

Comparison of spray pyrolyzed FTO, ATO and ITO coatings for flat and bent glass substrates

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Abstract

Transparent conductive FTO, ATO and ITO films were synthesized by spray pyrolysis technique on flat 12 × 12 cm borosilicate glass substrates at 500–550°C and investigated with respect to their electrical and optical properties. The resistivity of sprayed ITO films decreases with the thickness down to $3.0 \times 10^{-4} \Omega \text{ cm}$ (300 nm). The optical transmission in the visible range is 80% and the near IR reflection up to 96% for thicknesses larger than 300 nm. A reducing treatment at 400°C in forming gas still decreases the resistivity by a factor of two. Bending of the coated glasses in air at 650°C for 1.5 h increases the resistivity of the coatings on the tensile side of the substrate by a factor of 3–4 and by a factor 2 on the compressed side. A subsequent reducing treatment in forming gas at 400°C leads to a drastic decrease of resistivity in both cases by a factor of 5–7 with resulting value $\rho = 2\text{--}3 \times 10^{-4} \Omega \text{ cm}$. ATO layers have lower visible transmission (70–75%) due to stronger absorption and a higher resistivity ($\rho = 1 \times 10^{-3} \Omega \text{ cm}$). Spray pyrolyzed FTO coatings have a resistivity $\rho = 5 \times 10^{-3} \Omega \text{ cm}$ for film thicknesses >350 nm.

Keywords: Coatings; Deposition process; Indium Tin oxide; Tin oxide

1. Introduction

The high transmittance in the visible spectral region in combination with a high conductivity, and a high reflectance in the IR region of non-stoichiometric and doped films of oxides of tin, indium, cadmium and zinc is still of wide interest due to their broad applications in electronic and optical devices, like transparent electrodes for display devices, gas sensors, heating elements in aircraft and car windows for defogging and deicing, etc. [1]. These coatings have been deposited by various methods such as chemical vapor deposition (CVD), reactive RF sputtering, evaporation, atomic layer epitaxy, spray pyrolysis and sol-gel processes [2].

This paper compares the properties of pyrolytically sprayed ATO, FTO and ITO films deposited under nearly identical conditions. The effect of dopant concentration and coating thickness as well as heat treatment under a reducing atmosphere on the electrical and optical properties of the films are described. The influence of a bending process on the electrical properties of ITO films is also reported.

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2. Experimental

2.1. Spray process and sample characterization

The solutions were sprayed on hot borosilicate substrates of 12 × 12 cm size, heated from the backside by a ceramic heater. The temperature of the glass surface was measured with a pyrometer (Heimann KT 19.43, 7.5–8.2 μm). The spraying process was done with a conventional hand spray gun (SATA Mini Jet) equipment with a 0.5 mm nozzle using compressed air (1–2 bar) and a solution flow rate of 13–17 ml/min. To avoid a too strong cooling of the substrate by the compressed air an interval spraying procedure of 3 s of spraying period followed by an interruption for about 30 s was used.

The film thickness, t , was measured with a Tencor P10 profilometer and the sheet resistance, R_{\square} , as well as carrier density, n , and Hall mobility, μ , were measured with the Van der Pauw method (MMR Technologies, Inc.). The electrical resistivity, ρ , was determined by the relation $\rho = R_{\square}t$. Transmission and near normal (7°) reflection of the sprayed layers were measured with a Cary 5E spectrometer from 300 nm to 3 μm and the reflection in the IR from 3 to 20 μm IR range with a Bruker IFS 66v FTIR spectrometer.

