Zusammenfassung

In dieser Arbeit wird der Einsatz von Kohlenstoffnanoröhren in der Realisierung flexibler Displays untersucht. Die Gitterstruktur der Nanoröhren besteht aus einer monomolekularen Lage aus Kohlenstoffatomen, die in einem Wabengitter angeordnet sind. Sie haben Durchmesser im Bereich von 1 nm bei Längen von 1 µm oder mehr. Aus dieser speziellen Geometrie ergibt sich eine einmalige Kombination aus elektrischen und mechanischen Eigenschaften. So gibt es sowohl metallisch leitende sowie halbleitende Kohlenstoffnanoröhren. Bei der Synthese entsteht in der Regel ein Mix der zu 1/3 aus metallischen und zu 2/3 aus halbleitenden Kohlenstoffnanoröhren besteht. Um diese nanoskopischen Molekühle grossflächig anwenden zu können werden Sie in dieser Arbeit als ungeordnete Netzwerke verwendet.

Zwei Anwendungen werden in Theorie und Experiment untersucht. Die Erzeugung transparenter, leitfähiger Schichten, die als Bildpunktelektroden Verwendung finden, sowie die Herstellung von Dünnschichttransistoren mit einem Nanoröhrennetzwerk als halbleitende Schicht. Hierfür wird das Perkolationsverhalten von metallischen und halbleitenden Nanoröhren anhand von Monte-Carlo Simulationen näher untersucht.

In der praktischen Umsetzung werden zuerst Kohlenstoffnanoröhren in Pulverform mit Hilfe von Tensiden zu einer stabilen Suspension dispergiert. Diese kann anschliessend mit einfachen und kostengünstigen Prozessen grossflächig aufgebracht werden. Für die transparenten Elektroden werden realtiv hohe Netzwerkdichten benötigt, die sich mit einem Aufsprühverfahren erzeugen lassen. Das halbleitende Netzwerk im Kanal von Dünnschichttransistoren benötigt eine feinere Kontrolle der Netzwerkdichte und wird mit einem speziellen Aufschleuderverfahren realisiert. Die Schichten werden im Anschluss per Fotolithographie und zwei möglichen Ätzschritten strukturiert.

Neben der elektrischen und optischen Charakterisierung der erzeugten Schichten werden Produktionsprozesse entwickelt, die mit der bestehenden Displaytechnologie kompatibel sind. Besonderer Wert wird dabei auf Niedertemperaturprozesse von <100 °C gelegt, um eine Produktion auf Glas- sowie flexiblen Kunststoffsubstraten gewährleisten zu können.

Für die Anwendung als transparente, leitfähige Schichten wurden komplette Displays mit Nanoröhrenelektroden hergestellt. Einfachere, segmentierte Flüssigkristallanzeigen wurden auf Glas und flexiblen Kunststoffsubstraten hergestellt. Eine auf Glas realisierte vollfarbige Aktivmatrix Flüssigkristallanzeige mit herkömmlichen Dünnschichttransistoren aus amorphem Silizium und einer Auflösung von 320xRGBx240 Bildpunkten und 4 Zoll Bilddiagonale demonstriert die Anwendbarkeit solcher Schichten und die Kompatibilität mit standardisierten Industrieprozessen. Ausgehend vom Substrat konnten die Anzeigen komplett im Rahmen dieser Arbeit hergestellt werden. Eine organische lichtemittierende Diode (OLED) mit einer Kohlenstoffnanoröhren-Anode konnte ebenfalls realisiert werden.

Es wird gezeigt wie es möglich ist, trotz des Anteils an metallischen Nanoröhren halbleitende Kanäle in Dünnschichttransistoren zu erzeugen. Mit dem stetigen Fortschritt von Aufbereitungsverfahren sind nun auch Nanoröhren mit nahezu ausschliesslich halbleitendem Anteil verfügbar. Dies führt zu einer Verbesserung der Transistorleistung. Es wird ausserdem beschrieben wie durch eine Linearbewegung der Flüssigkeitszuführung während des Schleuderprozesses die Homogenität der abgeschiedenen Schicht und somit der Transistoreigenschaften verbessert werden konnte. Der Einfluss der Netzwerktopografie auf das Transistorverhalten wird näher analysiert.

