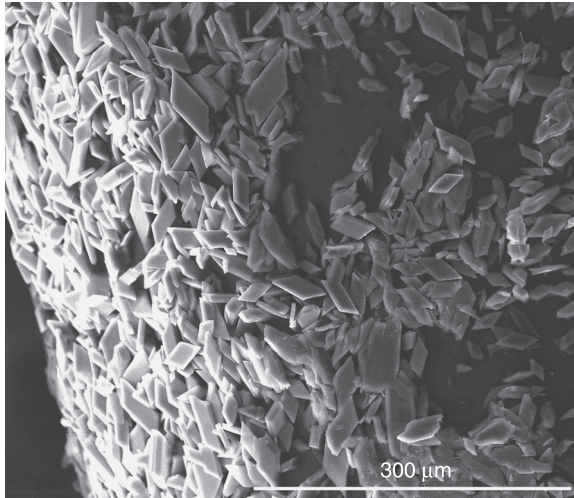
electron affinity and *p*-type by a low ionization potential. Most successful organic semiconductors are *p*-type, because of their stability in air and relative high mobility. *n*-type semiconductors have, in most cases, a tendency to react with air and moisture under operating conditions and have relatively low field-effect mobilities, making them less suitable for practical applications (Bao, 2004).

A distinction between organic semiconductors is typically made based on their size. Short organic semiconductors comprise polycyclic aromatic compounds, such as anthradithiophene (e.g. α -sexi-thiophene) and acenes (e.g. pentacene). Common polymeric semiconductors are polyacetylene, including PPy and PANi, poly(3-hexylthiophene) (P3HT) and polythienylenevinylene. Some examples are shown in Fig. 2.12.

With regard to textiles, the most explored oligomeric semiconductor is pentacene. Macconi *et al.* (2006), for instance, demonstrated the evaporation of pentacene on a cylindrical metal fibre. However, the main disadvantage is the poor solubility of pentacene molecules in organic solvents at room temperature (Afzali *et al.*, 2002). Despite its price, high-vacuum vapour deposition of pentacene is therefore still the most used technique for its deposition onto surfaces (Lee *et al.*, 2010). Another disadvantage of pentacene is that it is relatively unstable in oxidation conditions (Maliakal *et al.*, 2004). Hence, much work has been focused on using a soluble precursor allowing the fabrication of solution-cast unsubstituted pentacene (Wurthner *et al.*, 2006; Kwon *et al.*, 2008) or to permanently functionalize the structure with substituents. This allows the processing of pentacene with low temperature and cost technologies, such as drop casting, dip coating or inkjet printing. Hence, soluble TIPS-pentacene has been explored as a dip-coated layer on a PI-copper-coated polyester fibre (Genabet, 2010) (Fig. 2.13). In the area of polymeric semiconductors, PANi (Fryczkowski *et al.*, 2005), PPy (Corporation, 2011, Wallace *et al.*, 2008) and PEDOT (Skrifvars *et al.*, 2011) are mostly explored in textiles, as semiconductive properties can be achieved with the right amount and type of dopant.



2.12 Structures of selected oligomeric semiconductors.



2.13 TIPS-pentacene dip coated on a polyester filament surface.

2.8 Processing electro-conductive and semiconductive materials into textile structures

As discussed in Section 2.3, conductive textile materials can be classified into two general categories, namely intrinsically conductive textile structures and textile structures that are specially treated to gain conductivity. Materials of these two groups can also be distinguished by their production technologies (Table 2.3). This section summarizes the most common production technologies applied to produce intrinsically conductive fibres, yarns and fabrics, as well as textile structures that used an after-treatment to obtain conductive properties.

Table 2.3 Overview of production technologies to obtain conductive textile structures

	Fibre level	Yarn level	Fabric level
During production	Spinning, wire drawing, bundled wire drawing, cutting production method, melt extraction, melt spinning, wet spinning	Spinning, twisting	Weaving, knitting braiding with conductive filaments
After-treatments	Coating, ink-jet printing	Coating	Coating, ink-jet printing, screen printing

2.8.1 Intrinsically conductive fibres and yarns

In general, intrinsically conductive fibres and yarns are conductors without the addition of a conductive substance. These fibres are pure metals, such as nickel, stainless steel, silver, aluminium and copper, a metal alloy or carbon. Recently, the development of intrinsically conductive polymer fibres has also been reported, described at the end of this section. Different production methods are used to produce intrinsically electro-conductive fibres, among them wire drawing, bundled wire drawing, cutting production method, melt spinning and wet spinning.