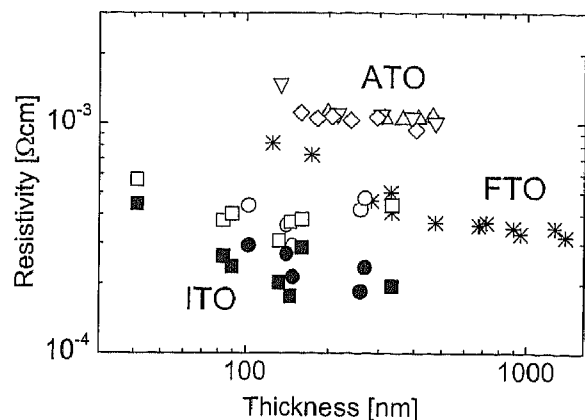


Fig. 1. Resistivity of ATO, ITO and FTO layers sprayed with different dopant concentrations versus film thickness. ATO layers: Sb concentration: (Δ), 1 mol.%; (∇), 1.5 mol.%; (\diamond), 3 mol.%. ITO layers: Sn concentration: (\circ), 2.4 mol.%; (\square), 4.8 mol.% Sn in the as-sprayed state and (\bullet), 2.4 mol.%; (\blacksquare), 4.8 mol.% Sn in the reduced state after forming gas treatment. FTO layers, (*3) wt.% HF.

2.2. Preparation of spraying solutions

For FTO layers a commercially available ethanolic solution (OTN 3-5, Goldschmidt AG) of monobutyltintrichloride (MBTC) doped with 3 wt.% HF was used. The substrate temperature was 500°C. For ATO layers a 0.24 M ethanolic solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (solid content 83 g/l ethanol) doped with 1–5 mol.% SbCl_3 (molar ratio Sb:Sn) was used. The substrate temperature was 550°C. For ITO layers a 0.36 M solution of InCl_3 in an ethanol/water mixture (weight ratio 1:1) was sprayed at a substrate temperature of about 520°C. The solution was stabilized by adding 7.5 g HCl to 100 ml of the mixture.

2.3. Bending and reducing treatment

Bending experiments were carried out for ITO layers in a furnace under air at 650°C. Flat coated substrates were laid on a curved steel mold with a radius of curvature of 50 cm

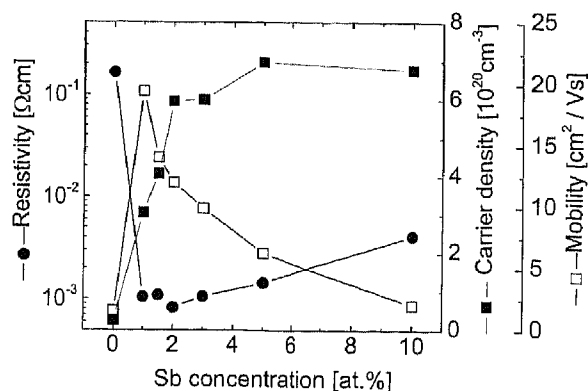


Fig. 2. Resistivity (\bullet), left scale, carrier density (\blacksquare), inner right scale) and mobility (\square), outer right scale) versus dopant concentration of sprayed ATO layers with about 300 nm thickness. The lines drawn are guides for the eye.

and bent under their own weight during 1.5 h. The experiments were done in two ways: the substrate was laid onto a steel mould such that the coating was either elongated (tensile bending) or compressed (compressive bending). A reducing treatment was then carried out for flat and bent ITO samples in forming gas (92% N_2 , 8% H_2 , flow rate 70 l/h) at 400°C during 15 min.

3. Results and discussion

3.1. Electrical properties of ATO coatings

In Fig. 1 the resistivity of ATO layers with different anti-dopant concentrations is plotted versus the film thickness. The lowest values are obtained for dopant concentrations in the range from 1 to 3 mol.% Sb. For lower and higher doping the resistivity is higher for all film thicknesses. Sheet resistance as low as 20 Ω_{\square} can be obtained for a film thickness of 400 nm (Fig. 4).

In Fig. 2 the resistivity, ρ , the carrier concentration, n , and the mobility, μ , are plotted for about 300 nm thick ATO films as a function of the antimony concentration. The undoped SnO_2 coating has very low intrinsic carrier density and mobility. For the doped ATO samples μ decreases always by almost the same factor by which n simultaneously increases. This behavior is the reason for the independence of ρ in the Sb concentration range of 1–3 mol.%.

