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Improvement of transparent conducting materials by metallic grids on transparent conductive oxides

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ABSTRACT

The trade-off between transparency and conductivity in transparent conductors used in optoelectronic devices is a major bottleneck towards higher device performances. Grid deposition on transparent conductive oxides was demonstrated using electrochemical deposition, which has the advantage of a high aspect ratio of 0.45 and the possibility to use very narrow lines. The sheet conductivity was increased more than two orders of magnitude at a transmittance loss of only a few percent. The figure of merit as defined by Haacke was improved with a factor of more than 50.

1. Introduction

Transparent contacts are vital in many optoelectronic devices, but also represent a major part of electrical and optical losses, thereby limiting the performance. Although properties of the transparent conductive oxides commonly used as contacts have improved considerably [1], there are still substantial losses related to their inherent material properties. The major trade-off for transparent conductive oxides (TCOs) is that between transparency and conductivity. TCOs exhibit a distribution of transmittance with the wavelength of light as illustrated in Fig. 1, which depicts the measured transmittance as function of wavelength for SnO_2:F. The different lines in this figure correspond to increasing carrier concentrations, which represent an accordingly increasing conductivity. Highly conductive TCOs generally have the disadvantage of absorbing large fractions of infrared (IR) photons [2]. As the conductivity increases, not only the amount, but also the energy of the absorbed photons increases [3,4]. As the energy of the photons absorbed in the transparent layer increases, the absorbed wavelength range shifts towards the visible and the effective transparency for wavelength range relevant for many optoelectronic devices, i.e. between 400 nm and 1200 nm, decreases.

All transparent conductors show a decreasing trend in transmittance with an increasing conductivity. The relation between the transparency (T) and the resistivity (R_s) of these materials can be described by a rather simple equation containing the ratio of the optical conductivity σ_{op} and the dc conductivity σ_{DC} [5]

$$T = \left(1+\frac{1}{2R_s}\sqrt{\frac{\mu_0}{\varepsilon_0}}\frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2} = \left(1+\frac{188(\Omega)}{R_s}\frac{\sigma_{op}}{\sigma_{DC}}\right)^{-2} \quad (1)$$

In which the free space permeability $\mu_0 = 4\,\pi \times 10–7$ s^2/F m and permittivity $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m. Fig. 2 shows reported values of the transmittance of TCOs, thin metal films and metallic grids as function of sheet resistivity, as well as curves fitted using Eq. (1), with a σ_{DC}/σ_{op} ratio of 500 (representing the various TCOs) and 180 (representing the metal) [6–18]. It can be seen that the TCOs, for which industrial processes are available [19], have a higher transmittance with similar sheet resistance than thin metal films. Reported transmittance values of both continuous metal films and metallic grids were below 80%. Interestingly, the metallic grids seem to have a trend that deviates from Eq. 1, which was derived for continuous films. The data suggests that a wide range of sheet resistances can be covered with only minor difference in transmittance, which contrasts with the trend observed with other materials. This is related to the fact that a fixed line width of 120 nm was used together with line heights of 40 nm, 60 nm and 80 nm, which leads to the different sheet resistances [6]. Moreover it should be noted that the metals gold, aluminum and copper all yielded equivalent results.

The trade-off between transmittance and conductivity has large consequences for optoelectronic devices, such as the efficiency of solar cells. In general for thin film solar cells, the optimum TCO properties lay around 10 Ω/sq at a relatively high transmittance above 85%. This optimum is positioned at the high end of the knee in the transmittance versus sheet resistance plot depicted in Fig. 2.

To minimize electrical losses, a high conductivity (i.e. low sheet resistance) is required, which is not compatible with a high transmittance. The application of a metallic grid can enhance the conductivity of a TCO contact [20]. One example of such metallic grids in applications is CIGS thin film solar cells, which have a surface area of several tens of cm^2 over which the current needs to be collected and use a metallic grid [21,22]. Monolithic integrated solar cells with a conductive grid have also been proposed [23], but little work have been published on this topic [24].

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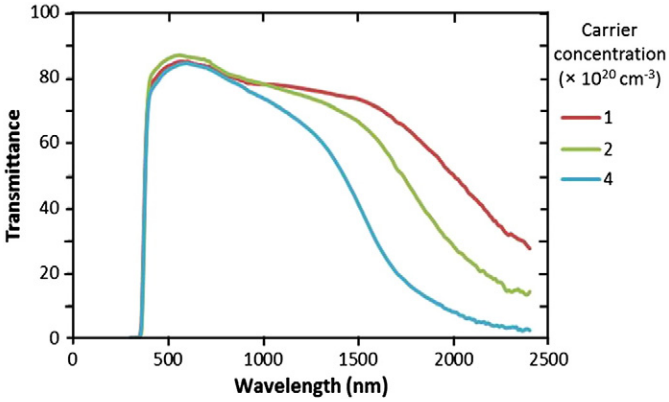

Fig. 1. Transmittance (%) as function of the wavelength for SnO_2:F layers with varying carrier concentration ($\times 10^{20}$ cm^{-3}).

In this paper we show the increased performance by application of a metallic grid on indium tin oxide (ITO) and ZnO:Al (AZO). Furthermore, we demonstrate the application of a grid on a TCO by electrochemical deposition [25].

2. Experimental details

Fluor doped tin oxide, of which the transmittance spectrum is shown in Fig. 1, was deposited on glass with atmospheric pressure chemical vapor deposition with a refitted Watkins Johnsons moving belt reactor. The source gases were monobutyl tin chloride, and water with trifluoroacetic acid as fluor precursor with flows between 0.01 and 0.1 slm, 0.005 and 0.05, and 0.01 and 10 slm, respectively. The temperature was 640 °C and the deposition rate was between 10 nm/s and 100 nm/s.

