Optical spectroscopic analyses of CVD plasmas used in the deposition of transparent and conductive ZnO thin films

A. Martín, J. P. Espinós, J. Cotrino*, F. Yubero, A. Barranco and A. R. González-Elpe

Instituto de Ciencias de Materiales de Sevilla (CSIC-Universidad de Sevilla). Avda. Américo Vespucio s/n. 41091 Sevilla (Spain)
(*) Departamento de Física Atómica, Molecular y Nuclear. Facultad de Física. Universidad de Sevilla. 41080 Sevilla (Spain)

Abstract

Transparent conducting ZnO:Al thin films have been prepared by remote plasma enhanced chemical vapor deposition. Emission line profiles were recorded as a function of different plasma gas composition (oxygen and hydrogen mixtures) and different rates of precursors (Zn(C₂H₃)₂ and Al(CH₃)$_3$) in the downstream zone of the plasma reactor. Optical emission spectroscopy were used to characterize the oxygen/hydrogen plasma as a function of hydrogen flow rate. The variation of plasma hydrogen content has an important influence in the resistivity of the films.

1. Introduction

Transparent conducting oxides have attracted much attention in several fields like flat panel displays and thin film solar cells[1]. ZnO is a material with a band gap of 3.3 eV that shows and excellent transparency for the entire visible spectrum. Although magnetron sputtering is widely used in the production of transparent conducting layers, the use of remote plasma enhanced chemical vapor deposition (PECVD) is a growing technique in the last years. In this paper we will address issues related to the use of an electron cyclotron resonance slotted antenna (ECR-SLAN) and low resistivity and highly transparent layers have been deposited by remote PECVD. The electric conductivity of ZnO is controlled by intrinsic defect, i.e., oxygen vacancies [2], and/or zinc interstitial [3], which act as n-type donors. The resistivity is lowered further by extrinsic doping with Al [4]. Transparent conducting layers of ZnO doped with Al (called ZnO:Al) are important because of their optoelectronic properties and low cost. Optical emission spectroscopy was applied to study the plasma discharge in oxygen/hydrogen, with different hydrocarbon precursors (Zn(C₂H₃)₂ and Al(CH₃)$_3$), to produced ZnO:Al layers. Control of the resistivity and UV-visible transparency of the films were achieved with hydrogen/oxygen plasma at various substrate temperature. The mass flow rate of precursors is maintained constant (0.25 sccm of Al(CH₃)$_3$ and 5 sccm of Zn(C₂H₃)₂). In an oxygen plasma this precursor flow rate gives the maximum atomic oxygen emission intensity. To get some insight into the plasma processes responsible for the ZnO:Al properties we performed optical emission spectroscopy. From these experiments we conclude that the feedstock ratio oxygen/hydrogen is an important step which determines the structure and properties of ZnO films.
2. Experimental procedure

A large volume microwave plasma source has been used for the production of an oxygen/hydrogen plasma. The plasma is generated in a 2.45 GHz SLAN microwave plasma source, which has been described in detail elsewhere [5], powered by a 2 kW microwave generator. The microwave power is coupled to the plasma inside a quartz bell jar by ten equally spaced slot antenna positioned equidistantly around the inside wall of a cylindrical ring cavity. A total of 10 SmCo magnet stacks are positioned between each slots. The plasma system is mounted directly to a stainless steel chamber. This vacuum chamber is cylindrical in shape (70 cm in diameter and 30 cm in height). Therefore, we are handling with remote plasma enhanced chemical vapor deposition. This plasma reactor that consists of two separated regions, i.e., plasma generation and deposition, can avoid radiation damage and reduce the contamination from the undesirable side reactions in the gas phase. In the upstream region, plasma is generated and in the downstream region, the precursors delivered to the reactor through a dispersal ring, mixed with reactive species generated in the upstream region. Excited species were monitored by optical emission spectroscopy, we used a scanning 0.25 m monochromator (Jobin-Yvon HR250). It is equipped with a holographic grating with 1200 lines/mm, giving a wavelength resolution of 0.1 nm, an a photomultiplier (Hamamatsu R928). Close to the downstream region the light was collected through a hole in the air cooling ring of the SLAN. This hole is separated 7 cm from the ECR layer zone and therefore, is close to the deposition chamber entry. The properties of the ZnO:Al films are significantly affected by the substrate temperature. To clarify the effect of substrate temperature, substrate were heated to a specific, elevated temperature (200-400 °C), prior to deposition and were maintained at that temperature during deposition. The films were deposited over silicon and quartz substrate at different temperatures. The substrate were oriented perpendicular to the gas flow. Optical constants (energy gap, absorbance and refractive index) were determined by transmittance data in the UV-visible region, while resistivities were obtained at room temperature by a in-line four point probe. Composition, texture, microstructure, crystallinity and thickness of the films were characterized by XRF, XPS, FT-IR, RBS, AFM, SEM and XRD. Homogeneous depth distribution of elements were also proved by RBS.