3.2. Electrical properties of ITO coatings

Fig. 1 shows also the resistivity of ITO layers with Sn dopant concentrations of 2.4 and 4.8 mol.% (atomic ratio Sn/In). For thicknesses $t > 100$ nm resistivities of 3–4 $\times 10^{-4}$ Ω cm are obtained for nearly all investigated samples. A reducing treatment in forming gas at 400°C slightly decreases the resistivity down to $\rho = 1.8$ – 2.8×10^{-4} Ω cm for thicknesses > 80 nm, the best results being reached with the highest dopant concentration. A reducing treatment

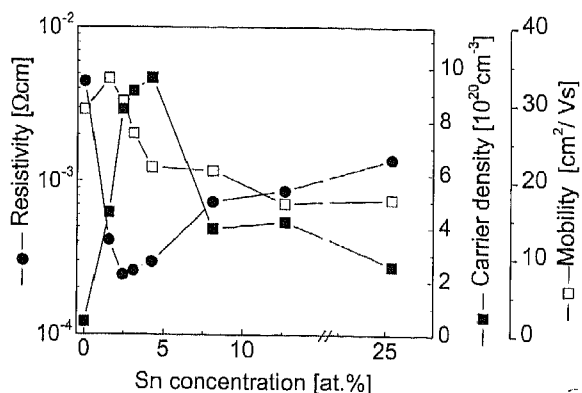


Fig. 3. Resistivity (\bullet), left scale, carrier density (\blacksquare), inner right scale) and mobility (\square), outer right scale) versus dopant concentration of sprayed ITO layers with about 240 nm thickness. The lines drawn are guides for the eye.

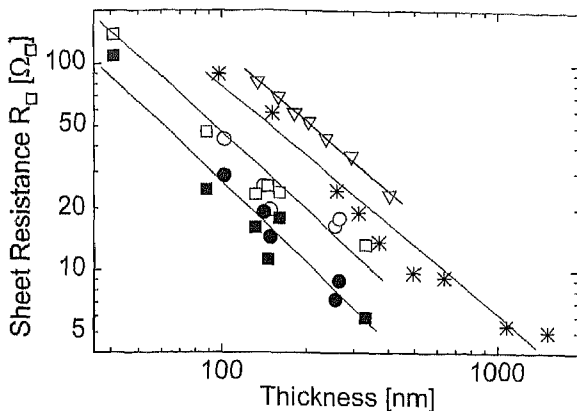


Fig. 4. Sheet resistance R_{\square} of ATO, ITO and FTO layers versus film thickness. ATO layers: (∇), 3 mol.% Sb; ITO layers: (\circ), 2.4 mol.% Sn; (\square), 4.8 mol.% Sn in the as-sprayed state and (\bullet), 2.4 mol.% Sn; (\blacksquare), 4.8 mol.% Sn in the reduced state after forming gas treatment. FTO layers: (*), 3 wt.% HF. The lines drawn reflect the t^{-1} dependence of the sheet resistance.

under forming gas for 15 min at 500°C increases the resistivity above the initial as-sprayed level in contrast to the reducing treatment at 400°C. In addition the samples show a slightly black metallic cosmetic appearance due to a partly reduction of the oxide layers into metallic indium.

In Fig. 3 the values of ρ , n and μ are shown as a function of the dopant concentrations. The thickness of all layers was about 240 nm. With increasing Sn concentration in the solution from 0 to 3 mol.%, n increases strongly reaching a maximum for about 5 mol.% Sn. For higher dopant content no more Sn-atoms can be embedded in the In_2O_3 -lattice, as the maximum solubility of Sn-atoms in the In_2O_3 -lattice is limited to about 5 mol.% [3]. The decrease of the carrier density for higher Sn concentration may be due to interstitial Sn-atoms in the lattice which act as charged trapping centers for the electrons. A phase separation of small SnO_2 -particles in the crystalline ITO-material does not occur since no Bragg reflexes belonging to a crystalline SnO_2 phase was detected in XRD measurements.

The mobility μ decreases from high values of about 35 cm^2/Vs for the undoped state down to below 20 cm^2/Vs for higher dopant content. This is due to the increasing number of Sn-atoms in the crystal lattice which act as ionized scattering centers when localized on interstitial lattice sites or to a strongly distorted crystal structure due to the radius mismatch. As a result the resistivity shows a minimum of $\rho = 2.5 \times 10^{-4} \Omega \text{ cm}$ around 3 mol.% Sn concentration. For lower and higher concentrations the resistivity exhibits higher values due either to low n values and/or to a decrease of μ . Only dopant concentrations between 2.4 and 4.8 mol.% were used for further investigations.

