Photoemission spectroscopy analysis of ZnO:Ga films for display applications

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We report the physical properties of ZnO:Ga-based films prepared by metalorganic chemical vapor deposition (MOCVD) using ultraviolet and x-ray photoemission spectroscopy (UPS and XPS). In addition, the surface characteristics of the films are modified with a series of cleaning and etching steps. The films were produced in an argon-oxygen atmosphere using metalorganic precursors at low pressure in a rotating disk reactor. The XPS results show a gallium oxide rich layer more than 20 Å on the surface of the as-received MOCVD films, with a small fraction of Zn. This oxide layer is removed by a cleaning and plasma treatment, which enhances the conductivity of the ZnO:Ga films. From UPS, the work function is 4.23 eV after an O_2 plasma treatment. Finally, we report on the surface morphology of the ZnO:Ga films after the cleaning process. The post-deposition treatment of these MOCVD films is important for the improved conductivity that is vital to display applications. [S0734-2101(99)22904-1]

I. INTRODUCTION

An important factor in the performance of most displays is the quality of at least one transparent conductive oxide contact layer. Presently, indium tin oxide (ITO) is predominantly used because it is an accepted standard and has a great deal of invested development. However, for several reasons, including work function, physical stability, and band alignment, ITO is not always the ideal contact layer for a given display technology. Recently, ZnO:Ga has attracted increasing attention as an alternative to ITO as a transparent conductor for solar cells[1] and potentially for displays.[2–4] In addition, ZnO:Ga has been shown to be a near-lattice-matched substrate for GaN-based devices.[5] Further, organic based light emitting diodes which typically utilize ITO as a hole injection layer could benefit from alternative oxides with better aligned electronic states.[6] ZnO:Ga has demonstrated a low resistivity of $<3\times10^{-4}\,\Omega\,\mathrm{cm}$[7] and a high optical transparency of 90%, making it very promising for present and future display applications.[7]

Several reports have utilized photoemission spectroscopy to probe the surface properties of ZnO:Ga.[8–11] Li *et al.* have reported the growth conditions of ZnO:Ga films and physical characteristics, including optical transmission, resistivity as a function of Ga concentration, and secondary ion mass spectroscopy (SIMS).[12] The ZnO:Ga sheet resistance was typically less than $\sim20\,\Omega$/square for Ga concentrations of less than $\sim4\%$. Further, the films are highly transparent in the visible spectrum, greater than 85%. In this report, we discuss the surface properties of ZnO:Ga prepared by metalorganic chemical vapor deposition (MOCVD) using photoemission spectroscopy. We have found that the ZnO:Ga films have a gallium-oxide-rich surface layer that can be easily removed by plasma etching. From x-ray photoemission spectroscopy (XPS), the films have a Zn/O ratio of 0.49 with approximately 5% Ga, which is in agreement with previous measurements.[12] The conductivity of the films is enhanced by more than a factor of 2 upon etching the surface. Further, the work function for ZnO:Ga films was 4.23 eV, somewhat lower than ITO.

II. EXPERIMENTAL PROCEDURES

The ZnO:Ga films were prepared using a Structured Materials Industries, Inc. low-pressure metalorganic chemical vapor deposition (LP-MOCVD) system as shown in Fig. 1. This system employs a vertical high-speed rotating disk reactor (RDR) with radially distributed multigas injectors on its top flange and a separate oxygen injector directly above the sample platter. The high-speed rotating disk can be rotated through 1500 rpm. The combined effect of the substrate rotation and high gas velocity induces laminar, nonrecirculating flow in the system. The substrate was heated by a radiative heater. The metalorganic vapors were carried from steel bubblers with an Ar carrier gas and O_2 to form the oxide. During the deposition, the substrate temperature was 400 °C. The films were doped with Ga to enhance the conductivity. In practice, after deposition, the films were allowed to cool to $<100\,^{\circ}\mathrm{C}$ in the flowing Ar–O_2 atmosphere. The details for the growth conditions, such as gas flows gas ratios, have been published previously.[12] The films thickness was approximately 1 μm.

