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Effect of doping elements on ZnO etching characteristics with $CH_4/H_2/Ar$ plasma

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Abstract

Effect of doping elements on the etching characteristics of doped-ZnO (Ag, Li, and Al) thin films, etched with a positive photoresist (PR) mask, and an etch process window for infinite etch selectivity were investigated by varying the CH_4 flow ratio and self-bias voltage, V_{dc}, in inductively coupled $CH_4/H_2/Ar$ plasmas. Increased doping of ZnO films decreased the etch rates significantly presumably due to lower volatility of reaction by-products of doped Li, Ag, and Al in $CH_4/H_2/Ar$ plasmas. The etch rate of AZO (Al-doped ZnO) was most significantly decreased as the doping concentration is increased from 4 to 10 wt%. It was found that process window for infinite etch selectivity of the doped ZnO to the PR is closely related to a balance between deposition and removal processes of *a*-C:H (amorphous hydrogenated carbon) layer on the doped-ZnO surface. Measurements of optical emission of the radical species in the plasma and surface binding states by optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS), respectively, implied that the chemical reaction of CH radicals with Zn atoms in doped-ZnO play an important role in determining the doped-ZnO etch rate together with an ion-enhanced removal mechanism of *a*-C:H layer as well as $Zn(CH_x)_y$ etch by-products.

Keywords: Doped-ZnO; Plasma etching; Inductively coupled plasma; XPS; OES

1. Introduction

As the increasing demand for digital information appliances continue, in particular, flat panel displays (FPD) including thin film transistor liquid-crystal display (TFT-LCD), plasma display panel (PDP), and organic light emitting diode (OLED) are increasingly under mass production or development stage. During fabrication of those devices, transparent conductive oxide (TCO) layer is used as an electrode transparent to visible light. For this purpose, ITO (indium tin oxide) has been used for the most of applications [1–3]. The greatly increasing use of TCO films for solid-state display devices has promoted research and development works on inexpensive TCO materials such as Al-doped ZnO and tin oxide (SnO_2) for the replacement of ITO that has some issues related to its cost and degradation of its properties upon plasma exposure [4,5]. Because ZnO or Al-doped ZnO has a good transmittance at the range of visible and IR, electrical conductivity, processibility at reduced temperature and low cost, recently there have been extensive research activities on ZnO or Al-doped ZnO for large-area display devices [6]. From the manufacturing viewpoint, TCO films including ZnO or doped-ZnO should be easily etched for formation of fine electrodes. Patterning of doped-ZnO is also required for the fabrication of other devices such as optoelectronic devices. Therefore, dry etch characteristics of ZnO and doped-ZnO films need to be investigated.

One concern in using $CH_4/H_2/Ar$ chemistry for ZnO dry etching is that *a*-C:H (amorphous hydrogenated carbon) or CH_x polymer-like layers can be easily deposited, in which the excessive deposition of *a*-C:H films on the surface of ZnO film can impede a continuous etching reaction. The *a*-C:H layers deposited during ZnO etching, therefore, can limit the process window in which the ZnO layer is continuously etched. However,

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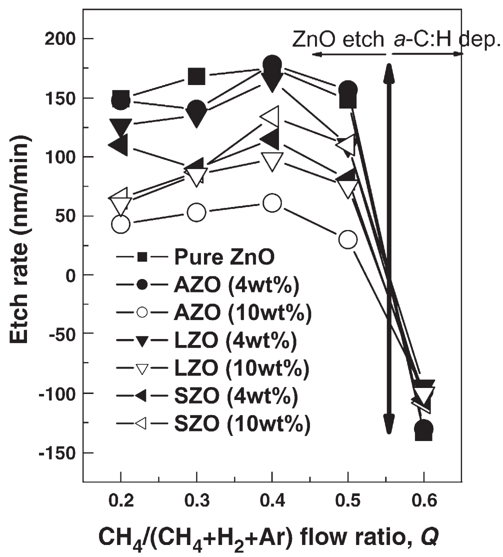

Fig. 1. Etch rates of pure ZnO and doped-ZnO as a function of the $CH_4/(CH_4+H_2+Ar)$ gas mixing ratio, Q, at a fixed Ar flow rate of 20 sccm.

the previous research works have not reported a detailed investigation on the process window during the doped-ZnO etching using $CH_4/H_2/Ar$ chemistry [7,9,10]. Our group has showed that an infinite etch selectivity of pure ZnO layer to PR could be obtained in the $CH_4/H_2/Ar$ inductively coupled plasma (ICP) [11].