Abstract

This work describes the use of carbon nanotubes in the realization of flexible displays. Such nanotubes are hollow fibers with diameters in the range of 1 nm and lengths of 1 μ m or more. They are built of a monoatomic lattice of carbon atoms, organized in a honeycomb lattice. This special configuration results in a unique combination of electrical, optical and mechanical properties. They can, for example, behave either like a metal or like a semiconductor with only slight changes in the orientation of the honeycomb lattice in reference to the nanotube circumference. As-synthesized nanotube powders typically contain a mix of 1/3 metallic and 2/3 semiconducting nanotubes. For using these nanoscopic molecules on large surfaces, they are implemented as a randomly oriented network.

Two distinct applications of carbon nanotubes in display technology are discussed in theory and experiment. The realization of pixel electrodes in the form of transparent conductive films as well as thin-film transistors that use carbon nanotube networks as the semiconducting channel. Monte-Carlo simulations are used to examine more closely the percolation probabilities of metallic and semiconducting nanotubes.

The description of the experimental part of this work starts with the methods to create stable surfactant suspensions from carbon nanotubes powders. The presentation of simple and cost-effective deposition processes for the creation of random networks from the liquid phase is followed by patterning procedures of the created films. Besides results from electrical and optical characterization, the realization of production processes, compatible with standard display technology is presented. High importance is put on a low temperature process chain for staying compatible with glass and flexible plastic substrates.

The realization of working displays is presented as proof of suitability of transparent conductive films made of carbon nanotubes. Simple segmented liquid crystal displays were realized on glass and flexible plastic substrates. The realization of a full-color active-matrix liquid crystal display with a resolution of 320xRGBx240 and 4 inch diagonal based on amorphous silicon thin-film transistors serves as proof for the compatibility of this new material with standard industry processes. All displays could be produced in the scope of this research project, starting from the bare substrate. As a further result, an organic light emitting diode (OLED) with a carbon nanotube network anode is also presented.

Functional thin-film transistors could be realized despite the metallic content in the nanotube network. Further improvements were gained by the use of nowadays available highly semiconducting nanotube feedstock and an optimized deposition process. The dependence of the TFT performance on the network density for both, mixed and highly semiconducting nanotubes, is discussed at the end of the document.

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1. Introduction

The realization of flexible displays is discussed and actively pursued since many years. The main arguments are a more versatile form factor permitting new products, big foldable or rollable screens in otherwise small mobile devices, ruggedness and general technology progress. The step from the formerly glass-based flat panel display technology to real flexible devices turned however out to be quite difficult. Two significant hurdles are for example the mostly brittle materials like oxides or nitrides and process temperatures that are not compatible with flexible and transparent plastic substrates. While the existing technology can be optimized to some degree to approach the targeted goal with established materials and processes, some unbreachable limits are to be expected. New materials are therefore investigated that can fulfill the mechanical demands, exhibit a high functional performance and can be processed at low temperatures. In this thesis, carbon nanotubes in the form of randomly oriented networks are investigated and applied as transparent conductive film for pixel electrodes and as semiconducting film in thin-film transistors. Carbon nanotubes are thin, hollow fibers, formed of a monolayer honeycomb carbon lattice. This unique structure leads to some remarkable properties.

The history of carbon nanotubes (CNT) is still quite young. The discovery of the C₆₀ bucky balls by Kroto, Curl and Smalley in 1985, that was later awarded with a Nobel price in chemistry, created a lot of interest in carbon nanomaterials [74]. The synthesis of this new species was however not yet well controlled. It took until 1990 that Krätschmer and Huffman published the synthesis of C₆₀ molecules with a relatively simple arc-discharge reactor that uses graphite electrodes [75]. In 1991 Sumio Iijima first reported the discovery of so-called multi-walled carbon nanotubes (MWNT) that he synthesized with a similar reactor as the one used by Krätschmer [57]. The nanotubes were discovered in the carbon soot with a high resolution transmission electron microscope. Finally in 1993 two research groups were able to simultaneously present the synthesis and discovery of the more fundamental single-walled carbon nanotubes (SWNT); Iijima with his colleague Ichihashi [58] as well Bethune et.al. [10]. It was the addition of metal nanoparticles, acting as catalyst during the arc-discharge process, that led to synthesis of single-walled carbon nanotubes with narrow diameter spread in the range of 1 nm to 2 nm. Mechanical and electrical properties, that were partly already postulated by theoretical calculations before discovery of carbon nanotubes, could now be confirmed by experiment. The prediction that 1/3 of all possible SWNT geometries will behave like a 1-dimensional metal and 2/3 like a 1-dimensional semiconductor for example was already postulated in 1992 [110]. Sumio lijima had paved the way to intense research of a new and fascinating form of carbon. CNTs already existed however long before their discovery. They could for example be discovered in an old Damascus saber from the seventeenth century [103].

