1 Introduction

The development of innovative materials is an essential part of modern research. In the recent years, researchers have been looking intensively at the use of nanomaterials due to their outstanding chemical and physical properties compared to bulk material. Today, nanostructured materials are already used, e.g., in lithium ion batteries to improve the energy storage capacity compared to batteries consisting of conventional material [1] . The influence of nanostructured materials in our lives shows a publication of ScienceDaily [2] where a rate of up to four new applications each week based on nanotechnology is announced.

Nanoparticles are nanomaterials with a size below 100 nm in all three dimensions. In this regime, many physical properties are size-dependent such as, e.g., the optical properties of silicon nanoparticles due to the quantum confinement. Also, the chemical reactivity increases with decreasing size due to the larger specific surface area and the particles are more affected by forces on the surface (van-der-Waals forces). The main focus of this work lies on the electrical properties of two nanomaterials systems, zinc oxide (ZnO) and silicon (Si) nanoparticles, to investigate their possible application in electronic devices.

Transparent conductive oxides (TCO) are optically transparent and electrically conductive. They are used as light transmitting electrodes in thin-film solar cells or flat-panel displays. Indium tin oxide (ITO) and ZnO are the most frequently used TCO materials for electronic applications but ITO is expensive due to the cost of the rarely available indium [3, 4]. In order to obtain cheaper devices, indium must be replaced by more abundant and therefore less expensive material with comparable optical and electrical properties [5–7]. For replacing ITO, aluminum-doped ZnO is the most promising alternative [8–11]. ZnO is a non-toxic material with a direct band gap of 3.37 eV [12] and the missing absorbance of visible light makes this material one of the best TCOs so far [9]. By using ZnO nanoparticles, it is possible to tune the optical and electrical properties in a wide range.

The optoelectronic properties of this material were investigated for progresses in light emitting diodes [13, 14], liquid crystal displays [15] or solar cells [4, 16, 17]. Also, the benefits of the large surface-to-volume ratio of the ZnO nanoparticles, which makes them a promising material for gas sensors [18, 19] and interesting for catalysis applications [14], were extensively studied. However, the electrical properties have not yet been investigated in detail. Therefore, the first part of this work aims at the characterization of the electrical transport mechanisms of ZnO nanoparticle-networks (powders). As application example, electronic devices made of ZnO nanoparticles are produced via ink-jet printing and tested. The raw ZnO nanoparticles are synthesized in the gas phase which provides control of the materials properties such as size and structural properties. Gas-phase synthesis also allows to synthesize large amounts of materials which is important to study subsequent processing steps.

The electronic properties of ZnO nanoparticles are investigated regarding doping, variable atmosphere, temperature and the influence of moisture. The resistivity can be changed by using doping by aluminum and the response of the material to different gases depends on the Al-doping level. The influence of moisture on the electrical behavior of ZnO is well known, but the influence of moisture on structural changes to the particulate material and the subsequent effect on the electrical behavior has not been investigated so far. Because this is crucial for practical applications, the respective effects have been studied in this thesis. Printable electronics made from nanoparticles enable printing of films on large areas at low cost, but only a few reports can be found for ZnO nanoparticles [20–22]

The second materials system used in this work are silicon nanoparticles. Silicon is one of the most abundant materials in the world and has the high advantage of biocompatibility and that it is already well established in the microelectronics technology [23]. One of the research fields with silicon nanoparticles are solar cells [24, 25], silicon-based lasers [26] and light-emitting diodes [27]. The electrical investigation for Si nanoparticles is rare due to the fact of the bad conductivity of the Si nanoparticles because of their stable oxide shell. It is known that the conductivity for etched Si nanoparticles is much higher but the particles have an affinity to oxidation and a stable surface functionalization to conserve the optical and electrical properties of etched Si nanoparticles has not been found yet. Because of this, the third aim of this work is to characterize the electrical properties of silicon nanoparticles with different surface morphologies. As-prepared, etched and functionalized Si nanoparticles are investigated with a focus on the influence of the oxide shell and the lengths of organic molecules and the temporal stability of the different surface configurations. In this thesis, the Si particles are functionalized with different long-chain alkenes after the oxide shell has been removed by etching. The stability in air and the long-term stability of the functionalized Si nanoparticles are investigated and the activation energies for the transport processes of the charge carriers are calculated and compared with the thickness of the surface coverage (oxide shell or organic alkenes) and the hopping distances of the charge carriers.