3.3. Electrical properties of FTO coatings

The resistivity of FTO coatings is also plotted versus the film thickness in Fig. 1. It slightly decreases with the

increase of the thickness and values as low as $\rho = 3.5 \times 10^{-4} \Omega \text{ cm}$ are reached for thicknesses larger than 500 nm. The mobility increases linearly with the film thickness from 10 to about 25 cm^2/Vs until a thickness of about 600 nm is reached. The reason may be a linear increase in the crystal size in the growing film with increasing film thickness resulting in a linear increase in mobility due to better contacts between neighbored crystallites. In the thickness range up to 600 nm the carrier density is nearly independent of thickness with showing values ranging between 4.5 and 6 $\times 10^{20} \text{ cm}^{-3}$.

For thicknesses higher than 800 nm the values of μ and n scatter in opposite direction resulting in an almost constant value in resistivity of about $3.5 \times 10^{-4} \Omega \text{ cm}$ as can be seen in Fig. 1. The scattering of the values may be a consequence of the long term heating at 500°C of the films during the spraying process which lasts for about half an hour for a layer thicker than 1 μm due to the interval spraying method.

3.4. Comparison of the electrical properties

A comparison of the plots shows that the resistivity of ATO films with an optimum Sn concentration of 3 mol.% is the highest for all film thicknesses. The ITO layers and especially the reduced ITO coatings show the lowest values whereas the values of the FTO layers lay in between. For technical application it is interesting to plot the sheet resistance versus film thickness. Fig. 4 shows a log-log plot of the results obtained for the different materials. As the resistivities do not vary drastically with the thickness all the results lie on straight lines as $R_{\square} = \rho/t$. Whereas the ATO coatings with optimum Sn concentration of 3 mol.% result in a sheet resistance as low as 20 Ω_{\square} for a film thickness of 400 nm, the FTO layers show lower values of about 15 Ω_{\square} for the same film thickness. The best results are obtained for

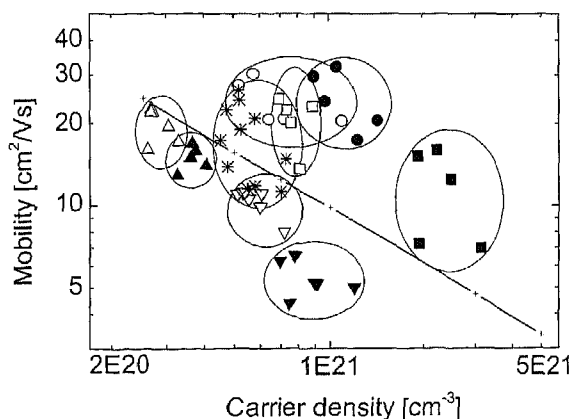


Fig. 5. Log-log plot of mobility μ versus carrier density n , for sprayed ATO layers (\triangle), 1 mol.%; (\blacktriangle), 1.5 mol.%; (∇), 3 mol.%; (\blacktriangledown), 5 mol.% Sb, as-sprayed ITO layers (\circ), 2.4 mol.%; (\square), 4.8 mol.% Sn, under forming gas reduced ITO layers (\bullet), 2.4 mol.%; (\blacksquare), 4.8 mol.% Sn) and FTO layers sprayed with 3 wt.% HF (*) versus film thickness. The corresponding samples are surrounded by circles. The straight line is a plot of the Johnson and Lark-Horovitz law for degenerated semiconductors.

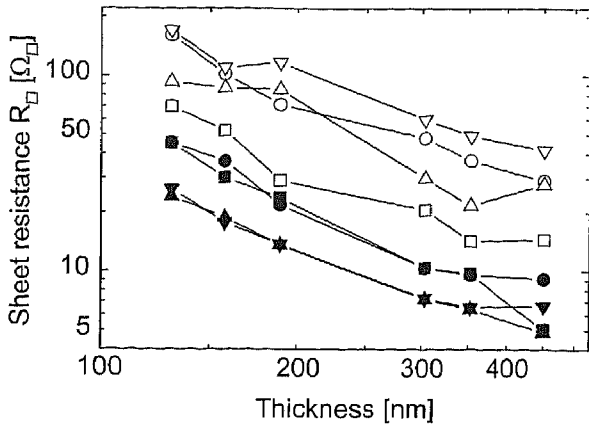


Fig. 6. Sheet resistance R_{\square} of sprayed ITO coatings doped with 2.4 mol.% Sn after different bending treatments and after reducing under forming gas at 400°C for 15 min: (\square), as-sprayed; (\circ), only heated at 650°C; (Δ), compressive bent; (∇), tensile bent; (\blacksquare), only reduced; (\bullet), reduced after heating at 650°C; (\blacktriangle), reduced after compressive bending; (\blacktriangledown), reduced after tensile bending. The lines drawn are guides for the eye.