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It is the combination of many remarkable intrinsic properties of SWNTs that caused an interest for a huge diversity of applications, reaching from compound materials over H_2 storage, AFM tips, transistors and sensors to quantum computers, to name only a few. Some of the properties that make SWNTs interesting for the applications discussed in this work are room temperature field-effect mobilities exceeding $100000 \text{ cm}^2/(\text{Vs})$ [28], the capability to carry currents with a density up to 10^9 A/cm^2 combined with a tensile strength and a Young's modulus exceeding any known material plus, at the same time high mechanical flexibility [1].

Extraordinary intrinsic properties of nanomaterials are however only one side of the medal. The crux lies in exploiting these characteristics in macroscopic systems. The highly flexible tubes of only 1 nm diameter and lengths going up to micrometers or more cannot be handled individually by some kind of nano-tweezers. Locating individual tubes on a wafer by means of atomic force microscopy and defining metal contacts with ion beam lithography is a viable way for fundamental research. Production processes need however faster and better controlled manners to place and contact the nanotubes. Fundamental research further revealed, that tunneling barriers to the outside world largely limit the extrinsic performance.

In this thesis carbon nanotubes are used in the form of randomly oriented networks. These can be deposited on large surfaces with simple and cost-effective deposition processes from liquid phase. The two application fields of interest are transparent conductive films, as well as the realization of thin-film transistors with SWNT networks as semiconducting layer. At the beginning of this research project, initial results for both applications were already presented by academic research. The main focus of this work is to elaborate to which degree the CNT networks can be applied to flexible display technology and to develop production processes that can be integrated into standard liquid crystal display (LCD) technology. CNT-based transparent conductive films are integrated into rigid glass and flexible plastic based segmented liquid crystal displays as well as glass based active-matrix displays. CNT thin-film transistors realized on glass and plastic substrates are evaluated on a single device basis, which is a precursor for being able to realize active-matrices or logic circuits later on.

This thesis is structured in the following way. First, the necessary theory to help understanding SWNT physics and the demands on the application side is explained. The formation of nanotube networks is then investigated by conducting Monte-Carlo simulations. In the experimental part, the preparation of dispersions from nanotube feedstock, the tested deposition methods as well as patterning of the realized layers is discussed. Results and fabricated demonstrators are then presented in two final chapters. The first chapter discusses the realization of transparent conductive films, while results of thin-film transistor fabrication and characterization are given in the second chapter. A summary concludes the main aspects.

2. Theory

2.1. Carbon Nanotubes

This thesis investigates the use of Carbon Nanotubes (CNT) in display applications. Understanding their structure and electronic properties is important for being able to use them in macroscopic systems. In this chapter the structure and electronic properties of CNTs are described. In both cases a single atomic layer of graphite, the so-called graphene is first discussed since carbon nanotubes are basically rolled up graphene ribbons. This holds up to the point that the electronic properties can be derived from the graphene band structure.

2.1.1. Structure of graphene and single-walled carbon nanotubes

A carbon atom has 6 electrons which according to the nuclear shell model have a configuration as shown in fig. 2.1. For chemical bonding, only the upper most energy levels 2s and 2p play a role. In graphene and carbon nanotubes the carbon atoms are sp^2 hybridized. This means that the 2s orbital and the $2p_x$ and $2p_y$ orbitals form three similar sp^2 orbitals that are all occupied by one electron. These sp^2 orbitals lie in one plane with 120° between each coil. The $2p_z$ orbital keeps the 4th electron and forms a double-coil perpendicular to the sp^2 plane (see fig. 2.2a).



Figure 2.1.: Electron configuration of carbon according to the nuclear shell model.

When the sp² orbitals of two carbon atoms overlap they form a strong σ -bond. The p_z orbitals overlap as well and form a so-called π -bond with two clouds of electron probability above and below the σ -bond. The result is a so-called double bond. When several carbon atoms are connected in this way a hexagonal or honeycomb structure is formed. A single hexagon consisting of 6 carbon atoms and the remaining open sp² orbitals saturated with hydrogen atoms is called benzene (see fig. 2.3a). In this hexagon the π -bonds are not localized between distinct carbon atom pairs but rather form a delocalized π electron system in which the



Figure 2.2.: Orbital configuration of and bonding between sp² hybridized carbon atoms.

electrons can move freely without barriers. This is indicated by the clouds above and below the molecule in fig. 2.3a.