3. Results and discussion

Appearance of the spectra

Before performing detailed studies of the effect of hydrogen on the plasma parameters and on the intensities of particular emission features, typical spectral of oxygen plasma were recorded to identify prominent atomic and molecular emission transitions. The survey spectra extended from 200 to 900 nm. In the middle of Fig. 1 a representative spectra is given. This spectrum is dominated by sharp line features due to emission from atomic oxygen (the intense atomic line 777.3 nm and other less intense lines like 844.5 nm, 435.8 nm, 615.8 nm or 533.07 nm) and several broad O$_{2}^-$ bands. These are bands of the second negative system of O$_{2}^+$ in the region surrounding the 350-400 nm and bands of the first negative system of O$_{2}^+$ between 500 and 700 nm, with sharp peaks near 526, 558, 597 and 638 nm. No evidence of strong O$_{2}^+$ emission was found. Under these conditions the survey spectra thus suggest that the major neutral and ionic species are O and O$_{2}^-$, respectively. In the bottom and upper part of Fig. 1 are shown the influence in the upstream plasma of the introduction of two precursors in
the downstream region. These metalorganic precursors are Al(CH₃)₃ (bottom) and Zn(C₂H₅)₂ (upper). Optical emission spectra of the oxygen plasma with precursor in the downstream chamber exhibit strong emission from H⁺, CO⁺, CO⁺, and OH⁺ in addition to O and O₂⁺ emission. No emission from CH species could be observed. The absence of CH indicates that the oxygen atom density is high enough to react with all the carbon atoms. The optical emission bands observed in the plasma are identified as CO (the third

![Graph showing optical emission spectra](image)

Figure 1. Optical emission spectra of oxygen microwave plasma (b) and the influence of two precursors, Zn(C₂H₅)₂ (a) and Al(CH₃)₃ (c).

positive system and the Angstrom system), OH (the 306.4 nm system), CO⁺ (the comet-tail system) and very sharp lines from atomic hydrogen H (H₅ 656.2 nm, H₆ 486.1 nm, H₇ 434 nm and H₈ 410.1 nm). The molecular bands seen to be more intense in the plasma with Zn(C₂H₅)₂ precursor. The decomposition of hydrogen molecules to hydrogen atoms effectively occurs in the discharge since the spectrum shows the presence of the Balmer lines, with intensities of one-hundredth of that any band. Gas-phase precursors are fragmented by electron, ion, or metastable species impact and also by chemical reactions with gas-phase radicals such as O atoms. These partially decomposed precursors species can physisorb, chemisorb, or diffuse on the substrate surface. The increase of precursor flow corresponds to a decrease in the oxygen atom emissions and an enhancement of the Balmer line emissions. The decrease in atomic oxygen emission is attributed to the consumption of O by oxidation reactions and the increase of Balmer line intensities is likely the result of increased fragmentation of precursors in the downstream zone.
Oxygen/hydrogen plasma

First, only oxygen plasma, with a flow rate of 15 sccm, was used to produced ZnO:Al films and the flow rate of Al(CH₃)₃ and Zn(C₂H₅)₂ was kept constant at 0.25 and 5 sccm, respectively. The gas pressure in the deposition chamber was 0.01 torr and the microwave power was 150 W. Resistivity was high in the ZnO:Al film deposited by oxygen plasma. A decrease of the resistivity with increased substrate temperature above 200 °C has been obtained. Film composition and deposition rate are strongly affected by the ratio of the feedstock gases used (O₂:H₂) and substrate temperature. The addition of hydrogen to the feed results in much better quality thin films than for films deposited without hydrogen. Optical constants (energy gap, absorbance and refractive index) remain with good optical quality with and without hydrogen. Figure 2 shows the film resistivity as a function of hydrogen flow rate. Resistivity was lower in the ZnO:Al film deposited by hydrogen in the plasma. The increase of substrate temperature (200-400 °C) results in a lower value of resistivity. The increase of hydrogen in the plasma correspond to a increase in the Balmer line emissions and a marked decrease in the atomic O emissions. Figure 3 shows the decrease in the atomic oxygen emission (O: 777.3 nm) and a first increase and further decrease of the atomic hydrogen emission (H₆ and H₈) as a function of hydrogen flow rate. Balmer lines are a powerful tools for plasma diagnostics. By using the Balmer lines H₆ and H₈, the electron temperature can be measured and the H₆ line permit to obtain the electron density [6]. The electron temperature and density versus hydrogen flow rate are shown in Fig. 4. Both plasma parameters decrease with increasing hydrogen flow rate. The decrease of electron temperature can be explained with the increase of the net gas pressure and the decrease of electron density is a consequence of the lack of electrons with sufficient energy to ionize.

Figure 2. Dependence of the resistivity on the hydrogen flow rate. Substrate temperature is 200 °C.
Figure 3. Emission intensities of spectral lines of transitions O (777.3 nm) (a) and Balmer lines (b) as a function of hydrogen flow rate. Microwave power is 150 W.

Figure 4. Electron temperature (a) and electron density (b) as a function of hydrogen flow rate for a microwave power of 150 W.

4. Conclusions

Resistivity of the ZnO:Al films deposited with hydrogen and oxygen plasma at various substrate temperature are dependent of the ratio oxygen/hydrogen. When this ratio is
close to the unity the maximum of the Balmer line emissions (Fig.3) and the lower resistivity values (Fig.2) are obtained. Two effects can be considered. First, hydrogen plasma cleaning is effective in removal of impurities. The atomic hydrogen reacted with surface impurities and reaction products were desorbed as a form of volatile compounds. Hydrogen plasma is effective in removing oxygen and carbon impurities and also induces surface roughening which gives favorable adsorption sites for crystalline film growth [7]. Second, hydrogen can cause considerable improvement in the structure of ZnO:Al films prepared by remote PECVD. This behavior is likely the result of gas-phase hydrogen atoms reacting with hydrocarbon radicals. These reactions serve to increase the concentration of carbon precursors in the plasma. The decreasing behavior of plasma parameters (electron density and temperature) versus hydrogen flow rate can explain the existence of an optimal deposition conditions. In this conditions the impinging ions from the plasma enhance the surface mobility of adatoms, thereby leading to an improved crystal quality. Thus, in the thin film, small grains and defects like zinc interstitials and oxygen vacancies are formed.

References