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Electrical resistivity of assembled transparent inorganic oxide nanoparticle thin layers: Influence of silica, insulating impurities and surfactant layer thickness

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Abstract

Transparent, conductive layers prepared from nanoparticle dispersion of doped oxides are highly sensitive to impurities. Currently investigated cost efficient and fast production of thin conducting films for use in consumer electronics relies on wet processing such as spin and/or dip coating of surfactant-stabilized nanoparticle dispersions. This inherently results in entrainment of organic and inorganic impurities into the conducting layer leading to largely varying electrical conductivity. Therefore this study provides a systematic investigation on the effect of insulating surfactants, small organic molecules and silica in terms of pressure dependent electrical conductivity as a result of different core/shell structure (layer thickness). Application of high temperature flame synthesis gives access to antimony-doped tin oxide (ATO) nanoparticles with high purity. This well-defined starting material was then subjected to representative film preparation processes using organic additives. In addition ATO nanoparticles were prepared with a homogeneous inorganic silica layer (silica layer thickness from 0.7 to 2 nm). Testing both organic and inorganic shell materials for the electronic transport through the nanoparticle composite allowed a systematic study on the influence of surface adsorbates (e.g. organic, insulating materials on the conducting nanoparticle's surface) in comparison to well-known insulators such as silica. Insulating impurities or shells revealed a dominant influence of tunneling effect on the overall layer resistance. Mechanical relaxation phenomena were found for 2 nm insulating shells for both large polymer surfactants and (inorganic) SiO₂ shells.

Keywords

conductive oxides; antimony tin oxide; charge transport; core-shell nanocrystals; thin films

Introduction

In the last decades transparent conductive oxides (TCO) have gained more and more importance in electrical devices: Thin films of the highly conductive inorganic materials are used as top electrode materials in solar cells, liquid crystal displays, light emitting diodes.¹⁻³ Beside their transparency and conductivity, they reflect thermal infrared heat,^{2,4-6} which is an advantage for most of the above mentioned applications as well as for future use as low-energy windows.

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Among the different TCO materials, indium tin oxide is the best known composition. It exhibits a high electrical conductivity combined with high light transmission. However, the rare occurrence of indium on earth^{7,8} demands the search for other doping materials of tin and zinc oxides. Antimony, aluminum or fluorine are heavily investigated and a balance between optimal performance and abundance/cost has to be found.^{3,4,9-14}

Vacuum deposition methods like sputtering and CVD are most common to produce these traditional polycrystalline films of different oxide materials¹⁵⁻¹⁸ on rigid substrates as for example glass. Scale up processes and cost reduction of electronic devices as well as the growing interest in producing flexible electrodes on polymer substrates led to a focus on new film production methods.¹⁹⁻²¹ This technical challenges demand improvements in low temperature processing of transparent conductive oxide films.²²⁻²⁴ Sol-gel routes, spray pyrolysis as well as spin and dip coating or even printing of TCO-nanoparticle solutions have been investigated and showed promising results for cheap transparent conducting layers.²⁵⁻²⁹

For these economically interesting coating processes of thin nanoparticle films often wetting agents or functionalization of the particles are necessary to prohibit the aggregation of the nanoparticles during the processing steps and to provide proper film formation properties.³⁰⁻³² These surfactant- and functionalization-molecules play a tremendous role in the performance of nanoparticle assemblies.^{33,34} The electrical conductance, however, can be seriously affected by an adsorbate shell around the particles, especially when low-temperature processing is needed for flexible devices, where no heat treatment is possible to remove the organic materials (sensitive polymer substrates). Therefore, it is necessary to deal with the impact (positive and negative) of those organic impurities.

