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Technical requirements, manufacturing processes and cost efficiency for transparent electrodes based on silver nanowires and carbon nanotubes

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ABSTRACT

We outline the reasons why indium tin oxide is still not replaced in transparent electrodes although enormous research has been carried out in the past decade. We evaluate the advantages and drawbacks of possible alternative materials with regard to material performance and cost-efficiency. As a result, we state that graphene is a very promising material but the production costs are very high. Without a technological breakthrough towards an energy- and material-efficient synthesis of graphene, this material will remain unfeasible for the use in industrially scaled production of transparent electrodes. Silver nanowires are easier to process but they exhibit high haze. Within our approach we produce ultra-transparent silver nanowire films and silver nanowire/carbon nanotube hybrid films with low haze. Our manufacturing technique is scalable on conventional smart phone glass and we present a conceptual production cell for the fabrication of ultra-transparent electrodes with optical transmission higher than 97 % and sheet resistance lower than 70 Ω/sq. The optoelectrical performance of these films is superior to most of the recently published silver nanowire films. The theoretical material range for 1 g of AgNWs is 165 m^2.

Keywords: Transparent electrodes, silver nanowires, carbon nanotubes, indium replacement, electrical percolation, display components, liquid film coating, energy-efficient manufacturing

1. INTRODUCTION

Shorter product life cycles of displays and decreasing prizes of solar cells increased the demand for transparent conductive films (transparent electrodes) within the past years. Transparent electrodes are fundamental components in displays and touch panels. Emerging markets like flexible electronics do not only increase the demand for transparent electrodes. Several aspired future devices such as bendable touchscreens require new mechanical functions. Conventional transparent electrodes are made of indium tin oxide (ITO). ITO is a brittle mixed crystal. Its chemical composition is $(In_2O_3)_{0.9}(ZnO_2)_{0.1}$. Therefore ITO is often referred to as tin-doped indium oxide. The existence of a solid material which exhibits both electrical conductivity and optical transparence is somehow contradictory. On the one hand, electrical conductivity demands a delocalized electron gas and on the other hand the electrons absorb photons. The trick of creating a material which is conductive and sufficiently transparent is doping. The presence of tin atoms as n-dopands within an indium oxide lattice structure influences the band gap and allows delocalization of the electrons [1, 2, 3]. The optical transmission of ITO is slightly lower than of indium oxide.

Although ITO exhibits excellent optoelectrical performance there has been developing a research trend for its replacement. There are both economical and technological drawbacks accompanied with the use of ITO in transparent electrodes. Indium is a rare metal (but not a rare earth metal which is a chemical term) and a by-product from zinc and lead mining. The pure element is produced by an electrolytic process. Due to these circumstances the production of indium and hence of ITO is expensive with regard to the material prize. Figure 1 illustrates the development of the indium prize during the past decades. The full thin curve represents the

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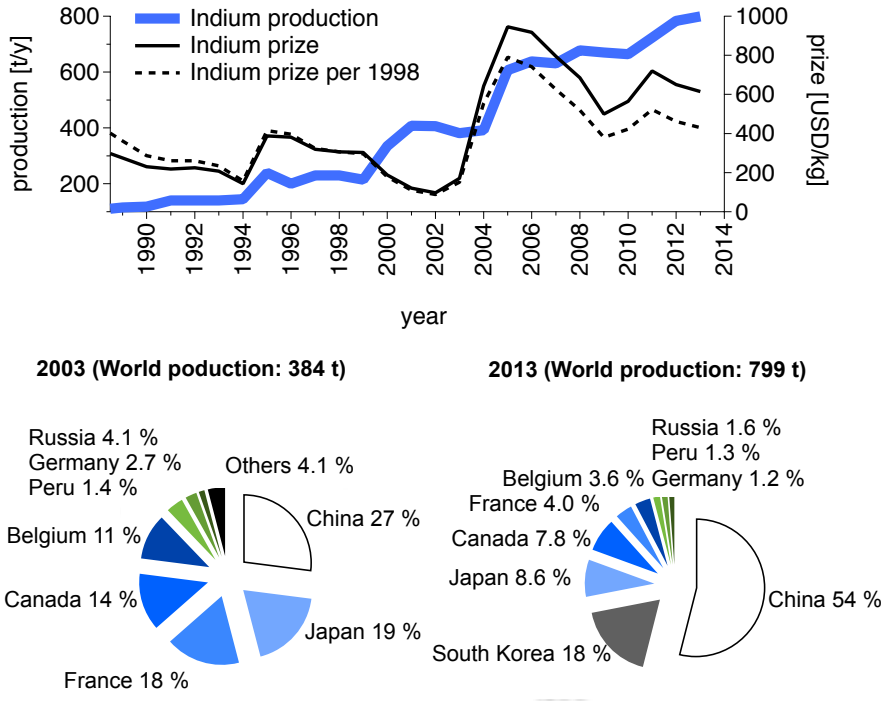