The ZnO:Ga film properties were measured as a function of surface treatment. The as-received films were processed with and without an O_2 microwave plasma treatment using a plasmatic plasma preen. The films were exposed to an average plasma power of 100 W for 4 min. For all photoemission studies, the treated and untreated samples were transferred in

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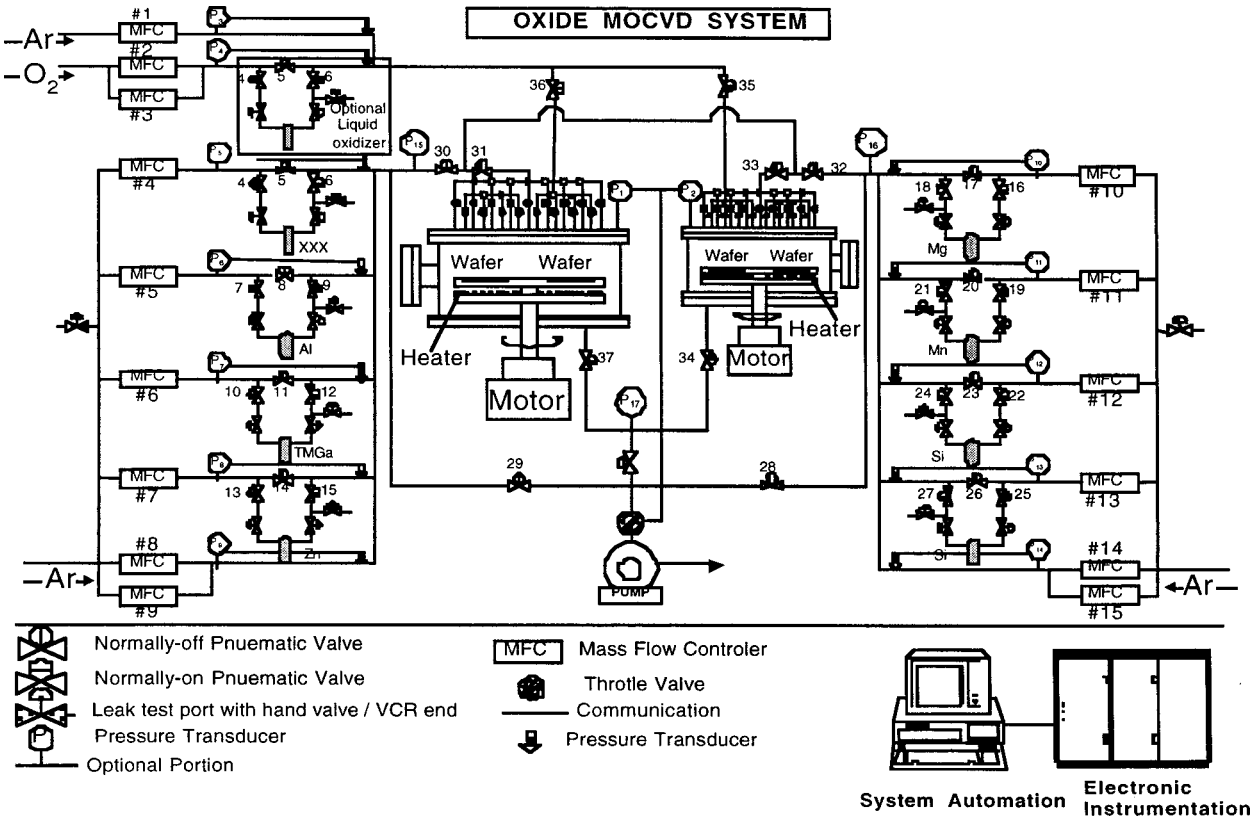

FIG. 1. Generalized schematic of the rotating disk reactor for the low-pressure chemical vapor deposition system. This system was used to prepare the ZnO:Ga-doped films. The details of the reactor and growth can be found in Ref. 12.

air to a sample transfer section of the ultrahigh vacuum (UHV) chamber.