As shown by Maksimenko et al.³⁵ additives as polyvinylpyrrolidone (PVP) can even enhance the conductivity of TCO thin films due to shrinkage in the drying process. Several works focused on understanding the influence of molecules,^{36,37} polymers³⁸⁻⁴⁰ and insulating barriers on the conductivity in nanoparticle composites. Models for percolation and hopping of electrons through nanoparticle assemblies have been investigated.⁴¹ Moreover, tunneling of electrons through thin insulating shells or filler materials in a nanocomposite play an important role.⁴² However, these reports have shown a considerable spread of data and various explanations for the electron transport in shells.

In the present study we therefore attempt to present systematic investigations on how insulating shells on TCO nanoparticles influence the overall conductivity of assembled nanoparticle thin films. High temperature derived antimony tin oxide (ATO) nanoparticles (guaranteed no adsorbed organics) were optionally coated with different dispersing agents or directly produced as SiO₂ coated ATO particles (one step coating and production process). Flame spray synthesis allowed a controlled antimony dopant level⁴³ in ATO and the in-situ deposition of a SiO₂ shells with a well controlled thickness.⁴⁴ The organic coatings were made by drying different surfactant-stabilized dispersions. We then compared the insulating silica shells with no possibility for rearrangement (SiO₂ layers are hard) as model core/shell conductor/insulator particles to typical nanoparticle preparations containing small (molecular) and large (polymer) surfactants or dispersion additives (such soft additives may re-arrange during preparation). Using a systematic study on pressure dependent resistance allowed us to investigate the accurate role of shell thickness and mean conducting core distance between nanoparticles on the overall resistivity in the nanoparticle assembly.

Experimental Methods

Materials

2-(2-(2-methoxyethoxy)ethoxy)acetic acid (TODA) and Tin(II) 2-ethylhexanoate (~95 %) were purchased from Aldrich Fine Chemicals. Ethanol absolute (analytical grade, ACS) was purchased from Scharlau (Scharlab S.L.), ethylene glycol from Acros Organics and tetrahydrofuran (HPLC grade) from Fisher Scientific. DISPERBYK®2164 was given by BYK-Chemie GmbH. Antimony(III) n-butoxide was purchased from ABCR-Chemicals. Technical grade xylene and 2-ethylhexanoic acid was used.

ATO-particle synthesis

The antimony tin oxide particles (10 wt% Antimony in SnO₂) were synthesized by an enclosed single step flame spray pyrolysis (FSP) setup. In analogy to the setup for the reducing flame synthesis among Grass et al.⁴⁵ a hermetically sealed glovebox including the flame spray set-up was built (3 glove-system, GS GLOVEBOX Systemtechnik GmbH). The glovebox can be purged by air to prevent the environment from nanoparticle exposure, as used here, or N₂ for non-oxide particle production. The multicomponent precursor was prepared by mixing the right amount of Sb(III) n-butoxide and Tin(II) 2-ethylhexanoate in 2-ethylhexanoic acid.⁴⁶ The precursor was diluted with THF (2:1) and had a total metal concentration of 4 wt%. The precursor was then dispersed (5 l min⁻¹ O₂, 5 ml min⁻¹ liquid) by a nozzle into a premixed flame (2.4 l min⁻¹ O₂, 1.13 l min⁻¹ CH₄). In the off gas above the flame, the nanoparticles were collected with a glass filter (Whatman GF/A, 25.7 cm diameter). A detailed description of a similar flame spray setup (without enclosure) has been described by Madler et al.⁴⁷

Organic functionalization

To functionalize the as-prepared particles, dispersions of 5 wt% particles were made by Nanograde LLC in a variety of solvents: The ethylene glycol functionalization was made with pure ethylene glycol (EG). To functionalize the particles with 3,6,9-trioxadecanoic acid (TODA) ethanol was used as solvent, and for the polymer functionalization DisperBYK 2164 (polymer) is taken as surfactant and xylene as solvent.