Figure 1. The development of the indium market. Data taken from the U.S. Geological Survey [7].

absolute prize and the dashed thin curve represents the prize normalized to the year 1998. Besides a rise since 2002 there has occurred a tremendous price fluctuation which is an economical problem for manufacturers of display components. Figure 1 also illustrates the world production of indium and it is seen that the overall growth rate is 108 % between 2003 and 2013. Today most of the indium is produced in China whereas ten years ago the market share was only about a quarter. As a country where several large display manufacturers are located, South Korea has developed its production to 18 % of the world production.

Besides the aforementioned economical drawbacks there are several technological disadvantages concerning the use of ITO in transparent electrodes. As the material costs are only 2 % of the total production, the technological drawbacks are a much stronger motivation for the replacement. The most tremendous disadvantages of ITO are its brittleness and the requirement of high-energy processes for the production. Furthermore ITO exhibits undesired yellowish color. The brittleness makes ITO useless for the production of flexible electronics such as bendable displays. Furthermore, roll-to-roll manufacturing on flexible foils is not possible. Moreover ITO cannot be coated on polymer foils directly since the manufacturing process demands high temperatures of several hundred °C. ITO is produced by a sputtering process at 350-1000 °C and low pressure of ≈ 0.1 mbar [4]. Hence, the production rate is slow and the energy costs are high. These two factors are causing the high cost of ITO films. Other ceramic ITO-alternative materials such as fluorine-doped tin oxide (FTO) [5, 6] and aluminum-doped zinc oxide (AZO) [8] are discussed but the use of these materials will not cause cheaper process costs or add further product characteristics such as mechanical flexibility. FTO and AZO are rather used in solar cells than in display and touchscreen devices. For the latter application other materials have shown promising properties the past years. In particular, these materials are graphene, carbon nanotubes (CNTs), metallic nanowires (mainly silver nanowires, AgNWs) and conductive polymers (mainly poly-3,4-ethylenedioxythiophene:polystyrolsulfonate, PEDOT:PSS). This paper presents the chances and bottlenecks of these materials and illustrates why ITO is still the only material for the usage in displays and touch screens, and how the drawbacks of the other materials can be mastered. Besides the properties of the transparent electrodes we put a strong focus on scalable production techniques. The criteria are energy-, material- and time-efficiency. Finally we present a conceptual production cell for AgNW-based transparent electrodes which fulfill industrial requirements.

2. ALTERNATIVE MATERIALS FOR TRANSPARENT ELECTRODES

2.1 Why ITO is still used in displays and touch panels

As mentioned in the previous section, the major motivations for the replacement of ITO are the creation of further functions or the implementation of energy-, time- and material-efficient manufacturing processes. The prize of indium is high but it contributes only 2 % to the overall production costs of ITO-based transparent electrodes [9]. Hence, alternative materials either have to allow further functionalities like bendabilty or cheaper manufacturing processes.

The principle of electrical conductivity is different for the aforementioned ITO-alternatives. Graphene and PEDOT:PSS are laminar films like ITO whereas carbon nanotubes and silver nanowires create jackstraw-like percolating networks based on one-dimensional conductors. It is important to mention that there are two types of percolation, structural and electrical percolation. Structural percolation represents a continuous physical pathway along a macroscopic area. Electrical percolation means that the electrons are able to diffuse along the network continuously. Structural percolation is a requirement for electrical percolation (we exclude tunneling effects) but it does not necessarily cause electrical conduction. The contact resistances of the rods have to be sufficiently low to allow the electrons to pass from one rod to another. As a result of the different principles of function for the electrical conductivity there are different production methods for graphene, CNT, AgNW and PEDOT-PSS films. Let us go step by step through the alternative materials discussed in literature during the past decade.