For grid deposition, commercially sputtered 50 Ω/sq ITO on polymer foil (Southwall Technologies, UK) and 50 Ω/sq AZO on glass (Philips Innovation Services), were used as substrates. Before grid application the ITO and AZO were ultrasonically degreased in iso-propanol for 5 min. The ITO was subsequently etched ultrasonically in 15% HNO_3 for 3 min to improve the adhesion of electrodeposited grids. As a benchmark for technological feasibility a standard commercially available (Microresist Technologies, D) photolithography procedure was used to make grid patterns on the TCO substrates. To prevent TCO degradation, in particular of AZO, during photoresist development, the negative photoresist SU-8 that it is dissolved in an organic solvent, was chosen. Photo masks with perpendicular straight line grid patterns forming squares, with grid line widths of 8, 20, 30, 45 or 60 μm, and a grid line pitch of 0.2, 1 and 2 mm were used. These different grid configurations yield grids with a surface coverage varying from 1 to 20%. Nickel metal was electrodeposited in the photoresist patterns from a commercial bright Nickel Watt's-type solution (Enthone, NL) at a current density of 4 A/dm^2. The applied charge for Ni electrodeposition was chosen such that a grid line thickness of half the lines width, i.e. an aspect ratio of 0.5, would be obtained. Due to some lateral growth over the photoresist film, the actual aspect ratios were about 0.45. After Ni electrodeposition the photoresist film was removed from the TCO. The sheet resistance was measured by four point probe measurements and the values are an average of 20 measurements. The transmittance was determined by a Shimadzu UV-3600 spectrophotometer over a range between 300 nm and 2400 nm, whereas the average transmittance values represent the range between 400 nm and 800 nm.

3. Results

Grid lines were deposited on commercial ITO on polymer foil and ZnO on glass, both with a sheet resistance of 50 Ω/sq. Fig. 3 shows a typical layout of such a grid. For display purposes a relatively wide line width and large pitch is shown. The grids used for this study have dimensions as presented in Table 1. It also shows the transmittance without taking into account optical losses caused by the substrate. The ITO layer is responsible for a transmittance loss of about 6%. The addition of a grid with a 6% coverage (30 μm line width and 1 mm pitch) decreases the transmittance proportionally, while the sheet resistance drops more than 400 times. Extremely low sheet resistances of 0.05 Ω/sq can be obtained with increased grid surface coverage of 20% (20 μm line width and 0.2 mm pitch). However, it is compromised by a considerable loss in transmittance.

Fig. 4a shows a summary of the transmittance values as function of the sheet resistance for 'bare' ITO [9,13–16] and some of the best results for a silver layer sandwiched between TCO layers as reported in the literature [26]. Furthermore, experimental results of metallic grids deposited on top of ITO from our laboratory are presented. The ITO on which the metallic grids were deposited is represented by the data point on the far right with a sheet resistance of 50 Ω/sq. The application of grids on top of this ITO film results in a much lower sheet resistance than obtained for TCO/metal/TCO sandwiches. This is related to the fact that the metal is accumulated on only a small part of the total surface, thereby reducing the impact on transmittance. In contrast to the reported values of grid without TCO [6], these results were obtained with a variety of line widths as shown in Table 1. For such a combination of patterned materials, it is not known whether Eq. (1) gives an accurate representation. Nevertheless, we included a trend line according to Eq. (1) with a σ_{DC}/σ_{op} ratio of 27000 as to make a comparison with the other transparent conductor materials.

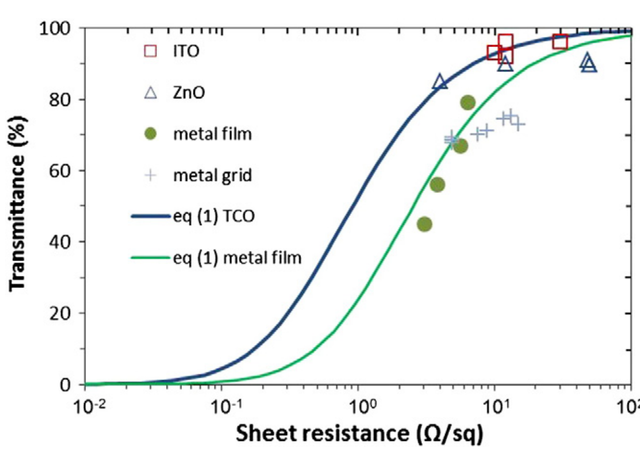

Fig. 2. Transmittance as function of sheet resistance for ITO, thin silver layer and metallic grids by nanoimprinting as reported in the literature [6–18]. Solid are according to Eq. (1).

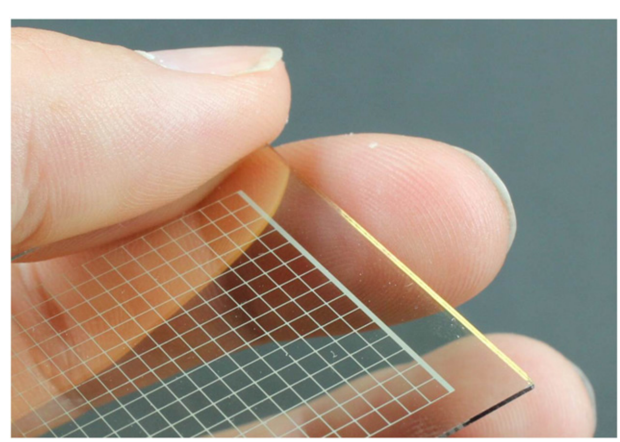

Fig. 3. Photograph of a typical grid layout with relatively wide gridlines.