ITO coatings that are treated in a forming gas atmosphere. This reducing treatment results in a decrease in the sheet resistance, R_{\square} , of nearly a factor 2. For example, a 250 nm thin film with $R = 18 \Omega_{\square}$ in the as-sprayed state decreases to about $R_{\square} = 8 \Omega_{\square}$ after reduction. For thicknesses >400 nm sheet resistances as low as $5 \Omega_{\square}$ can be reached by this reducing treatment.

In Fig. 5 μ is plotted versus n for all investigated ITO, FTO and ATO samples. The values obtained from various spraying solutions are always situated in a limited region independently of the individual film thickness. The ATO layers follow a specific trend with increasing Sb concentration from 1 to 5 mol.%: n increases steadily whereas μ decreases. All data points in this plot are below the straight line given by the Johnson and Lark-Horovitz law which describes how much the mobility decreases in fully degenerated semiconductors when the carrier density increases [4,5]:

$$\mu \approx (4elh)(\pi/3)^{1/3} N^{-2/3} \quad (1)$$

The data for the FTO and ITO layers are above this line. The reducing treatment of the ITO layers in forming gas shifts the data simultaneously to higher n and smaller μ values on a line parallel to the calculated line. Hence these reduced samples also follow the trend of the law of Johnson and Lark-Horovitz but the values for the ITO samples are shifted to higher values.

3.5. Effect of bending on the electrical properties

Bending treatments were done with the sprayed ITO coatings of 2.4 and 4.8 mol.% Sn concentration. To examine the influence of the bending process each as-sprayed substrate was cut into four individual smaller pieces which were submitted to the following procedures:

1. Piece one was measured, forming gas (FG) treated, and measured again.
2. Piece two was subjected to tensile bending, measured, FG treated, and measured again.
3. Piece three was subjected to compressive bending, measured, FG treated, and measured again.
4. Piece four was only heat treated without bending under the same heating conditions (650°C for 1.5 h), measured, then FG treated, and measured again.

Fig. 6 shows the resulting sheet resistances, R_{\square} , as a function of the film thickness of samples sprayed with the solution containing 2.4 mol.% Sn. A similar behavior has been obtained with the 4.8 mol.% Sn doping. R_{\square} increases by a factor of 1.8 for layers submitted to compressive bending and by a factor 3 for layers submitted to tensile bending. The samples heated under the same conditions without bending show values between these for most of the investigated thicknesses (factor 2.2). The FG treatment results in a strong decrease of R_{\square} for all four types of samples. The as-deposited samples show a decrease to 0.55 of the initial as-sprayed state. The strongest decrease is observed for the samples subjected to tensile bending (factor 7.2), those ones subjected to compressive bending show a decrease by a factor of 4.6 while the only heated samples show a decrease by a factor of 3.5. It is interesting to note that both types of bent samples exhibit nearly identical results after the reducing treatment with values of sheet resistances lower than those of flat samples directly reduced from the as-sprayed state. The bending and subsequent reducing treatment results in values of about 5–7 Ω_{\square} for film thicknesses between 280 and 430 nm.