Graphene is a very promising material for several applications in electronics, lightweight construction and barrier layers. With regard to the application in transparent electrodes, graphene has sparked huge interest since Wu et al. predicted that a sheet resistance of $R_s = 62.4/N\ \Omega/sq$ is possible, where N is the number of graphene layers [10]. The optical transmission is %T = 100 - 2.3N [11]. As of yet, the technologically feasible sheet resistance is higher and the best value for the sheet resistance is reported by Samsung in cooperation with several research institutes ($R_s = 125\ \Omega/sq$, %T = 97.4) [12]. The industrial requirements for transparent electrodes are $R_s < 100\ \Omega/sq$ and %T > 90 [13]. Hence, with more layers of graphene the required sheet resistance can be achieved and the optical transmission is still higher than 90 %. However the manufacturing process of such high-quality graphene is rather inefficient. The production of graphene is usually performed by chemical vapor depostion (CVD) from short hydrocarbons at $\approx 1000\ ^\circ C$ [14]. Moreover, a copper or nickel foil is required as substrate since these metals function as a catalyst within the graphene formation. Consequently, besides that most of transparent substrates do not resist such high temperatures (exceptions are quartz and sapphire glas), the metal foil cannot be replaced for the process. Direct coating of quartz glas is possible but results in sheet resitance which is higher by orders of magnitude. Moreover, lower temperatures of down to 300 °C are possible with plasma-enhanced chemical vapor deposition (PE-CVD) on copper foils. However this approach results in higher sheet resistance than the thermal CVD process. In order the transfer the graphene on a transparent substrate, it is coated with a polymer layer. Afterwards the copper is dissolved in a bath of nitric acid and the graphene-containing carrier polymer is roll-pressed on the final substrate (e.g. a PET foil) and removed by dissolving. The treatment with nitric acid has a further function. It causes p-doping of the graphene which increases the conductivity [12]. It is obvious that the high temperatures, the need of oxidizing acids and the large-scale consumption of copper is not energy- and material-efficient. Moreover, the coating velocity is rather low. Hence, the manufacturing of graphene-based transparent electrodes is not feasible for large-scale production.

Several works report on the liquid-film coating of graphene and CNTs. Thereby the nano carbon material is dispersed as colloids in a liquid, usually water. After the drying of the liquid the graphene flakes or the CNTs create an electrically percolating network. Compared to CVD-graphene the optoelectrical performance of dispersion-based graphene films is significantly lower [15]. Dispersion-based CNT films exhibit better optoelectrical performance than dispersion-based graphene films but underperform compared to CVD-graphene. Most of the CNT-films do not fulfill the industrial requirements of $R_s < 100\ \Omega/sq$ and %T > 90. CNTs are usually dispersed in water with a tenside using a tip sonicator. The tenside is needed in order to avoid bundle formation. These tensides reduce the optoelectrical performance due to insolation. They can be removed by treating the CNT films with nitric acid. Additionally it is estimated that the nitric acid causes p-doping of the CNTs as it was mentioned for graphene previously. Only two publications report on conductivity closely sufficient to the

	ITO	Graphene	CNTs	AgNWs	PEDOT:PSS
CVD	possible	standard	no	no	no
Sputtering	standard	no	no	no	no
Liquid film coating	possible (1)	possible (1)	standard	standard	standard
Prozess temperature	350-1000 °C	300 - 1000 °C	RT - 100 °C	RT - 300 °C	RT
Acid needed	no	yes	yes	no	no
Typical sheet resistance [Ω/sq]	5-100	30-3000	60-300	1-50	60-900
Typical transmission at 550 nm [%]	80-97	80-97	80-91	80-97	75-95
Corrosion stability	+	++	++	- to + (2)	- -
Flexibility	- -	++	++	/ to ++ (2)	++
Haze	/	+	+	- -	/
Adhesion	+	+	+	- - to + (2)	/

(1) The optoelectrical performance is significantly lower than for CVD/Sputtering

(2) Can be improved by encapsulation of the AgNW film into a polymer matrix

Table 1. Comparison of ITO and the alternative materials discussed in the text.

industrial requirements [16, 17]. Both apply the approach of dispersing the CNTs in chlorosulfuric acid without the need of encapsulating substances such as tensides.

