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Sol-gel deposited aluminum-doped and gallium-doped zinc oxide thin-film transparent conductive electrodes with a protective coating of reduced graphene oxide

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Abstract. Using a traditional sol-gel deposition technique, we successfully fabricated aluminum-doped zinc oxide (AZO) and gallium-doped zinc oxide (GZO) thin films on glass substrates. Employing a plasma treatment method as the postannealing process, we produced thin-film transparent conductive electrodes exhibiting excellent optical and electrical properties, with transmittance greater than 90% across the entire visible spectrum and the near-infrared range, as well as good sheet resistance under 200 Ω /sq. More importantly, to improve the resilience of our fabricated thin-film samples at elevated temperatures and in humid environments, we deposited a layer of reduced graphene oxide (rGO) as protective overcoating. The stability of our composite AZO/rGO and GZO/rGO samples improved substantially compared to that of their counterparts with no rGO coating. © 2016 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.JNP.10.026001]

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1 Introduction

Transparent conductive electrodes (TCEs) are crucial components of optoelectronic devices such as thin-film photovoltaic modules¹⁻³ and touch-screen displays.^{4,5} Among the existing materials, indium tin oxide (ITO) is the most common commercially viable TCE, owing to its good visible light transmittance and excellent electrical conductivity.⁶⁻⁸ However, the diminishing indium supply of the world may not be able to meet the rapidly growing demand for TCEs. In recent years, thin films of zinc oxide (ZnO) containing n-type dopants have been considered as promising substitutes for the ITO material. In particular, aluminum-doped zinc oxide (AZO) and gallium-doped zinc oxide (GZO) have been extensively studied as suitable TCEs for a wide variety of applications. These thin-film electrodes can be deposited via a number of different techniques such as spray pyrolysis,⁹ chemical vapor deposition,¹⁰ molecular beam epitaxy,¹¹ sputtering,^{12–17} and the sol-gel process.¹⁸⁻²³ Long-term stability in ordinary, as well as harsh environments, is necessary for successful commercialization for all applications. However, the electrical conductivity of AZO and GZO thin films suffers from material degradation when these films are exposed to ambient air or harsher environments.^{15,16} Many approaches have been proposed and investigated by various researchers to improve the stability of AZO and GZO thin films under adverse conditions.^{24,25} However, to our knowledge, no one has reported the stability of AZO or GZO thin films protected by a cover layer of reduced graphene oxide (rGO).

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In this work, we deposited AZO and GZO thin films on glass substrates using the sol-gel process, and applied plasma treatment to the deposited films to improve their electrical conductivity. More importantly, to alleviate a well-known degradation problem which afflicts ZnO-based thin film TCEs, we deposited layers of rGO on top of our plasma-treated AZO and GZO films as passivation coating layers. Our rGO-protected AZO and GZO films exhibit significant improvements in stability in ambient air as well as in a harsh environment.

2 Methods

The deposition and annealing of AZO and GZO thin films is described in our previous work.²⁶ In brief, equimolar mixtures of diethanolamine and zinc acetate are dissolved in 2-methoxyethanol at a concentration of 0.5 M. Subsequently, $Al(NO_3)_3$ or $Ga(NO_3)_3$ is added to the solution at 2 or 1 atomic percent (at. %) relative to its Zn^{2+} content (e.g., [Al]/[Al + Zn] = 2% or [Ga]/[Ga + Zn] = 1%), and the solution is stirred for 1 h. The precursor solutions are aged for at least 24 h before spin-coating. Our AZO and GZO thin films are subsequently deposited by repeating the sequence of spin-coating and preannealing processes. Once the films are deposited, they are exposed to low-pressure (i.e., below 5 torr) air plasma in a plasma-cleaner (PLASMA-PREEN-II-862) for 10 min.

In order to deposit the rGO overcoating, an aqueous suspension of graphene oxide (GO) platelets with 0.2 mg/mL concentration is spin-coated (at 1000 rpm for 45 s) atop our solgel deposited and plasma-treated AZO and GZO films. Following the spin-coating of GO platelets, the samples are annealed in a forming gas environment at 180°C for 1 h to (partially) reduce the GO material.