Synthesis of silica coated ATO-particles

Silica coated ATO-particles were prepared in an enclosed flame spray pyrolysis reactor.⁴⁸ The same ATO-precursor as for the production of pure ATO-particles was dispersed by 5 l min⁻¹ oxygen into a 1.5 l min⁻¹/3.2 l min⁻¹ methane/oxygen flame. Additionally, sheath gas (40 l min⁻¹ O₂) surrounding the flame was also provided to ensure complete combustion. The flame was enclosed by a 20 cm quartz glass tube, on top of which a metallic ring with 16 equidistant opening was placed. Through these openings, hexamethyldisiloxane (HMDSO, Sigma-Aldrich, purity >98 %) vapor was injected along with 15 l min⁻¹ N₂ carrier gas. The HMDSO vapor was supplied by bubbling N₂ at appropriate flow rates through a HMDSO containing flask. The reactor was terminated by a 30 cm quartz glass tube.

Particle analysis

Transmission electron microscopes (TEM) images of the pure and SiO₂-coated particles (not shown) were made by a FEI Tecnai F30 (FEG cathode, operated at 300 kV, point resolution ~2 Å). The particle size as well as the SiO₂-shell thickness was determined out of these images (log-normal fitting, 1 nm step). X-ray diffraction spectra were carried out on a X'Pert PRO-MPD (Cu KR radiation, X'Celerator linear detector system, step size of 0.05 °, 45 kV, 40 mA, ambient conditions) and the as-prepared particle size was calculated by the

Debye-Scherrer-equation.⁴⁹ Nitrogen adsorption measurements were carried out with the inorganic particles (Brunauer-Emmett-Teller (BET) method, Tristar Micromeritics Instruments) with a heat pre-treatment of 3 h at 140 °C under vacuum. Thermogravimetric analysis (not shown) was made to determine the organic content (functionalized-shell) on a TG STAPT1600 (Linseis) with a heat rate of 10 °C min⁻¹ under air up to 800 °C. The shell thickness of the organic/ATO composites was calculated from the following geometric consideration, assuming spherical particles and a density of the organic phase of 1 g cm⁻³:

$$\frac{V_{shell}}{V_{core}} = \frac{V_{Total} - V_{core}}{V_{core}} = \frac{\frac{4}{3}\pi(r_{core}+x)^3 - \frac{4}{3}\pi r_{core}^3}{\frac{4}{3}\pi r_{core}^3} = \frac{(r_{core}+x)^3 - r_{core}^3}{r_{core}^3} = \frac{m_{shell}}{m_{core}} \cdot \frac{\rho_{core}}{\rho_{shell}}$$

where V denotes the volume, r the radius, m the mass and ρ the density of either the core or the shell material. x is the shell thickness, which can then be calculated from the mass ratio gained from the thermogravimetric analysis. This procedure is in line with the strong, irreversible adsorption of surfactants and polymer monolayers.^{50,51} For the polymer/ATO composite, the volume content of polymer is high and we can assume that all interparticle voids are filled with polymer. Since the packing is clearly random, a volume filling $\psi = 0.5$ can be assumed as generally accepted in powder technology⁵² and affords a smaller shell thickness of 0.8 nm.

Resistivity measurements

The resistance of the pestled powder was measured by a two-point measurement under different pressures at a constant current with a Keithley Series 2400 SourceMeter (measurements were conducted about 10 s after pressure appliance). The pressure was applied by manually compacting the powder in a press (IR-Press-25T, manual, hydraulic, Maassen GmbH). The thickness of the pill was determined either by an optical microscope (Zeiss, Axio Imager.M2m, z-stacking) or by a caliper (Sylvac, S_Cal Work).