Transparent electrodes based on AgNWs exhibit sufficient optoelectrical performance, especially since the synthesis of AgNWs with higher aspect ratio [9, 18]. The films are usually created with liquid-film coatings such as mayer-rod coating, slot-die coating or knife-coating. Furthermore spay-coating has been applied. However we found that spray-coating is not material-efficient due to the high overspray. Moreover, AgNWs sediment quickly which results in inhomogeneities within the dispersion, especially in tight channels of slot dies. Mayer-rods can be clogged by AgNWs and coating of larger surfaces results in inhomogeneities. Though, the processing of silver nanowires is much more feasible than for graphene or carbon nanotubes as there is no demand of high temperatures or oxidizing acids. Nonetheless AgNW networks exhibit several drawbacks too. The stability towards bending is not as good as for graphene or CNTs and AgNWs suffer from corrosion. These disadvantages have been handled by encapsulating the AgNW network into a polymer matrix [19]. This approach also improves the weak adhesion of AgNWs on the substrate. The biggest disadvantage of AgNWs is their hazy appearance which does not meet today's quality standards in display industry. The human eye is able to detect haze higher than H = 2 %. The haze depends on the AgNW diameter and the fractional area coverage which is inverse proportional to %T. Hence, the higher %T, the lower %H. Best reported haze values are still > 2 % at %T = 96 [18].

Conductive polymers used to be a very promising ITO-alternative material. Until 2010 PEDOT:PSS exhibited better optoelectrical performance than graphene and CNTs. By now, nano carbon materials have outperformed PEDOT:PSS. Its instabilty towards several environmental influences such as oxidation, heat and UV-light makes PEDOT:PSS to the weakest ITO-alternatives. Table 1 summarizes the aforementioned properties and manufacturing techniques for ITO and the alternative materials.

2.2 An approach for the production of ITO-free transparent electrodes with cost-efficient processes

It is seen from Table 1 that neither of the alternative materials is able to fulfill all of the industrial requirements. Graphene performs well if it is produced by energy-consuming CVD, followed by a slow and copper-consuming transfer process onto a flexible substrate. PEDOT:PSS is cheap and the processes for the production of the

PEDOT:PSS films are cost-efficient. However it has insufficient optoelectrical performance and is unstable towards environmental influences. The advantages and drawbacks of graphene and PEDOT:PSS are somehow reverse. Graphene exhibits sufficient material properties whereas PEDOT:PSS allows cost-efficient processing. However, both of these materials are hard to justify for the replacement of ITO.

There is another inverse trend between two ITO-alternatives. Films made of CNTs are very stable towards corrosion without a polymer matrix and exhibit haze which is low enough. But suffer from insufficient optoelectrical performance. The optoelectrical performance of AgNW networks can compete with the one of ITO but the haze of the AgNW films is a serious limitation for the use in displays. Despite of these disadvantages, CNTs and AgNWs appear to be the most promising materials for the industrial replacement of ITO, as long as well-performing graphene can be only produced with inefficient processes. This leads to two approaches towards industrial use. The first approach is further improvement of the optoelectrical performance of CNT films. The second approach is reducing the haze of AgNW films. As there has been a lot of work published about CNT films for transparent electrodes and the best optoelectrical performance was reported in 2011, it seems that CNT films have reached their peak with regard to the optimization of conductivity [20]. Furthermore there is still the need of acids for best performance. On the other side, the research on AgNW films is more dynamic and there has been developing a continuous and ongoing improvement of the optoelectrical performance, although AgNW networks are already performing very well compared to the other ITO-alternatives. The most important reason for this development is the availability of AgNWs with high aspect ratio. It is known that the use of longer AgNWs results in better conductivity since the electrons can diffuse along an AgNW without hitting on a high-resistance junction point for a longer distance in case of long AgNWs. Consequently we decide for the second approach and use AgNWs as a material for our transparent electrodes. In order to overcome the problem with haze we produce ultra-transparent AgNW films, where haze should not be detectable for the human eye. The term ultra-transparent is not clearly defined and means the optical transmission is significantly higher than 90 %. Here we refer to films with %T $>$ 97 as ultra-transparent. In case of insufficient optoelectrical performance we add CNTs to the AgNW network. The co-percolation of CNTs within an AgNW network increases the conductivity significantly as we have reported previously [33]. As a manufacturing technique we apply a simple dip-coating method. In any case, the AgNWs sediment but it is easier to homogenize a dispersion where a substrate is dip-coated than doing so for a reservoir which is linked to a meyer-rod or a slot-die device. Moreover, there is no problem with clogging.