Fig. 7 shows a plot of μ versus n of the samples shown in Fig. 6. Samples that have been subjected to the same treatment are surrounded by a circle or an ellipse. As-sprayed samples subjected to tensile bending as well as samples only heated at 650°C exhibit a strong decrease of n and μ ,

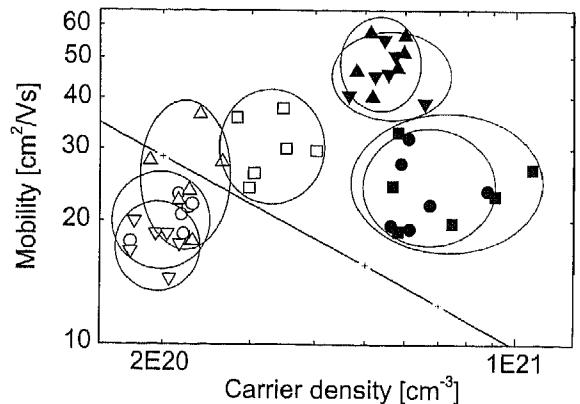


Fig. 7. Log-log plot of mobility μ versus carrier density n of the sprayed ITO layers doped with 2.4 mol.% Sn already shown in Fig. 6 after different bending treatments and after reducing under forming gas at 400°C for 15 min. The symbols are the same as in Fig. 6. The straight line is a plot of the Johnson and Lark-Horovitz law for degenerated semiconductors.

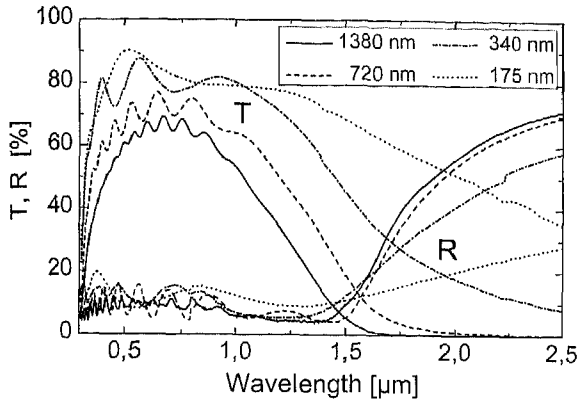


Fig. 8. Transmission T and reflection R versus wavelength of FTO coatings sprayed with 3 wt.% HF for different film thickness.

whereas the compressed coatings show only a decrease in n . It is believed that in compressive bending a closer contact and a higher densification occurs at the contact areas between the crystalline particles in the layer which roughly compensates the decrease in μ detected in the only heated and tensile bent layers.

The observed decrease in n in all cases is probably due to an oxidation of the non-stoichiometric oxide layers subjected to the high temperature of 650°C. This results in a decrease of the number of vacancies in the oxygen sublattice and probably also to an increasing number of excess oxygen atoms situated at interstitial sites in the crystal lattice. These electrically charged excess oxygen atoms lead to ionic scattering centers which decrease the mobility in the ITO films. The subsequent FG treatment reverses this effect and results in a higher oxygen deficiency in the oxygen sublattice than it was present in the initial as-sprayed state. As a consequence n increases from the initial value of $3.5 \times 10^{20} \text{ cm}^{-3}$ to about $6 \times 10^{20} \text{ cm}^{-3}$ for the bent and only heated samples. At the same time the mobility increases significantly for both kinds of bent samples probably because of a decrease of the number of the ionic

oxygen scattering centers in the crystal lattice due to the loss of oxygen ions at the interstitial sites.

3.6. Optical properties

Fig. 8 shows the as measured transmission and reflection curves for sprayed FTO coatings with different thicknesses ranging from 175 to 1380 nm. The transmittance in the visible region is significantly lowered for thicker layers whereas the reflectance in the region $\lambda > \lambda_p$ is increased for thicker layers. The observed plasma-wavelength of all studied FTO coatings is $\lambda_p \approx 1.5 \mu\text{m}$.

In Fig. 9 the optical properties of a 470 nm thick 2.4 mol.% Sn-doped ITO layer are shown in the as-sprayed and reduced state. The transmittance is higher in the optical range ($\approx 80\%$) than for an ATO coating with a comparable thickness ($\approx 72\%$). This indicates a lower absorbance in the ITO layer than in the ATO film. The steep increase in reflection begins at $\lambda \approx 1.8 \mu\text{m}$ (plasma-wavelength) for the as-sprayed ITO coatings. A shift of the reflectance onset of about 400 nm towards shorter wavelengths is observed for ITO coatings after the FG treatment. The reason is an increase in n after the reduction treatment which decreases the value of λ_p following the equation [6]

$$\lambda_p = 2\pi c_0 \left(\frac{ne^2}{\epsilon_0 \epsilon_L m_{\text{eff}}} \right)^{-0.5} \quad (2)$$