Results and Discussion

Nanomaterial dispersions and film preparation

Antimony tin oxide (ATO) nanoparticles with an antimony (Sb) content of 12 wt% have been prepared by flame spray synthesis. This high temperature preparation method has routinely been used for oxide preparation with high purity (high temperature results in destruction of organic surface impurities).⁵³⁻⁵⁵ The as-prepared pure ATO nanoparticles were characterized with complimentary methods and showed a log-normal primary particle size distribution (mean 4.5 nm, $\sigma = 0.3$) with an average diameter of 5.2 ± 2.3 nm (157 particles optically counted using transmission electron microscope images; Figure 1 a). Specific surface area measurements according to the BET method revealed a surface area of 124 m² g⁻¹ (Table 1) which results in a surface-equivalent particle diameter of 7.1 nm if assuming spherical particles and a density of 6.8 g cm⁻³ for the antimony tin oxide.⁴⁵ X-ray diffraction pattern of the material confirmed its chemical identity (match of crystal phase to literature data) and yielded a mean crystallite diameter of 6.9 nm (applying the Debye-Scherrer-equation on the main reflection peaks). These measurements confirmed the optical (electron microscopy) characterization of the material and showed that it consists of about 7 nm, rather single-crystalline particles of ATO. For mechanistic investigations, a series of SiO₂ coated ATO nanoparticles with different shell thickness' (nominal values: 0.7 nm, 1.4 nm, 2.1 nm and 2.8 nm; calculated by assuming shells around monodisperse spheres (core diameter from uncoated particles from BET) were prepared using a modified flame spray synthesis setup⁴⁸ where a gaseous Si-precursor vapor was injected further downstream of the freshly-formed core ATO-nanoparticles at a height of 20 cm. The flame is surrounded by

a glass tube to provide a better turbulent flow mixing of the different components⁵⁶ and inhibit the air entrainment in the reactor.

High quality dispersions are needed to inhibit aggregate formation during processing as spin or dip coating since such premature aggregate formation results in film inhomogeneity, rupture or holes. As known from colloid science, stabilization of small particles in a fluid can either be done electrostatically or sterically.⁵⁷ Steric stabilization is usually done by adding (bulky) surfactants to the fluid or by chemically functionalizing the particles. In both cases, a spacer is introduced between the particles, thus reducing their attractive force. High quality nanoparticle dispersions are the key condition to form good, conducting films and today mainly rely on certain optimized, organic additives (usually rather high molecular compounds). After film formation and evaporation of the solvent, the stabilizing agents remain in the nanoparticle film. These insulating (non-conducting) surfactants are traditionally removed by annealing the films under high temperature which may also induce a usually beneficial side-effect, namely sintering, which maximizes the contact area between adjacent particles and improves conductivity. The now ongoing transformation to flexible (usually polymer based) film substrates, however, severely limits the application of such high temperature post-treatment. Surfactant removal, hence, has become more difficult and demands for alternative film preparation strategies.

In order to better understand the effect of such insulating additives, a number of samples with varying contents and size of commercially used surfactants were prepared and compared to assembled ATO nanoparticles without any additives (e.g. absence of impurities as far as technically possible). Dispersions with 5 wt% ATO were either stabilized by a polyurethane-based dispersion additive (polymer) and supplied in xylene (sample a; i.e. the thickest coating) or using a small molecular surface modifier, trioxadecanoic acid (TODA) and supplied in ethanol (b) or prepared without additional surfactants (c) in ethylene glycol (EG) where a direct adsorption of ethylene glycol molecules on the particle of the oxide surface has been assumed.⁵⁸ Thin films were made by spin coating (1500 rpm, 42 s) the dispersions with a thickness of about 100 nm (Figure 1 b) and a quite dense packing of nanoparticles (Figure 1 c) after post-treatment of 550 °C for 10 min. Nevertheless, some defects, as small cracks and shallow pits, are introduced into the film during the post treatment and show how volume loss due to surfactant removal may result in film imperfections.