3. RESULTS AND DISCUSSION

3.1 Optoelectrical performance of the produced transparent electrodes

For a comprehensive measurement series we used microscopy glass slides (75x25 cm) as substrates. AgNWs are dispersed in ethanol. The withdrawal speed of the AgNW dispersion was 300 mm/min. The concentration of the AgNWs was adjusted in a way that one dip was sufficient. The optical transmission was adjusted by changing the AgNW concentration. We used two AgNWs with two different dimensions (length L, diameter d): (11 μm, 31 nm, Blue Nano) and (19 μm, 25 nm, Nanopyxis). After the coating, the films were annealed in an oven (Gestigkeit PR 5-3T) in order to decrease the overall sheet resistance by reducing the junction resistances. The thicker AgNWs were annealed at 150 °C and the thinner at 120 °C. These values are the input values to the control unit of the oven. We prepared AgNW/CNT films by applying a second dip-coating step with 20 mm/min with an aqueous CNT dispersion (CoMoCat CG200). The dispersion was prepared as follows: 0.1 w% of the CNT raw material was added to an aq. 0.2 w% sodium docedylbenzenesolfunate (SDBS) dispersion and sonicated with a tip sonicator (pulsation: 0.5 s on, 0.5 s off) for 20 min. Afterwards the dispersion was centrifuged at 9 krpm for 20 h and filtered with a 5 μm and then with a 1.2 μm pore size syringe filter. In Figure 2a the optical transmission is plotted versus the sheet resistance. It is seen that the AgNW(11 μm, 31 nm)/CNT hybrid films exhibit better optoelectrical performance than the pure AgNWs(11 μm, 31 nm) films, as we have reported previously [33]. Figure 2b shows a scanning force micrograph of an AgNW/CNT hybrid film. The CNTs create additional pathways for the electrons and close to the percolation threshold the electrical conductivity can be increased by a factor of up to 70. The dashed rectangle in Figure 2a illustrates the commonly stated quality window of R_s $<$100 Ω/sq and %T $>$ 90 and the shaded rectangle is the quality window under consideration of haze for AgNW films. For the AgNWs used in this work the optical transmission has to be %T $>$