There have been also no detailed research works on the etch selectivity to the mask materials during doped-ZnO dry etching. Some research works had utilized metal masks such as NiCr and Cr instead of photoresist [8,12] and in case of using photoresist mask the etch selectivities of doped-ZnO to the PR have not been reported in detail. [7,9,12]. In this work, ICP etching studies of doped-ZnO using $CH_4/H_2/Ar$ gas chemistry were carried out in order to investigate the effect of doping on the etch characteristics of the ZnO layers.

2. Experiment

A modified commercial 8-inch inductively coupled plasma (ICP) conductor etcher having a 3.5 turn spiral copper coil on the top of chamber separated by a 1cm-thick quartz window and a turbo pump backed by a dry/booster pump was used in this experiment [11]. An rf power of 13.56 MHz was applied to the top electrode coil to induce ICP. Bottom bias electrode power of 13.56 MHz was applied to the substrate holder to induce a bias voltage to the wafer. Doped-ZnO thin films with the thickness of 300 ~ 350 nm and different metal(Al, Li, and Ag) doping concentrations were prepared on 10 × 10 mm^2 Si wafer substrates by RF magnetron sputtering and photolithographic patterning of a positive photoresist (PR) mask (AZ 7220) on doped-ZnO/Si substrates was followed. The samples are attached on the 8-inch Si wafer placed on the 8-inch wafer chuck. The backside temperature of the wafer chuck during etching was held at 18 °C.

Plasma etching of doped-ZnO thin films was investigated by varying the gas flow ratio and bottom electrode power. Etch rates of patterned doped-ZnO thin films and deposition of *a*-C:H layers were measured by the field emission scanning electron microscopy (FE-SEM) operating at an acceleration voltage of 10.0 kV. In order to understand the etching mechanism of doped-ZnO, optical emission spectroscopy (OES) are used in orde1r to investigate the species in the plasma and X-ray photoelectron spectroscopy (XPS) in order to examine the chemical binding states and composition of the etched doped-ZnO surface. A multi-channel optical emission spectrometer (Ocean Optics) with the spectral range of 270 ~ 900 nm was used for an analysis of the optical emission from the radicals in the plasma. Species with optical emission are monitored as the peak intensities of characteristic optical lines. The emission line at CH (431.4 nm) and H1 (486.12 nm) were mainly monitored in the work. After the etched samples were removed from the etching system they were exposed to the atmospheric environment for 1 day prior to XPS analysis. The surface binding states of etched doped-ZnO thin films were investigated using an XPS system (AES-XPS ESCA2000). The XPS Mg (Kα) source provides nonmonochromatic X-rays at 1253.6 eV. XPS narrow scan spectra of all the interesting regions were recorded with 20 eV pass energy in

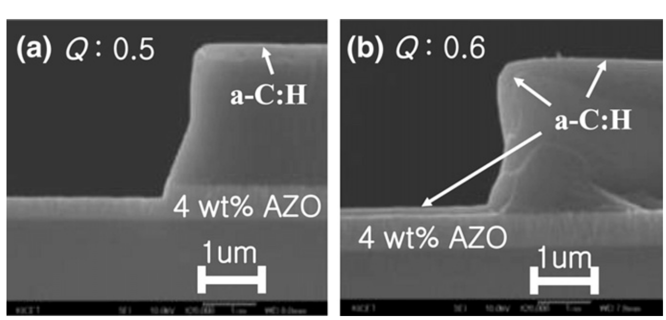

Fig. 2. FE-SEM images of the etched Al-doped ZnO (4 wt % AZO) films at the $CH_4/(CH_4+H_2+Ar)$ gas mixing ratio, Q, of (a) 0.5 and (b) 0.6 at a fixed Ar flow rate of 20 sccm.

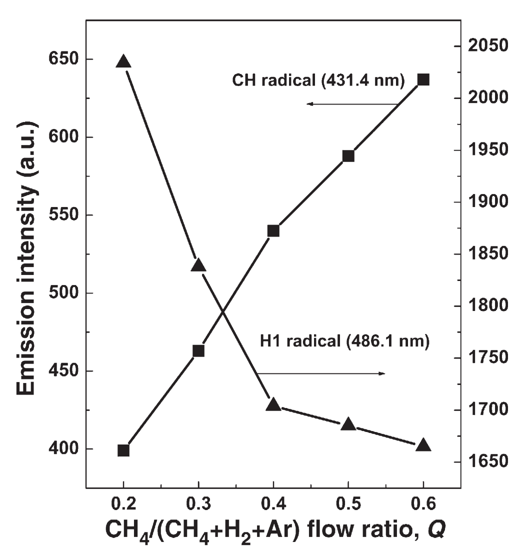

Fig. 3. Optical emission intensity of CH radicals and H1 radicals by OES as a function of the $CH_4/(CH_4+H_2+Ar)$ gas mixing ratio, Q, at a fixed Ar flow rate of 20 sccm.