Electrical conductivity in the presence of insulating shells

In order to correlate electrical conductivity to impurities and/or formation of insulating shells on the particles, the organic impurity content was measured from drying the organic molecule-coated particles (i.e. stabilized suspensions) after centrifugation and supernatant removal in vacuum at 60 °C. Since pressure dependent conductivity measurements provide a more detailed insight into governing conduction mechanism in assembled nanoparticles, pills were pressed using the slightly pre-pestled powder (breaking the centrifugation pellets manually). Pills with systematically increasing organic shells around the ATO particles were prepared from the original dispersions based on ethylene glycol (EG, smallest molecule, less than 0.6 nm), trioxadecanoic acid (TODA, about the size of a fatty acid, 1-2 nm long) and polymeric dispersion additives (size above 2 nm; see subsequent sections for characterization). Figure 2 shows how the resistivity of pure ATO pills drops upon increasing pressure (from little load applied on the pill and a pressure of less than 10¹ bar to around 10⁴ bar). Mechanical relaxation (irreversible or reversible nanoparticle compaction during these experiments) was investigated by releasing the pressure after applying the maximum pressure (10⁴ bar) back to 10³ bar and showed no relaxation for pure ATO samples (i.e. no insulating shells). A similar behavior was found for the thin organic layer

coated samples derived from ATO coated/stabilized with the trioxadecanoic acid (TODA) and ethylene glycol (EG) These samples irreversibly compact (see Figure 2 b, insert).

In contrast, polymer dispersant stabilized/coated ATO nanoparticle derived samples showed a reversible mechanical relaxation and resistance came back to initial values upon pressure reduction (see Figure 3 b). We repeated the measurements for a number of times applying pressure cycles between 0.8 kbar (1 t) and 5.9 kbar (7.5 t). Multiple cycles (see Figure 4 for 5 consecutive compression/expansion cycles) clearly demonstrate reversible behavior, thus excluding irreversible compaction events as a cause of the here discussed effects. However a minor drift in resistance is observed, which may be an effect of charge accumulation and discharging of single-nanoparticles working as capacitors in the composite as proposed by Oldfield et al.⁵⁹ An equilibrium state was generally reached after 3 hours (no more drift). Using such long time equilibration conditions afforded a drift-free, constant and reversible behavior as demonstrated over 3 additional cycles (Figure 4). The polymer/ATO samples can therefore be considered non-compacting and fully relax after releasing pressure (Figure 3 b).

Origin of pressure dependent conductivity in core/shell composites

Pressure dependent changes in electrical resistivity may originate from several effects: The piezoresistance may be explained by formation of a higher number of percolation paths through a pill (or any assembly of nanoparticles) as a result of powder compaction and denser packing.⁶¹ Alternatively, the organic molecules forming the insulating shell are mobile and subsequent shell deformation and displacement increases the contact area between the conducting particle cores improving conductivity. Another possibility is that the electron transport through the insulating shells is not negligible and depends on the detailed molecular composition. The last possibility has been originally described by Athanassiou et al.⁶⁰ as altered electron tunneling through nanometer thick insulating shells as a result of shell compression during pressure load (i.e. shorter tunneling path and higher tunneling probability, thus higher conductivity).

Do insulating surfactant layers behave like ceramic shells?

Assuming, that the so far investigated organic shells are in principle non-conducting, we expect electron tunneling through the organic layer (EG, TODA surfactant or polymer). Shell displacement effects could be excluded based on above observation of reversible behavior (A) and by using a second, independent argument: Comparison of a rigid insulating shell (e.g. ceramic or silica shell) with a similar organic shell of the same thickness affords a similar piezoresistance. This was demonstrated by comparing the conductivity of compacted polymer/ATO composites to earlier investigations on ceramic coated metal nanoparticles by Athanassiou et al. (Figure 3 a).

In order to systematically investigate the role of insulating shell thickness, we directly compared composites from ATO either with organic shells (EG, TODA, polymer) or silica for various layer thicknesses (Figure 5). The relative change in resistivity as function of pressure is used to directly compare these two otherwise most different set of samples. At first, it becomes most evident, that the organic shells show a more pronounced change in resistivity, which can be well understood if considering the much easier compaction of organic matter than silica (i.e. organic matter being much softer than silica). The behavior of the thinnest silica samples is best understood based on the absolute resistivity data given in Figure 6 which includes data for compaction and relaxation measurements (i.e. pressure was increased or decreased subsequently). For samples with no silica or a very thin, possibly only partially-coated layer⁶² (nominal thickness of 0.7 nm silica), the materials irreversibly compacted similar to the previously discussed samples of ATO with no coating, EG or

TODA surfactants. Less pronounced effects and overall greater resistance arise from increasing the silica layer thickness. A comparison of nominal shell thickness and optically measured values for the higher silica shells is given in Table 1.