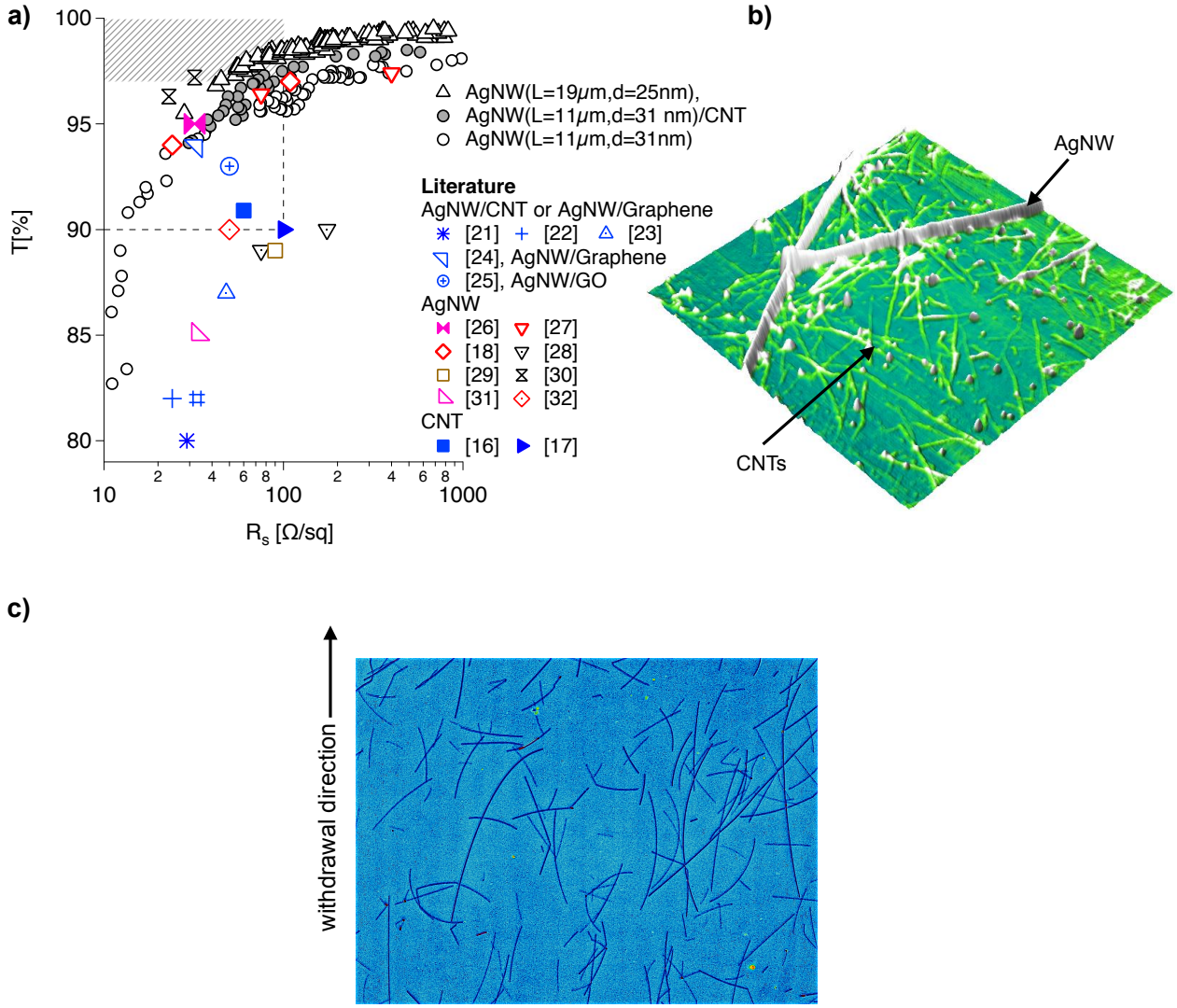

Figure 2. a) The optoelectrical performance T(R_s) for of the different AgNW and AgNW/CNT films produced in this work compared to values from recent literature. b) Scanning force micrograph of an AgNW/CNT film. c) Laser scanning micrograph of an AgNW film with very low area coverage.

97 in order to exhibit acceptable haze. As the AgNWs used in this work belong to the thinest AgNWs generally, and haze increases with the AgNW diameter, we expect that AgNW films always have to have transmission in the ultra-transparent range. It is seen that the pure AgNW(11 μm, 31 nm) networks do not meet the haze-corrected optoelectrical requirement whereas they do after CNTs have been added. However, using the longer AgNWs(19 μm, 25 nm) results in even better optoelectrical performance. Adding CNTs to these AgNWs also results in a decrease of the sheet resistance but only at very low area coverage were both the AgNW and the AgNW/CNT films are significantly outside the quality window. Within and close to the quality window the addition of CNTs does not influence the optoelectrical performance as it does in case of the shorter AgNWs. Our experiments show that low-haze transparent electrodes with sufficient conductivity are possible by using long AgNWs without adding further co-percolating materials. Compared to our previous work we do not need to add CNTs in order to achieve sufficient optoelectrical performance. With regard to the process efficiency these results are very promising as we do not have the need of a second dip coating step which is slower than the coating of AgNWs. We plot several %T(R_s) values from previous works in Figure 2a. We observe that only

our films and the films from Ref. [30] fulfill the haze-corrected industrial requirements. Moreover we observe significantly better optoelectrical performance for the same AgNWs(19 μm, 25 nm) produced by dip coating compared to spray coating by Woo et al., who used AgNWs from the same material supplier [27].

Dip-coating causes anisotropic alignment of the AgNWs. Figure 2c shows a laser scanning micrograph of AgNWs with L = 19 ± 9 μm and d = 25 ± 5 nm. The sample is aligned along the withdrawal direction of the dip coating process. We found that about 75 % of the AgNWs are aligned rather parallel than orthogonal to the withdrawal direction (45° to 135° where 90° represents the withdrawal direction). For random percolation this value is 50 %. The image in Figure 2c is a micrograph of a sample with very low area density to allow visible evidence for anisotropic structural percolation. In order to evaluate whether or not the anisotropic structural percolation induces anisotropic electrical percolation we measured the sheet resistance of the films parallel and orthogonal to the withdrawal direction. Anistropy of electrical percolation is not observed for samples with %T = 98.0. It starts to set on at %T = 98.5 where R_s(orthogonal)/R_s(parallel) ≈ 1.3. Such a difference is still acceptable but for %T > 99.0 the ratio increases up to ≈ 30. For %T = 98.0 a sheet resistance of R_s ≈ 70-150 Ω/sq can be achieved. For %T = 97.5 a sheet resistance of R_s ≈ 55-75 Ω/sq is possible. These values are within the quality window of sufficient haze and structural anisotropy does not cause electrical anisostropy. For %T = 98 the haze is %H ≈ 1.5 on microscopy slides. The bare substrates exhibit haze of %H ≈ 0.5.