The sheet resistance of our samples was measured by the four-point probe method using a Keithley 2400 Source Measurement Unit. Optical transmittance was measured using a Cary-3000 spectrophotometer, with the bare glass substrate used as baseline. Film thickness was measured by a Vecco DEKTAK 150 profilometer.

3 Results

In our previous work,²⁶ we demonstrated that AZO and GZO thin films prepared by the sol-gel process have extremely poor electrical conductivity (>200 MΩ/sq) before plasma treatment. However, after plasma treatment, these AZO and GZO films exhibit sheet resistances as low as 200 and 130 Ω/sq , respectively. In addition, our plasma-treated AZO and GZO films have over 90% optical transmittance across the visible and in the near-infrared range of wavelengths. A comparison of the various parameters of our sol-gel deposited and plasma-treated thin films versus those reported in the literature is given in Table 1.

 Table 1
 Properties of sol-gel deposited AZO and GZO thin films.

Material	Film thickness (nm)	T (%)	$R_{\rm s}~(\Omega/{ m sq})$	Annealing method	References
AZO (2 at. %)	330	>92	200	Plasma treatment	This work
AZO (1 at. %)	313	>80	130	500°C in air	18
AZO (2 at. %)	200	~90	2200	Laser irradiation	19
AZO (1 at. %)	150	>85	4400	650°C in air	23
GZO (1 at. %)	353	>94	130	Plasma treatment	This work
GZO (2 at. %)	65	91.5	$4.3 imes 10^7$	500°C in air	20
GZO (3 at. %)	200	>80	950	IR lamp + 600°C in vacuum	21
GZO (1 at. %)	200	~85	2.1 × 10 ⁷	550°C in air	22
GZO (1.5 at. %)	200	>85	3300	650°C in air	23

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Improvement in the electrical conductivity of our plasma-treated aluminum-doped and gallium-doped ZnO thin-film samples was accompanied by a change in the morphology of these samples. The scanning electron microscope (SEM) images of our AZO and GZO films, both before and after plasma treatment, are shown in Fig. 1. It is seen in Figs. 1(a) and 1(b) that the AZO/GZO crystalline nanoparticles with sharp and clear boundaries are individually distinguishable before plasma treatment, whereas the plasma-treated samples shown in Figs. 1(c) and 1(d) have sintered and interdiffused nanoparticles across the film's surface. It appears that, during plasma treatment, bombardment by energetic particles causes partial melting followed by merging of the nanometer-sized AZO and GZO particles, thus producing a more homogeneous and fairly continuous thin film. It is this sintering and merging of the nanoparticles that we believe to be responsible for the improvement of the electrical conductivity of our plasma-treated samples.

Previous work has shown degradation of ZnO, AZO, and GZO films due to exposure to heat and/or humidity.^{15,16} This is true of sol-gel deposited as well as sputtered films, even though the latter typically have a more compact structure and are consequently more stable than the former in hot/humid environments.²⁵ In our previous work,²⁷ we have shown that an rGO cover layer can protect a transparent and conductive thin film of copper nanowires (deposited on a glass or plastic substrate) from degradation caused by heat and moisture. In an attempt to improve the stability of our ZnO-based thin-film samples, we spin-coated graphene oxide (GO) platelets in the form of a passivation layer on top of the plasma-treated AZO and GZO films and, subsequently, reduced the GO film in a forming gas $(5\%H_2 + 95\%N_2)$ environment at moderate temperatures (180°C) for 1 h. The effectiveness of partially reducing GO by this particular process has been discussed in our previous work.²⁷ As can be seen in Fig. 2, the resulting films (both AZO and GZO) had slightly lower optical transmittance due to the presence of the rGO coating. The sheet-resistance of the samples after passivation with the rGO layer, however, remained essentially the same as before passivation (<200 Ω/sq).



Fig. 1 SEM images of (a) AZO and (b) GZO films before plasma treatment. The corresponding images after plasma treatment are shown in (c) and (d).