Wire drawing

The conventional process to produce metal fibres is wire drawing, a mechanical production process. This process is characterized by its various drawing steps, called coarse, medium, fine and carding trains. The drawing die, used to draw the fibre, consists of a steel mount with a core out of ceramics, carbide or diamond. The initial diameter of the metal wire varies, depending on the material. For copper, for example, it is usually 8 mm, while for iron it is 5 mm. After drawing, the wire is annealed in steel at temperatures ranging between 600 and 900°C. Subsequently, they are quenched. The fine metal wire is then wrapped onto a revolving wire drawing cylinder.

The wires produced in this way are used today in metal spun yarns, which are produced by wrapping the wire around a core yarn or are used to be processed further, for example by the bundling wire drawing process (Association, 2011).

Bundle wire drawing

Another mechanical metal fibre production process is the bundle wire drawing procedure. In this process, 1000 to 2000 conventional drawn wires are bundled into one strand and are wrapped by a thin metal cylinder.

The thin cylinder is used to enable further drawing of the whole bundle, because the drawing of a single wire would lead to wire breakage. As the cylinder material is chemically less stable than the wires, it can be removed by dissolving the whole system in an acidic bath. Finally, the process results in individual and parallel fibres of adjustable diameter between 4 to 25 µm. These can afterwards be spun to multifilament or broken into staple fibres with a length of 50 to 150 mm (Association, 2011).

The company Bekaert Fibre Technologies credits a US patent with the description of the bundle drawing production process of metal fibres. Their product range includes BEKINOX® VS, a 100% metal fibre in silver form or bulk, and BEKINOX® VN out of 100% stainless steel that can be applied in antistatic textiles, for signal and power transfer, cut resistant fabrics, heat resistant sewing and thermal conductivity. Therefore, the yarn is suitable for

application in the sector of protective clothing, but also in fashion for the metal look (Bekaert, 2011).

Cutting production method

Besides using the bundle drawing procedure, Bekaert also produces metal fibres by shaving them endlessly off the edge of a rolled metal foil. With this process, it is possible to obtain several fibres per cutting section. Subsequently, the metal fibres are bundled into fibre skeins and wound onto a bobbin (Bekaert, 2011).

These fibres are branded under the name Bekinit[®]. In contrast to bundle-drawn fibres, they have a rectangular cross section. In addition, they are thicker, composed of more crimp and are less expensive due to a shorter production processing time. It has to be noted that the bundle-drawing process takes approximately six months.

Melt spinning

Metal fibres may also be produced by thermal methods based on processing the fibres through direct extrusion from the melt. The challenge of metal melt spinning compared to melt spinning of glass or polymers is that the melt viscosity of metals is approximately 100 times lower than that of glass and polymers. Thus, melt fractures can easily arise and instead of fibres, only droplets are formed. In the following, we refer to some methods for metal fibre production by using a coagulation bath.

In the Taylor process, a metal rod is utilized, which is placed into a glass tube. Both the material and the glass tube need to possess a comparable melting point to draw them at the same time. When heating the whole system, the metal rod melts and the glass tube softens. In this state, the glass tube can be drawn and forms a very thin hollow glass thread, with the metal as the filler material. The glass casing is afterwards removed from the metal, either by crushing with a roller or by ultrasound or chemical separation, and the result is a very fine metal fibre (diameter <50 µm).

Continuous production of metallic fibres is achieved by melt spinning in a rotating fluid. During this process, metals or their alloys are molten and overheated in a gaseous atmosphere at high temperature and pressure. The liquid surface is charged with an inert gas excess pressure. Due to the high pressure, the melt can be pressed through a nozzle, after which the fibre is submerged as a free jet at a defined angle in a laminar flowing cooling agent. The solidifying fibre is accelerated through the rotation and through the density difference between the metal and the cooling agent at the inside of the drum, where it cools down to the temperature of the cooling agent. Extraction takes place either continuously or discontinuously, depending on the batch size.

A further way to produce melt spun metal fibres is the usage of the melt extraction process. In this procedure, a water-cooled extraction roller rotates in

the melt batch. The roller usually comprises a multiple blade with V-shaped edges with which the mass is solidified and short fibres are pulled out. A magnetic field is created at the top of the melt batch to prevent waves occurring at the melt's surface. With this procedure, it is possible to process materials such as aluminium and tin fibres that cannot be produced by conventional methods due to their brittleness.