where c_0 is the velocity of light and ϵ_0 the permittivity in vacuum, e is the elemental electron charge, ϵ_L the relative dielectric constant of the layer material, and m_{eff} is the effective mass of the free electrons in the electrical conductive layer. A value of $\lambda_p = 1.9 \mu\text{m}$ is obtained for as-sprayed ITO layers by taking $n = 3.2 \times 10^{20} \text{ cm}^{-3}$ and assuming that $m_{\text{eff}} = 0.35 m_e$ and $\epsilon_L = 3$. A value $\lambda_p = 1.3 \mu\text{m}$ is calculated for taking $n = 6.5 \times 10^{20} \text{ cm}^{-3}$ for the reduced state. These calculated values of 1.9 and 1.3 μm agree well with the values for λ_p (estimated by the intersection of the slope of the reflection curves with the x -axis) of 1.75 and 1.4 μm from Fig. 9. The observed values for the plasma-wavelength are nearly independent from the thickness of the coating. The only difference in the optical properties between the 470 nm thick and thinner ITO coatings is the height of the transmission and reflection values for the same wavelengths.

The onset in reflection at shorter wavelengths for the reduced ITO samples also results in higher values in reflection for all wavelengths $\lambda > \lambda_p$. Beyond $\lambda \approx 4 \mu\text{m}$ the IR reflection curves for the 470 nm thick ITO coating in the as-sprayed and reduced state can not be distinguished from each other. Both reflection curves reach a level of about 96% for $\lambda > 5 \mu\text{m}$.

4. Conclusion

A comparison of the electrical and optical properties of spray pyrolyzed FTO, ATO and ITO coatings has been

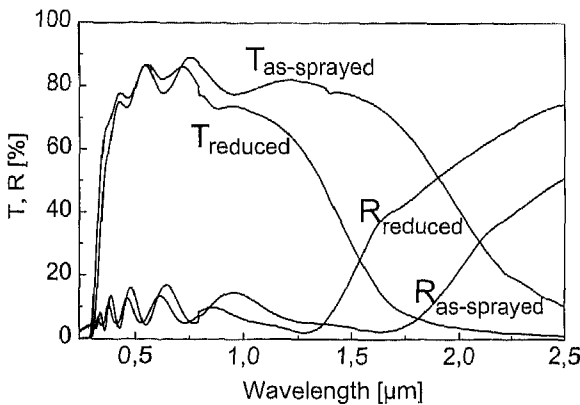


Fig. 9. Transmission, T and reflection, R versus wavelength of a 470 nm thick ITO coating in the as-sprayed state and reduced state after a reducing treatment for 15 min at 400°C in a forming gas atmosphere.

presented. The experimental data show that ITO layers especially after an optimized reduction treatment under forming gas exhibit the best properties i.e. lowest electrical resistivity and highest optical transmission. The reduced ITO layers show a resistivity of only $2.1\text{--}2.8 \times 10^{-4} \Omega \text{ cm}$ which is comparable to the resistivity of sputtered ITO coatings. The sprayed ITO layers show an optical transmittance larger than 80% in the visible range. In comparison sprayed ATO layers show poorest properties. Their resistivity is about $1 \times 10^{-3} \Omega \text{ cm}$ and their transmittance is only $\approx 75\%$ due to a stronger absorption in the ATO layers which also shows a blackening tendency. The FTO layers produced by spraying with an ethanolic solution of organic monobutyltintrichloride show a low electrical resistivity of about $5 \times 10^{-4} \Omega \text{ cm}$ and high transmittance for thickness $< 500 \text{ nm}$. Values of sheet resistances $< 10 \Omega_{\square}$ can be reached for film thicknesses of about 200 nm with reduced ITO coating or 500 nm as-sprayed FTO, respectively.

As-sprayed ITO coatings that are subjected to a bending

process at 650°C show for tensile as well as for compressive bending treatment a strong increase in sheet resistance independent of film thickness. A forming gas treatment is able to decrease these values by a factor of 4.5–7 to small values. These values are even lower than those that are obtained by a direct forming gas treatment of the as-sprayed layers without bending. For thicknesses of about 300 nm sheet resistance values of $< 10 \Omega_{\square}$ can be obtained for both kinds of bending process.

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