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Fig. 2 Optical transmittance spectra of sol-gel-deposited and plasma-treated thin film TCEs across the visible and near-infrared range of wavelengths. (a) Transmittance spectra of AZO and passivated AZO/rGO samples fabricated on glass substrates; inset: photographs of both samples placed over the OSC logo. (b) Transmittance spectra of GZO and passivated GZO/rGO samples fabricated on glass substrates; inset: photographs of both samples placed over the OSC logo.

To test the effectiveness of the rGO coating as a passivation layer, we stored the samples in an environment with 50% relative humidity at room temperature for a period of 30 days. The sheet resistances of the samples were measured during the test period and normalized to the original values of as-fabricated samples. Normalized plots of sheet resistance versus time for these samples are shown in Fig. 3(a). On the one hand, the electrical conductivity of AZO and GZO samples without rGO coating is seen to have degraded rapidly during the first 7 days, and continued to degrade afterward, resulting in a 50-fold increase in their sheet resistance. On the other hand, samples with rGO passivation coating exhibit significantly improved stability over the entire 30day period; in particular, the sheet resistance of the GZO/rGO sample at the end of the month is less than double its initial value. Another test was conducted under a harsh environment with 80% relative humidity at 80°C for a period of 48 h, and the sheet resistance was monitored every 12 h; the results are shown in Fig. 3(b). Once again, the stability of rGO-coated samples is seen to have improved substantially relative to that of the uncoated samples. Whereas the unprotected AZO and GZO samples showed a 25- and 15-fold increase of sheet resistance, respectively, the sheet resistance of the passivated AZO/rGO sample just about tripled during the same period, while that of the GZO/rGO sample remained essentially intact.

The SEM images in Fig. 4 show the coverage of rGO on the surface of our AZO and GZO samples. Figure 4(a) is a representative view of a typical AZO/rGO sample, in which the rGO passivation layer almost completely covers the surface of the AZO film. The bright ridges seen in this SEM image are wrinkles in the rGO layer. The full and uniform coverage by rGO across



Fig. 3 Normalized sheet resistance versus the time during which the samples were exposed: (a) for days to 50% relative humidity at room temperature and (b) for hours to 80% relative humidity at 80°C.

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Fig. 4 SEM images of: (a) an rGO layer fully covering an AZO thin film sample; wrinkles in the rGO protective sheet are clearly visible in this image. (b) An rGO layer partially covering an AZO thin film sample; sintered and partially merged nanocrystalline AZO particles are visible in the areas not covered by rGO. (c) An rGO layer fully covering a GZO thin film sample; wrinkles in the protective rGO sheet are visible in the image. (d) An rGO layer partially covering the lower-right half of a GZO thin film sample; nanocrystallites of GZO are visible in the unprotected upper left-half of the image.

the surface protects the sample against moisture attacks. Upon closer inspection, however, one finds isolated spots where the AZO surface is not seamlessly covered. Figure 4(b) shows an instance where only a fraction of the imaged region is protected by the rGO layer; where the sample remains unprotected, the nanocrystallites of AZO are clearly visible. Similarly, a GZO thin film fully covered by an rGO layer is shown in Fig. 4(c), and a half-covered region of a GZO/rGO sample is shown in Fig. 4(d).

4 Conclusion

We employed the conventional method of sol-gel deposition to fabricate AZO and GZO thin film TCEs on glass substrates, and applied plasma treatment to these films following deposition. Our best samples are a 1 at. % GZO with sheet resistance $R_s < 130 \ \Omega/sq$, and a 2 at. % AZO with $R_s < 200 \ \Omega/sq$. The AZO and GZO samples prepared in this work both exhibit over 90% optical transmittance across the visible and near-infrared wavelength range. We imaged the fabricated TCEs using a SEM, and observed surface morphology changes due to plasma treatment, which we believe explains the significant enhancement of the electrical conductivity over those samples that were treated solely by thermal annealing. Lastly and most importantly, we deposited an rGO protective layer over our plasma-treated AZO and GZO films for purposes of passivation. The smooth and continuous rGO layer almost completely passivates the AZO and GZO thin films. The rGO-coated TCEs exhibit substantial improvement in sample stability in both ambient air and harsh (i.e., 80% relative humidity at 80°C) environments.

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