The surface and microscopic properties of the ZnO:Ga films were tested with several analytical tools. The surface composition was determined with nonmonochromatic XPS in an ultrahigh vacuum chamber at a base pressure of 10^{-10} Torr. The x-ray source was a Mg $K\alpha$ line at 1253.6 eV. The XPS was also measured at 75° to normal incidence. Reducing the take-off angle for the photoelectrons by rotating the energy analyzer off normal incidence reduces the probe depth because of the finite mean free path. The effective mean free path changes from ~ 20 Å at normal exit angle to ~ 5.0 Å at 75° from the normal. For ultraviolet photoemission spectroscopy (UPS), He I 21.22 eV discharge emission was used at a base pressure in the high 10^{-9} Torr, due mainly to He. The photoelectrons were detected with an angular resolved energy analyzer. The combined energy resolution of the x-ray source and energy analyzer was 1.2 eV. For UPS, the energy resolution was 0.1–0.2 eV depending on the analyzer pass energy. Finally, the ZnO:Ga surface morphology was measured with a Topometrix Explorer atomic force microscope (AFM) in contact mode.

Using the secondary electron cutoff from UPS, the work function of the ZnO:Ga films was measured before and after plasma treatment. This method[13,14] depends on one experimental parameter, the He I energy of 21.22 eV. The Fermi level of the ZnO:Ga film could not be measured due to the low number of occupied states. Thus, the Fermi level was determined from a thick metal film. As the ZnO:Ga films were properly grounded, the Fermi level of the system is the fermi level of the films. Finally, a -5.00 V bias was applied to the films to shift the secondary electron cutoff.

III. EXPERIMENTAL RESULTS

A. XPS surface analysis before and after plasma treatment

In Fig. 2, the Zn $2p$, O $1s$, and Ga $2p$ core level XPS data are presented for untreated and treated films, with the elec-

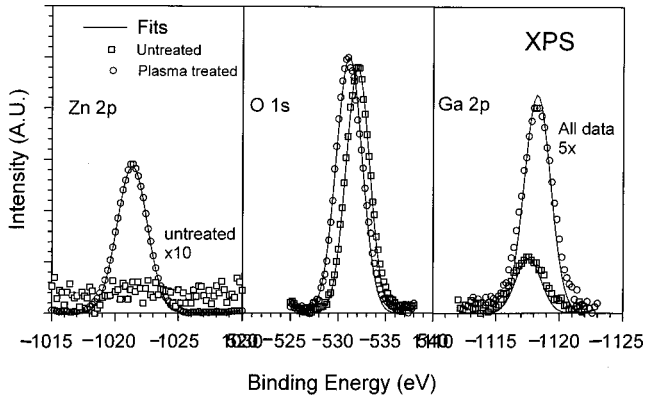

FIG. 2. X-ray photoemission data at normal exit angle for ZnO:Ga films before and after plasma treatment.

TABLE I. Percent concentrations of elements at the surface.

Element	Untreated % 0° to normal	Untreated % 75° to normal	O_2 plasma treated 0° to normal	O_2 plasma treated 75° to normal
Zn 2*p*	0.0%	0.0%	21.5%	18.0%
O 1*s*	30.2%	30.8%	42.5%	43.4%
Ga 2*p*	1.0%	0.0%	4.7%	0.0%
C 1*s*	68.8%	69.2%	31.3%	38.6%

tron energy analyzer at normal incidence. The solid lines are gaussian fits to the experimental data. Each spectrum was scaled by the maximum O 1*s* core level and the corresponding atomic structure factor for each element. The Ga 2*p* spectra were multiplied by 5 to properly observe the spectra within the scale used. From the data shown in Fig. 2, the untreated films present a predominately gallium-oxide-rich surface. After the O_2 plasma treatment, at least 20 Å of the film, the escape depth for photoelectrons, was removed from the surface. Further, the O 1*s* and Ga 2*p* spectra shift to higher binding energy, indicating the bulk oxide is a different oxide than the surface contaminant.