Wet spinning of carbon nanotubes from solutions

Researchers have explored the wet spinning process of lyotropic liquid crystalline suspension of SWCNTs. In this process, a dispersion of carbon nanotubes is dissolved in sulphuric acid. After being stored in a piston, the mixture is subsequently extruded through a spinneret into the air before entering a coagulation bath containing diethyl ether, aqueous sulphuric acid or water. The fibres are washed and dried before collecting them on a take-up bobbin (Ericson *et al.*, 2004).

2.8.2 Specially-treated conductive and semiconductive fibres, yarns and fabrics

Various coating techniques are currently in use to provide fibres, yarns and fabrics with conductive properties. This section gives an overview of the most applied techniques.

Electroless deposition

An electroless deposition is a process in which a metal is deposited onto a surface by an autocatalytic reduction. In the deposition solution, a metal salt (often in the form of a complex ion) and an appropriate reducing agent are dissolved.

To be of practical use, the reaction between dissolved metal species and the reducing agent must continuously occur only on the surface areas where metal deposition is desired and not in the bulk of the solution. Hence, electroless deposition is often referred to as autocatalytic deposition, because the deposited metal acts as catalytic surface for further deposition of the metal (Schwarz *et al.*, 2011).⁴

In the field of textiles, electroless deposition is mostly applied to polymeric fibres, yarns and fabrics. Various research groups deposited copper (Cu) onto fibres and fabrics (O'Connor and Capistran, 1986; Kim *et al.*, 2001; Oh *et al.*, 2004; Westbroek *et al.*, 2006; Gan *et al.*, 2008; Guo *et al.*, 2009; Jiang *et al.*, 2009; Schwarz *et al.*, 2009).

Other metals that can be applied in this way include nickel (Ni) (Pinto *et al.*, 2003; Yuen *et al.*, 2007) and silver (Ag) (Jiang *et al.*, 2005). Moreover, Cu-Ni alloys were deposited by electroless deposition on polyester fabrics (Gan *et al.*, 2008).

Silver-coated yarns have already been introduced to the market by different companies. For example, *X-Static*TM by Sauquoit Industries (2011) and *Shieldex*[®]

by Statex (2011) are both silver-coated polyamide yarns, either based on staple fibres or filaments.

Electroplating

Electroplating is a deposition process using electrical current to obtain a metallic layer on a sample's surface. The sample is immersed into an electrolyte solution and used as a cathode. The anode is made of the depositing material, which is dissolved in the depositing solution in the form of metal ions. These cations travel through the solution and are reduced to their metallic form on the cathode surface, resulting in a metallic layer. As the sample to be coated acts as cathode, it needs to be electro-conductive prior to the electroplating process.

In textiles, different conductive structures have been utilized to apply an additional metal or metal oxide layer to the surface. For instance, carbon fibres have been used to electroplate nickel and silver onto the surface (Morin, 1982). The additional metallic layer ensures a good bonding strength between the carbon fibre used for reinforcement and the matrix material in a composite structure.

Another approach was followed by the Textile Research Institute of Thuringia-Vogtland (TITV Greiz). Researchers used polyamide filaments that were coated with a thin silver layer as the base material, which were normally used for antistatic purposes and thus possessed a low conductivity. In a subsequent electrochemical treatment, the yarns could be modified with different metals, ranging from gold, to platinum, copper and silver (Gimpel *et al.*, 2003; Scheibner *et al.*, 2003). These yarns are registered under the name *ELITEX*[®] yarns.

The same base material was used to electroplate zinc oxide on the yarn's surface (Schlettwein *et al.*, 2009). The resulting semi-conductive yarn could then be used for the development of textile-based photovoltaics.

Physical vapour deposition (PVD)

In physical vapour deposition, a metal is evaporated in a vacuum. The vacuum allows metal vapour particles to travel directly to the target sample, where they condense back to a solid state. This condensation is achieved by cooling the sample surface, thus drawing energy from the metal particles as they arrive, allowing them to form a solid layer at the sample's surface.

This process, capable of uniformly depositing coatings on fibres, was implemented in various research labs to create metal-coated fibres by depositing metallic alloys (Subramanian *et al.*, 1998; Suzuki and Umehara, 1999) as well as metals, such as copper (Wei *et al.*, 2008a, Bula *et al.*, 2006) and silver (Scholz *et al.*, 2005, Hegemann *et al.*, 2009) on a fibre's surface. It is a technique that was also used to coat ceramic fibres with a metal layer, to ensure good shear strength in ceramic matrix composites (Miller *et al.*, 2001).