Figure 2.3.: Hexagonal carbon molecules

A sheet of graphene results if a large number of sp^2 hybridized carbon atoms are connected. This is a monolayer crystal of hexagonally bonded carbon (see fig. 2.3b). Also in graphene the delocalized π electron system forms, giving good electrical conduction along the sheet. Graphite consists of a large number of stacked graphene sheets. Interaction between the sheets is rather weak, leading to e.g. a high anisotropy of electrical conductivity in graphite.

A single-walled carbon nanotube (SWNT) can be imagined as a rolled up finite sheet of graphene. Due to the high symmetrie of the hexagonal lattice this can be done in various manners. An unambiguous nomenclature was defined by Dresselhaus et.al. [26] (see fig. 2.4).

First the unit vectors of the honeycomb lattice $\vec{a_1}$ and $\vec{a_2}$ are defined which form an angle of 60°. Their length is

$$|\vec{a_1}| = |\vec{a_2}| = a_0 = \sqrt{3}a_{C-C} = 2.46\,\text{\AA}$$
(2.1)



Figure 2.4.: Definition of carbon nanotube nomenclature in the hexagonal graphene lattice; Example shows graphene lattice with chirality vector \vec{C}_h , chiral angle θ and translation vector \vec{T} of a (4,2) chiral SWNT.

where the distance between two carbon atoms is

$$a_{C-C} = 1.42 \,\text{\AA}$$
 (2.2)

The chirality vector

$$\vec{C}_{h} = n\vec{a}_{1} + m\vec{a}_{2} \equiv (n,m); \quad \{n,m\} \in \mathbb{N}; \quad 0 \le |m| \le n$$
(2.3)

describes the circumference of the nanotube. It connects two crystallographic identical positions that are superimposed when the sheet is theoretically rolled up to form the tube. The 2-tuple (n,m) non-ambiguously describes the single-walled carbon nanotube and all geometric parameters can be calculated thereof [27, p.7]. Also physical properties like e.g. the electronic behavior can be derived as will be shown in the next section. The length of the chiral vector and therefore the circumference of the nanotube can by calculated as:

$$C_h = |\vec{C}_h| = \sqrt{\vec{C}_h \cdot \vec{C}_h} = a_0 \sqrt{n^2 + nm + m^2}.$$
(2.4)

The angle between \vec{C}_h and \vec{a}_1 is called the chiral angle.

$$\theta = \arctan \frac{\sqrt{3}m}{2n+m} \tag{2.5}$$

Due to the high symmetry it holds $0^{\circ} \le |\theta| \le 30^{\circ}$. There are three distinct classes of SWNTs depending on the value of θ - zigzag, armchair and chiral nanotubes. A list of the specifications for these three classes is given in table 2.1 while representative images are shown in fig. 2.5. The upper part of the displayed tubes indicate where the names are coming from. They describe the form of the lattice along the chiral vector.

Name	θ	(n , m)
zigzag	0°	(n,0)
armchair	30°	(n,n)
chiral	$0^\circ < \theta < 30^\circ$	$n \neq m; n,m \neq 0$

Table 2.1.: SWNT categories and their specific properties.



Figure 2.5.: Single walled carbon nanotubes with $d_t = 1.49$ nm, left: zigzag (19,0), center: armchair (11,11), right: chiral (16,5), red molecules indicate origin of type name.

The diameter of the tube is easily calculated from the length of the chiral vector.

$$d_t = \frac{C_h}{\pi} = \frac{a_0}{\pi} \sqrt{n^2 + nm + m^2}$$
(2.6)

Another characteristic parameter is the translation vector \vec{T} that stands perpendicular on \vec{C}_h and therefore is parallel to the cylinder axis. Both vectors start in the same origin point *O*. The length of \vec{T} is determined by the closest intersection with a crystallographic identical atom in the lattice. It can also be described by *n* and *m* as [138, p.80]

$$\vec{T} = \left(\frac{2m+n}{g_d}, -\frac{2n+m}{g_d}\right) \tag{2.7}$$

where g_d is the greatest common divider of 2m + n and 2n + m or

$$g_d = GCD(2m+n, 2n+m).$$
 (2.8)

It's length is derived thereof as

$$|\vec{T}| = \frac{\sqrt{3\pi}d_t}{g_d}.$$
(2.9)

 \vec{C}_h and \vec{T} span up the unit cell of the SWNT which is in contrast to the rectangular form indicated in fig. 2.4 in reality a cylinder with diameter d_t and length T.