3.2 Conceptual design of a production cell for transparent electrodes based on silver nanowires

We scaled the dip coating process on commercial smart phone glass and found the film homogeneity to be sufficient. The optoelectrical performance and film homogeneity is reproducible for withdrawal speeds between 150 and 1000 mm/min. The coating time and the drying time are opposed because higher withdrawal speeds result in thicker liquid films which dry slower. Figure 3a shows six commercial smart phone cover glasses coated with AgNWs from this work. The optical transmission is %T = 97.5-97.7 and the sheet resistance is R_s ≈ 55-70 Ω/sq. Figure 3b illustrates a conceptual production cell for the coating of smartphone cover glass with our approach. Ten substrates are coated simultaneously into a dispersion with a volume of 3750 ml (250x10x15 mm). The AgNW (L = 19 ± 9 μm and d = 25 ± 5 nm) concentration is 0.25 w%. One dip results with withdrawal speed of 300 mm/min in an optoelectrical performance of %T(R_s) = 97.5(55 Ω/sq). The coating process consists of three sub processes: (1) positioning, (2) dipping in and (3) dipping out. The velocity of steps (1) and (2) do not have a direct influence of the coating process, step (1) has to be chosen with regard to previous steps such as adjustment of the substrates and step (2) should not cause waves on the liquid surface. For the velocities (1) 1000 mm/min, (2) 1000 mm/min and (3) 300 mm/min we calculated a production rate of ≈ 17,000 substrates per 24 h. This is about 3.4 % of the daily Iphone production in industry. Hence, we need at least 30 of these production cells. It is important to mention that our calculations do not include breaks of the process due to homogenization of the dispersion. The homogenization is needed since the AgNWs sediment. For the illustrated dip coating processes, homogenization is easy to handle. The process is stopped and the dispersion is stirred for a few seconds. Afterwards, the coating process can continue. The process can be controlled by measuring the absorbance of the AgNW dispersion. After the absorbance reaches a critical minimum, further AgNWs are added.

For the calculation of the material range we need to know the area coverage A_C of the AgNWs. Bergin et al. found the following relation between the area coverage and the optical transmission [28].

$$A_C = \frac{100 - \%T}{a_1} \tag{1}$$

The fitting parameter a_1 depends on the wavelength of the incidenting light (which is conventionally 550 nm) and the diameter of the AgNWs. Bergin et al. found that a value of a_1 = 87 is in agreement with the experimental data for AgNWs with a diameter of 41 nm. Araki et al. calculated higher values for thicker AgNWs [18]. Recently we found a very similar result (a_1 = 85) for AgNWs with a diameter of 31 nm [33]. Hence, we estimate that we can rely on this value for the AgNWs with a diameter of 25 nm. For %T = 97.5 the area coverage is A_C ≈ $2.94 \cdot 10^{-2}$. The number of AgNWs per area unit N_{AU} can be calculated from the length L and the diameter d