A quantitative comparison using the tunneling formalism for such insulating shell/conducting core particles⁶⁰ affords a composite resistivity ρ as a function of pressure P as

$$\rho(P) = \rho_0 \exp(-2X_t d_0 P/M) \quad (1)$$

where d_0 is the mean distance between two particles (note that $d_0 = 2x$, where x is the shell thickness). M is the bulk compressive modulus of the coating material and X_t is defined as $X_t = (8\pi^2 m_{\text{eff}} V / h^2)^{1/2}$ with m_{eff} as the effective electron mass, V the potential barrier height at the material junction and h the Planck constant. The same exponential behavior of resistivity and conductivity for small biases is described by Zabet-Khosousi and Dhirani⁴² for metal-insulator-metal junctions. For organic composites, polymer science describes piezoresistive behavior in the context of flexible sensors, where the pressure dependence of resistance is described as:⁶³

$$\frac{R(P)}{R_0} = \frac{d}{d_0} \exp(-2X_t(d_0 - d)) = (1 - P/M) \cdot \exp(-2X_t d_0 P/M) \quad (2)$$

with $d = d_0 \cdot (1 - P/M)$ and the resistance R . R_0 is the resistance measured at a given reference

pressure. The expression $\frac{R}{R_0}$ is similar to $\frac{\rho}{\rho_0}$ as long as the pill thickness is not largely affected by compaction. For amorphous SiO_2 (bulk compressive modulus = 36.9 GPa), P/M is very small in the pressure range of $10^3 - 10^4$ bar and therefore the pre-exponential factor in equation (2) $(1 - P/M)$ is nearly 1. Therefore, the two models are congruent in this case. For an assumed electron mass of $0.39 \cdot m_0$ ⁶⁴ and a potential barrier of 3.9 eV at the transition from ATO to amorphous SiO_2 ,^{65,66} we can evaluate the present data (e.g. the nominal 1.4 nm SiO_2 shell sample) using equation (1). The data in Figure 7 a shows a good qualitative match of purely physical models (calculated data) and experimental finding yielding a shell thickness of about 2 nm. This is in the same size range than the experimentally observed shell thickness using electron microscopy images, where we found a mean shell thickness of 1.7 nm.

Note that above formalism assumes measurement at a small, constant voltage applied. The here performed experiments, however, were done at constant current and afforded voltage variations in a range of 10^{-1} to 10^0 V with peak values below 1.6 V. As the energy of these electrons is still significantly smaller than the potential barrier of 3.9 eV,^{65,66} the tunneling phenomena above is not significantly suppressed. In order to quantitatively estimate the maximum deviations arising from this mode of measurement, we re-run the above calculations at a reduced barrier height of 2.3 eV (i.e. using 3.9 – 1.6 eV, the most extreme potential effects that may have arisen from choosing this type of measurement method) which afforded only minor changes in the resulting shell thickness (less than 30 %). We can therefore still use the above model to qualitatively describe our systems (inorganic and organic shells).