Chemical vapour deposition (CVD)

Chemical vapour deposition of films and coatings involve the chemical reactions of gaseous reactants on or near the vicinity of a heated substrate surface. This atomistic deposition method can provide pure materials with structural control at atomic scales (Choy, 2003).

CVD is a commonly-used method to coat textile structures with layers of conductive polymers (Malinauskas, 2001). Fibrous materials, prepared from chemically-modified polyacrylonitrile (PAN), which possesses ion-exchange properties, were charged by sorption with iron chloride (FeCl_3), provided from an aqueous or etheric solution. Then they were treated with pyrrole vapour in vacuum yielding PPy-coated composite material (Cvetkovska *et al.*, 1996).

Cotton yarns were coated with FeCl_3 and exposed to pyrrole vapour, resulting in a coating with a layer of PPy (Tan and Ge, 1996). Similarly, cotton yarns were saturated with ammonium persulphate, and then exposed to aniline vapour, resulting in polymerization on the cotton surface (Tan and Ge, 1998).

Conductive aramid and PPy composite fibres (Cho and Jung, 1997), as well as wool and PPy composite yarns (Kaynak *et al.*, 2007), were obtained by vapour-phase polymerization of pyrrole using FeCl_3 as an oxidant. Furthermore, PPy-poly(p-phenylene terephthalamide) composite fibres have been prepared by continuous vapour phase polymerization using FeCl_3 as an oxidant (Xu *et al.*, 1995). The technique was also applied to deposit thin silicon films onto PI substrates, which were subsequently integrated into a textile to shape a piezo-resistive sensor array (Alpuim *et al.*, 2009).

Lately, researchers have reported the idea of a PPy coating technique for fabrics using a screen-printing method, followed by vapour phase polymerization (Tsang *et al.*, 2007). An emulsion containing FeCl_3 was screen-printed onto the fabric, which was then transferred to a desiccator containing pyrrole for the deposition. After the deposition process, a layer of PPy had formed on the fabric surface.

Solution polymerization of conductive polymers

Conductive polymers, such as PPy, PANi or polythiophene, can also be applied onto textile surfaces through a solution polymerization. Here, their monomers are present in a polymerization solution. The solution also contains an oxidizing agent to start the polymerization of the monomers (Malinauskas, 2001).

In combination with textiles, mostly PPy and PANi are the polymers of choice. Different textile materials have been used to produce PPy-coated textiles obtained by chemical reaction, such as polyester (Kuhn *et al.*, 1995, Sparavigna *et al.*, 2008), polyamide (Wu *et al.*, 2005; Ferrero *et al.*, 2006), cotton (Bhat *et al.*, 2006) and wool (Kaynak *et al.*, 2002). Different methods are followed in chemical polymerization. While often a two-step polymerization is the method of choice (Lee and Hong, 2000), *in situ* polymerization (Reynolds *et al.*, 1998; Lee and Hong, 2000) and emulsion polymerization (Yanumet *et al.*, 2004) are also applied.

PANi has been applied as a coating on polyester and polyamide fabrics via *in situ* polymerization (Oh *et al.*, 1999; Kim *et al.*, 2004). Moreover, two-step polymerization of aniline on fabrics is also commonly used (Oh *et al.*, 2001). The chemical coating with conducting polymers (Scholz *et al.*, 2005; Shahidi *et al.*, 2007), or the reinforcement of polymeric materials with conductive compounds via spinning (Kumar *et al.*, 2002), are possible techniques.

Spin coating, drop casting and dipcoating

Spin coating (Park *et al.*, 2007; Kim Y H, 2007; Kim *et al.*, 2009), solution-drop casting (Reese, 2004, Park *et al.*, 2007, 2009) and dip coating (Park *et al.*, 2007) are popular ways of direct solution deposition. The basic working principle for all three is the same. By dropping or casting solutions to a certain rate, thin films can be obtained on a substrate when the solvent evaporates. In spin coating, a solution is deposited on a flat substrate and spun at a determined rate, usually in the order of magnitude of 10^3 rpm (Park *et al.*, 2007). For drop casting, the solution is deposited as a droplet on the substrate and the solvent slowly evaporates. Dip coating is a process in which the substrate is immersed in a liquid and lifted out of the solution at a preset speed controlled by a continuous motor. A part of the solution will remain on the substrate, which will form the coated film with a certain thickness after the solvent has evaporated.

These three techniques are frequently used to apply semiconductive layers onto different substrates, among them textiles. Dip coating, for instance, was applied to deposit TIPS-pentacene onto polyamide filaments (Van Genabet *et al.*, 2011).