2 State of the art

Semiconducting ZnO nanoparticles could be an alternative for ITO due to the stability in ambient air. ZnO is already used for a wide range of applications such as an additive in rubber [28], varistors [29], piezoelectric transducers [17], pigments in paint and suntan lotion [28, 30]. It is known, that the conductivity of aluminum doped ZnO (AZO) nanoparticles increases with higher Al content in ambient atmopshere and that the conductivity in hydrogen is even higher [31] but a detailed investigation of powders or thin films in different gases and temperature ranges is missing. In this work, the influence of the gaseous environment and the temperature-dependent conductivity of AZO nanoparticles synthesized by chemical vapor synthesis (CVS) in general are investigated. The stability of ZnO nanoparticles in ambient conditions were investigated by Ali et. al [32], having a view on the growth of ZnO nanoparticles with time. They found a significant growth of the ZnO nanoparticles in ambient conditions depending on the moisture concentration of the environment. The changing electrical properties which depend on the moisture concentration and the growth of the ZnO nanoparticles in moisture are therefore also investigated in the present work. This is done by using ZnO nanoparticles synthesized by the same route and having a similar size of about 12 nm. Another important part of this work is the production of a hydrogen sensitive ZnO thin film produced by ink-jet printing. The ink-jet printing method is already established for the production of diodes and light emitters [33, 34]. The method has some advantages compared to the preparation of thin films produced by magnetron sputtering [35] or spray pyrolysis [36]. The ink-jet printed ZnO films do not need any post-annealing and the ink-jet printing process does not require any high vacuum conditions. Also it is a very precise, selective deposition technique for particle dispersions. The selective deposition makes it possible to get well-defined patterns and structures of the ZnO film out of a dispersion and the waste of ZnO dispersion is strongly decreased compared for example with the doctor-blade method [37]. Up to now, there are only very few publications [38] about ZnO based gassensors. Shen et al. used the ink-jet printing method to print ZnO films. The influence of the amount of different layers on the sensitivty of acetone was investigated. They found that the resistivity decreases with more ZnO layers, but the best sensitivity was found for four layers of ZnO. In this thesis it will be shown that it is possible to produce gassensors based on ZnO nanoparticles prepared by ink-jet printing which do not need any post annealing.

The second material used in this work are silicon nanoparticles synthesized in a microwave plasma reactor. The interest in silicon is resonable because it is the second most abundant element on earth and it is the best established material for the use in electronics devices [39]. It is highly available and also non-toxic. Silicon nanoparticles could increase the effectiveness of the applications in solar cells, silicon based lasers or diodes [24, 26, 27, 40, 41]. They have a big surface area and the defect concentration is high [42, 43]. The oxide shell around the silicon core decreases the electrical conductivity and the optical properties of the silicon nanoparticles [44–46] are limited. By removing this oxide shell with hydrofluoric acid the optical and electrical properties can be changed [47–50]. The problem of the hydrosilylation is the reoxidation of the surface and a method to prevent the reoxidation has to be found [51]. The functionalization with organic molecules was done by several groups before [52–56]. The silicon carbon bonds (Si-C) have a strong bonding and a low polarity [48, 57]. The optical properties of these functionalized silicon nanoparticles were already investigated deeply but the electrical properties are quite unknown. The functionalization with dodecene and octene up to 300°C are investigated by Nelles et al. [58]. Their silicon films have a thermally activated conductivity process between 7°C and 156°C which depends on the thickness and polarity of the molecules used for the functionalization. The conductivities of functionalized silicon nanoparticles are decreased to the as-prepared and etched particles which is completely different to our results.

The objective of this work is to find out the electrical properties for ZnO and silicon nanoparticles in different conditions and the properties of ink-jet printed ZnO. The particles are all synthesized from the gas-phase. The ZnO nanoparticles are synthesized via chemical vapor synthesis (CVS) in a hotwall reactor while the silicon nanoparticles are synthesized also with CVS but in a microwave plasma reactor. The ZnO nanoparticles are prepared after the synthesis by producing a pellet consisting of compacted powder. The ZnO pellets are investigated by considering the aluminum doping, influence of changing humidity concentrations and the behavior of the electrical properties in different gaseous environments. From another part of the ZnO nanoparticles a stable dispersion is produced to perfom ink-jet printing of a thin film on an interdigital structure. The ink-jet printed film is tested with respect to its sensing properties in hydrogen atmosphere. To support the findings, additional measurements like x-ray diffraction (XRD) are performed. The main aim of the investigation of the silicon nanoparticles is the characterization of their electronic properties dependent on the type of preparation. The silicon nanoparticles are etched and functionalized with alkenes of different lenghts. To explain the findings of the electrical measurements, Fourier transformed spectroscopy (FTIR) and some other additional measurements (XRD, SEM) are also performed. The most important theory needed to understand the mechanisms are explained in the theory, chapter 3. The electrical properties of the ZnO are explained in chapter 4. The results for the ink-jet printed ZnO can be found in chapter 5 and for the silicon nanoparticles in chapter 6.