Based on the XPS results, Table I summarizes the composition of the ZnO:Ga films before and after plasma treatment and as a function of the photoelectron exit angle. The plasma treated ZnO:Ga films have a dramatically different surface composition as compared to the as-received films. From the angular-dependent XPS, the treated film composition is uniform through 20 Å, which suggests the surface contaminant is mostly removed by the cleaning and plasma treatment. For the 0° angular XPS measurement, the films have a Zn/O ratio of 0.49 with approximately 5% of Ga. These concentration are in good agreement with previous measurements of similarly grown films, which further confirms the surface contamination is mostly removed by the plasma treatment.[12] At 75°, the Ga signal could not be measured due to the low cross section and relatively low initial concentrations of the Ga in the films. As discussed, the Ga is added to the ZnO films to improve the conductivity. In addition to Zn, O, and Ga, the carbon concentration is reduced from 69% to 31% after plasma treatment. This post-treatment carbon contamination is due in part to the transfer in air from plasma treatment reactor to the UHV chamber. In addition, the residual carbon may result from the chemical reaction during film growth. From the angular-dependent XPS, the carbon concentrations increase from 31% at normal incidence to 39% at 75° suggesting that in part the contaminant is a monolayer on the surface, such as contamination during transfer in air.

We speculate the surface oxide contamination results from the time the samples spends cooling down in an overpressure of Ar and O_2 as well as subsequent handling. Further, some carbon may be due to the starting pressure, which suggests increasing the oxygen concentration during the deposition may be useful. This surface oxide contamination layer is removed with the above described plasma treatment. Here, we have used an O_2 microwave plasma as the ZnO:Ga films to further enhance the work function of the ZnO:Ga films, as observed for ITO.[15]

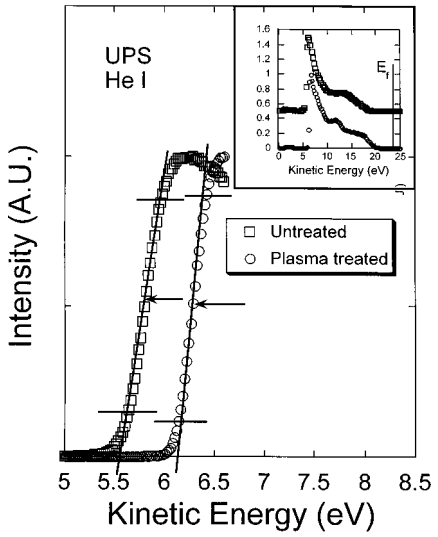

FIG. 3. Ultraviolet photoemission data showing the secondary electron cutoff before and after plasma treatment. The inset in Fig. 3 shows the full UPS spectra.

B. UPS surface analysis before and after plasma treatment

As shown in Fig. 3, the ultraviolet photoemission spectrum is measured for ZnO:Ga films before and after the O_2 plasma treatment. Both films were cleaned with an ultrasonic rinse as described above. In Fig. 3, the inflection point of secondary electron cutoff determines the vacuum level position. The inset in Fig. 3 shows the full UPS data for untreated and plasma treated ZnO:Ga films. In Fig. 4, the valence band tail is plotted along with the fermi level of the system as determined from a thick metal. From Figs. 3 and 4, the work function of the treated ZnO:Ga film is 4.23 eV.