Screen printing

Screen printing is a traditional way of printing that is applied in both the textile as well as electronic industry, as it is a low-cost and simple process. In this printing technique, the image to be printed is photographically transferred to a very fine fabric screen; the non-printing areas are coated with an impermeable substance and the fabric serves as a stencil. Ink is forced through the unblocked mesh by moving a squeegee across it. Hence, the ink is transferred to the underlying substrate.

Different research groups applied screen printing to cover a fabric with a conductive layer. Usually the applied inks contained silver particles and aluminium powder (Yip *et al.*, 2009a; Kazani *et al.*, 2012).

Ink-jet printing

Being developed in the early 1950s, ink-jet printing is a young technology compared to screen printing. In general, we can distinguish between two different ink-jet printing principles: continuous and drop-on-demand. In continuous ink-jet

printing, the charged drops are allowed to fly directly onto the media, while the uncharged drops are deflected into a gutter for recirculation. Depending on the mechanism used in the drop formation process, the drop-on-demand technology can be categorized into four major methods: thermal, piezoelectric, electrostatic and acoustic ink-jet.

Two distinct ways are followed to print conductive patterns onto textile substrates. Either conductive ink-jet inks contain a dispersion of metallic nanoparticles in an aqueous or organic vehicle. A major challenge is to formulate suitable inks. The inks must contain the appropriate precursors and a carrier vehicle. In addition, they may contain various binders, dispersants and adhesion promoters, depending on the nature of the precursor and the type of fabric.

Another approach is the two-step printing of a water-soluble metal salt and a reducing agent on the textile forming the metal *in situ* (Li *et al.*, 2009).

2.9 Future trends

From a textile point of view, the overall aim for smart textiles is to convert all related components, such as sensors, actuators, transmission lines, etc., into 100% textile materials. To achieve this aim, we have to face a large challenge from a technological point of view, as concepts, materials and treatments must be made appropriate for use in, on or as textile materials.

Basic components that will be needed for all smart-textile components are electro-conductive yarns and materials. To be fully applicable, research will have to concentrate on the properties' improvement of these materials. Hence, focus will be directed to increase the washability and textile character, as well as conductivity of yarns.

Yet there is another trend visible in that electro-conductive yarns still exhibit rather passive electronic functions and there is a great need to move one step ahead, such as by developing yarns that carry out an electronic function themselves. One possible function may be switching or amplifying, which can be realized by a transistor (Maccioni *et al.*, 2006; Schwarz *et al.*, 2010b; Krucinska *et al.*, 2011). Another possible approach may be to develop photovoltaic fibres, yarns and textiles to collect and store energy from sunlight (Ghosh *et al.*, 2006; Schlettwein *et al.*, 2009; Bedeloglu *et al.*, 2010).

2.10 Sources of further information and advice

Table 2.4 gives an overview of producers that currently offer electro-conductive filaments and yarns on the market.

An interesting link may be the wiki information database on flexible, organic and large area electronics (Association, 2011), which gives an overview on materials and processes that are currently applied in the world of flexible electronics, into which we may cluster electro-conductive yarns.

Table 2.4 Overview of producers of conductive yarns and textiles

Material	Companies Wires/filaments	Companies Yarns
Copper	Elektrisola Feindraht Drahtwerk Waidhaus	Syscom Advanced Materials R.Stat
Silver	Elektrisola Feindraht	Statex Sauquoit Industries TITV Greiz (Elitex) Syscom Advanced Materials Textronics Swiss Shield
Gold		Microcroax Syscom Advanced Materials
Aluminium	Imattec Gutmann	
Nickel	Western Metal Materials	Electro Fiber Technologies Syscom Advanced Materials
Stainless steel	Leoni Nippon Seisen	Bekaert Textiles Schoeller Epitropic Fibres R.Stat Créafibers IMATTEC International TibTech Innovation
Carbon black	SmartFiber	Kuraray Teijin Monofilament Ascend Performance Materials Shakespeare Conductive Fibers Unitika Fibers Barnet
Carbon nanotubes		Kuraray and Mitsui
Polypyrrole		Sterling Fibers Eeonix Corporation

2.11 Notes

- ¹ Inertness means not chemically reactive with other elements and hence forming few or no chemical compounds.
- ² The percolation threshold is the minimal amount of filler that needs to be added to create a conductive path in between the fillers.
- ³ Diamond is not addressed in this chapter as it is an isolator.
- ⁴ An electroless deposition process is truly autocatalytic when the rate of deposition is more or less independent of thickness. That is given when thickness of the deposited metal is linear with respect to deposition time at a given temperature.

2.12 References

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