Comparing the here investigated polymer/ATO composite to the recently reported ceramic/metal core/shell particles⁶⁰ again confirmed the here made observations in terms of reversibility and scaling of resistivity versus applied pressure (Figure 3). In the used pressure range, equation (1) and (2) are nearly congruent (see Figure 7b) for an assumed bulk modulus of 2 GPa for the here applied polymer (polyurethane co-polymer with tertiary amine groups, information given by the supplier).^{67,68}

Conclusion

This study shows the strong influence of non-conducting surface impurities in the preparation of conductive nanoparticle films in a quantitative way and relates the experimental observations to a quantitative understanding based on an electron tunneling mechanism. The direct comparison of conductivity behavior of assemblies made from hard shell ceramics (e.g. silica) on conductor nanoparticles (metals or ATO) with commonly used organic surfactants in the preparation of conductive thin films demonstrates the identical influence of such non-conducting materials, even at minor concentration. Understanding the role of surfactants, adsorbates or processing aids in thin film preparation will assist the development of improved film preparation methods as urgently required in photovoltaics and classical electronics.

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Figure 1.

(a) Particle size distribution of antimony-doped tin oxide (ATO) nanoparticles after preparation with a log normal curve fit and representative electron micrograph. (b) Dispersions containing 5 wt% ATO in xylene and resulting spin coated thin films (cross section, b) and (c) top view.

Figure 2.

The electrical resistivity of compacted ATO nanoparticles under various pressures and using different organic additives with increasing size (a) and detailed view on the behavior at high pressure (b). All samples undergo an irreversible compaction and maintain improved conductivity after pressure release.

Figure 3.

(a) Electrical resistivity of compacted ATO particles using a polymeric additive as dispersion agent (top series of data) and comparison to literature data on 1-3 nm ceramic coated metal core/shell nanoparticles (bottom data) and insulating 1 nm carbon coated copper nanoparticles (middle). (b) A detailed view on the high pressure region reveals reversible relaxation of such materials upon pressure release (see further investigations in Figure 4).

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Figure 4.

Cycles of 1 and 7.5 t (0.8-5.9 kbar) pressure applied to the polymer coated ATO pill show a reversible behavior of the resistance over more than 5 cycles. A drift in resistance is observed, but measurements after 3 h (equilibrium reached) showed the same behavior over more than 3 cycles. Therefore the polymer/ATO samples fully relax after releasing pressure.

Figure 5.

Relative changes in electrical resistance under elevated pressure for ATO samples with (a) increasing silica shell thickness allow a direct comparison of these samples. A thickness of around 1.4 nm results in the most pronounced piezoresistance (silica shells, left). (b) Organic material on the surface of conductor (ATO) nanoparticle provoked the same behavior: Small molecules (e.g. ethylene glycol) showed a similar pressure dependent resistance as low silica samples and polymeric shells (a few nm thick) afforded a stronger piezoresistance, similar to intermediate silica layers.

Figure 6.

An increasing thickness of silica (a well-known insulator) was deposited in situ on conductor particles of ATO and resulted in a successively reduced conductivity. While very thin layers (0.7 nm) behaved similar to pure ATO upon pressure release (irreversible compaction), the higher barrier samples (>2 nm silica) showed a less pronounced piezoresistance and partially relaxed upon pressure release.

Figure 7.

Evaluation of congruence of experimental data to theoretical models by fitting equation (1) and (2) to the measured data from (a) 1.4 nm SiO₂ on ATO particles and (b) polymer coated ATO particles. The models show a good agreement as well as for inorganic coated and organically coated ATO.

Table 1

Summary of BET-analysis and shell thickness measurements by TEM and thermogravimetric analysis.

	material	Specific surface area from BET ($\text{m}^2 \text{g}^{-1}$)	Shell thickness (nm)
Series 1	ATO (enclosed FSP - setup)	124	-
	ATO – polymer	-	2 ^a
	ATO – EG	-	0.7 ^a
	ATO - TODA	-	0.7 ^a
Series 2	ATO (SiO_2 – FSP - setup)	38	-
	ATO – 0.7 nm SiO_2	42	-
	ATO – 1.4 nm SiO_2	47	1.7 ^b
	ATO – 2.1 nm SiO_2	59	1.9 ^b
	ATO – 2.8 nm SiO_2	66	2.1 ^b

^aShell thickness determined by geometrical considerations from thermogravimetric analysis data^bShell thickness determined by TEM image analysis