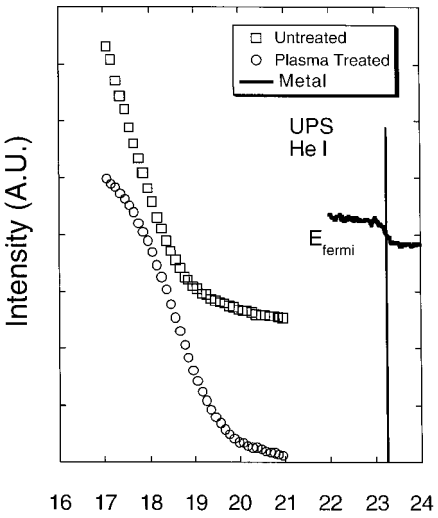

FIG. 4. Ultraviolet photoemission spectroscopy data of the valence band edge before and after plasma treatment.

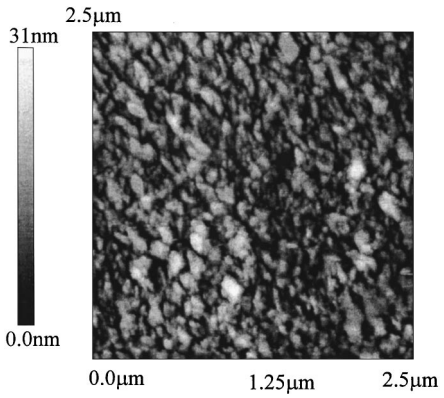

FIG. 5. Atomic force microscopy images of ZnO:Ga films after plasma treatment.

Further, the work function increases after the O_2 plasma treatment predominately due to the removal of the top oxide layers. In addition, O_2 plasma treatment has been shown to increase the increase the work function of ITO.[15] The larger work function is particularly important for organic based light emitting diode applications, where the anode must inject holes into the device.[6]

C. Surface morphology

Prior to taking AFM images, the ZnO:Ga film was cleaned as discussed in the experimental procedure section. In Fig. 5, the contact AFM images of ZnO:Ga films after the O_2 plasma treatment indicate a surface morphology, with an rms roughness of 45 Å. The bar graph to the left of Fig. 5 is a gray scale representation of the *z*-axis height for the AFM image. From the grain sizes in Fig. 5, the ZnO:Ga prepared by LP-MOCVD is a dense film, with few features observable at the scan range used for these measurements. From the AFM images, we do not observe a change in particle growth on the surface, within the spatial regions observed by AFM. However, the plasma treatment may cause microcrystalline changes to the ZnO:Ga films that cannot be observed by AFM.

IV. CONCLUSIONS

ZnO:Ga films were prepared by a Structured Materials Industries, Inc. low-pressure MOCVD reactor. We have measured the surface characteristics of the ZnO:Ga films before and after an O_2 plasma treatment. From XPS, the as-received ZnO:Ga films have a surface layer composition consisting of Ga, O, and C. We speculate this surface layer grows primarily during the cool down period after growth as well as subsequent handling. For XPS, the finite electron mean free path of ~ 20 Å indicates this top oxide layer is at least 20 Å thick. After the films are treated by an O_2 plasma, this top oxide layer is removed and the Zn/O and ratio is 0.49 with less than 5% Ga. The UPS data were used to determine the work function of the ZnO:Ga film. The treated ZnO:Ga film has a work function of 4.23 eV, which is more than 0.4 eV greater than the untreated films. The increased work function is especially important for display applications such as organic light emitting diodes, where holes must be injected from the ZnO:Ga films into an organic layer. Further, the surface treatment reduces the resistance by more than 50%, as measured by four-point probe. This improved resistance is important for all display applications. We believe the enhanced conductivity results from the removal of the top carbon-rich gallium-oxide layer. Further, the plasma treatment may cause some recrystallization of the bulk film. However, the AFM images before and after plasma treatment do not show particle growth. In summary, we have measured the surface properties of a ZnO:Ga film used for display applications. Further, we have found that an O_2 plasma treatment removes a surface layer and improves the overall conductivity of the films.

ACKNOWLEDGMENTS

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