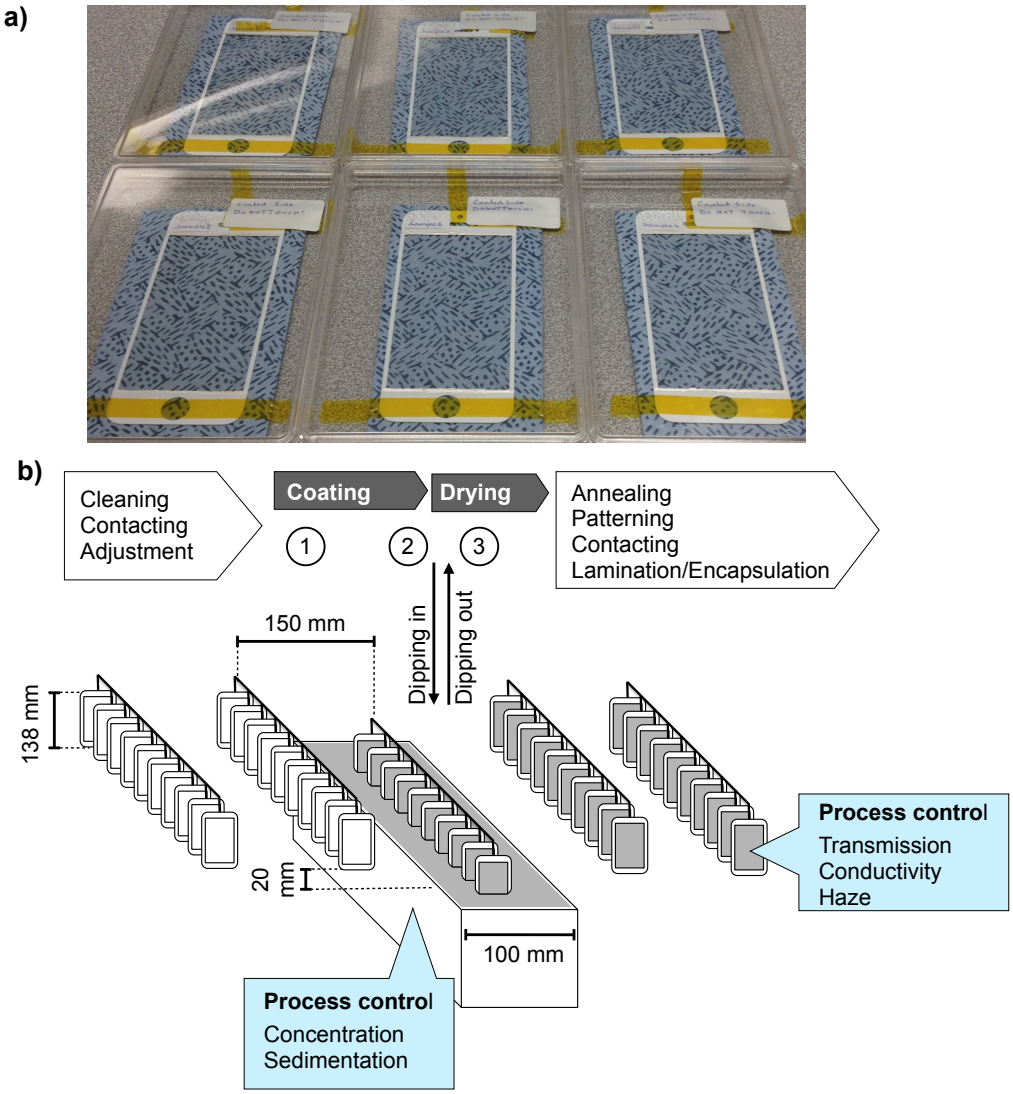

Figure 3. a) Conventional smart phone glasses coated with AgNWs. The optical transmission is %T = 97.5-97.7 and the sheet resistance is $R_s \approx$ 55-70 Ω/sq. b) conceptual setup of a production cell for AgNW-based transparent electrodes.

of the AgNWs with $A_C = N_{AU}Ld$. For cylindrical shape of the AgNWs the mass of Ag per area unit $m_{Ag/AU}$ is calculated from the density ρ_{Ag} as follows.

$$m_{Ag/AU} = N_{AU} \cdot \rho_{Ag} \pi \left(\frac{d}{2}\right)^2 L \tag{2}$$

The calculation results in 6.06 mg Ag/m^2 which is equivalent to a material range of 1 g AgNWs(19 μm, 25 nm) per 165 m^2. This value does not include material loss at the edges of the substrate. Moreover, AgNWs are not cylindric but have a pentagonal base [34]. Furthermore we did not consider the length deviation of ± 9 μm. However the order of magnitude of the determined material range with dip coating is significantly higher than for spray coating where we can reach only ≈ 10 m^2 with 1 g of the same AgNWs. The recent material price for AgNWs are 450 US$/g. Hence, the material costs for our AgNW films are 2.73 US$/m^2. Since AgNWs are only available in research scale so far, industrial scaling of the AgNW synthesis will decrease the material costs significantly.

4. CONCLUSION AND OUTLOOK

We have outlined why ITO is still not replaced by frequently discussed alternative materials. Basically there are two reasons: Either the manufacturing processes are not efficient or the materials underperform in at least one important requirement. With our approach, the production of ultra-transparent AgNW films we are able to create low-haze transparent electrodes with good optoelectrical performance. We were able to achieve such excellent values since we used AgNWs with high aspect ratio. Dip-coating is a feasible and cost-efficient technique for the production of transparent AgNW films on glass substrates. However, the roll-to-roll feasibility still has to be evaluated. Moreover the weak adhesion of the AgNWs is not only a drawback but it also offers the possibility of easy patterning with scratch lithography. We will report more about our ongoing research on transparent electrodes based on ITO alternatives in the future.

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