

Dry etching of bulk single-crystal ZnO in CH₄/H₂-based plasma chemistries

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Abstract

The effect of inert gas additive (He, Ar, Xe) to CH₄/H₂ discharges for dry etching of single crystal ZnO was examined. The etch rates were higher with Ar or Xe addition, compared to He but in all cases the CH₄/H₂-based mixtures showed little or no enhancement over pure physical sputtering under the same conditions. The etched surface morphologies were smooth, independent of the inert gas additive species and the Zn/O ratio in the near-surface region decreases as the mass number of the additive species increases, suggesting preferential sputtering of O. The plasma etching improved the band-edge photoluminescence intensity from the ZnO for the range of ion energies used here (290–355 eV), due possibly to removal of surface contamination layer.

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1. Introduction

Zinc oxide is a wide bandgap semiconductor material with many promising properties for blue/UV optoelectronics, transparent electronics, spintronic devices and sensor applications [1–6]. It has been commonly used in its polycrystalline form for over a hundred years in a wide range of applications: facial powders, ointments, sunscreens, catalysts, lubricant additives, paint pigmentation, piezoelectric transducers, varistors, and as transparent conducting electrodes [7–11]. Recent improvements in the growth of high quality, single crystalline ZnO in both bulk and epitaxial forms has renewed interest in this material [12–21]. ZnO has numerous attractive characteristics for electronic and optoelectronic devices. It has direct bandgap energy of 3.37 eV, which makes it transparent to visible light and operates in the UV to blue wavelengths. The exciton binding energy is ~60 meV for ZnO, as compared to GaN, ~25 meV; the higher exciton binding energy enhances the luminescence efficiency of light emission. ZnO has exhibited better radiation resistance than GaN for devices used in space and nuclear applications [15,16]. ZnO can be

grown on inexpensive substrates, such as glass, at relatively low temperatures. Nanostructures, such as nanowires and nanorods, have been demonstrated [22,23]. These structures are ideal for detection applications due to its large surface area to volume ratio. One main attractive feature of ZnO is the ability for bandgap tuning via divalent substitution on the cation site to form heterostructures. Bandgap energy of ~3.0 eV can be achieved by doping with Cd²⁺ [24], while Mg²⁺ increases the bandgap energy to ~4.0 eV [25].

Etching processes are crucial steps in device fabrication to form features and patterns. Numerous wet etchants have been reported for ZnO, including NH₄Cl, HNO₃/HCl and HF [26–29]; however, little is known about its dry etching characteristics and the associated mechanisms and effects on the optical properties of the material. Some initial results have appeared on plasma etching of sputter-deposited thin films [27,30], while plasma-induced damage from high ion density Ar or H₂ discharges was found to increase the conductivity of the near surface of similar samples and lead to improved n-type ohmic contact resistivities [30]. Initial results have shown that CH₄/H₂/Ar, Cl₂/Ar and BCl₃/Ar plasma chemistries are capable of ZnO etch rates of <0.3 μm/min at room temperature [30–32].

In this paper, the etching characteristics of high-quality, bulk single-crystal ZnO in inductively coupled plasmas (ICP) of CH₄/H₂ discharges with additives of He, Ar or Xe were studied.

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The effects of the gas additive were determined by etch rate measurements and by examining the effect on the luminescence efficiency and near-surface stoichiometry of the ZnO.

2. Experimental

The bulk, wurtzite(0 0 0 1) ZnO crystals from Cermet were nominally undoped ($n \sim 8 \times 10^{16} \text{ cm}^{-3}$, mobility $190 \text{ cm}^2/\text{V s}$ at 300 K from Hall measurements). Photoresist masked and unmasked samples were exposed to CH_4/H_2 discharges in a Unaxis 790 ICP reactor. We used inert gas additives of He, Ar or Xe to determine the effect of ion bombardment on the etch rates and near-surface properties of the ZnO. The 2 MHz power applied to the ICP source was held constant at 300 W, and the rf (13.56 MHz) chuck power at 200 W. The source power controls the ion density while the rf chuck power affects the ion energy. Etch rates were obtained from stylus profilometry measurements while PL spectra were obtained at 300 K using He–Cd laser excitation. Auger electron spectroscopy (AES) surface scans were used to determine the near-surface stoichiometry. The samples were fastened to a stainless steel mount using carbon paint. The sample mount was placed in the system load-lock, inserted into the analytical chamber and aligned to the focal point of the cylindrical mirror analyzer. Secondary electron imaging was used to locate and record areas of analysis. A survey spectrum (a plot of the first derivative of the number of electrons detected (c/s, i.e. counts/second) as a function of energy (eV, i.e. electron volts)) was used to determine the composition of the outer few nanometers of each sample. Elemental quantification was accomplished by using elemental sensitivity factors. A Physical Electronics 660 Scanning Auger Microprobe Electron Beam at 10 keV, $0.3 \mu\text{A}$, 30° from sample normal was used for the data collection, while for profiling the ion Beam conditions were 3 keV Ar^+ , $2.0 \mu\text{A}$, $(4 \text{ mm})^2$ raster with sputter rate $86 \text{ \AA}/\text{min}$ (SiO_2). Prior to AES data acquisition, secondary electron images (SEIs) were obtained from each sample. The SEIs were used to document analysis areas and surface morphology.

3. Results and discussion

Fig. 1(top) shows the ZnO etch rates as a function of the percentage of inert gas additive in the total gas flow rate of CH_4 , H_2 and the inert species. Except for the case of He addition, the effect of adding the inert species to the CH_4/H_2 is a very small increase in etch rate. However, the rates with these gas mixtures are still comparable or lower to that with pure sputtering in the inert gas plasma. The pure Xe plasma produces the highest rate, consistent with the heavy mass of its ions. The data in Fig. 1 are consistent with the etching being dominated by the physical component, with little or no chemical enhancement under these conditions where the average ion energy ranges from ~ 290 to 355 eV, as determined from the sum of plasma potential and the dc self-bias. The latter is shown at the bottom of Fig. 1.

The SEIs in Fig. 2 show that there was no apparent roughening of the ZnO surface during etching with any of the CH_4/H_2 -based mixtures. This was confirmed by the atomic

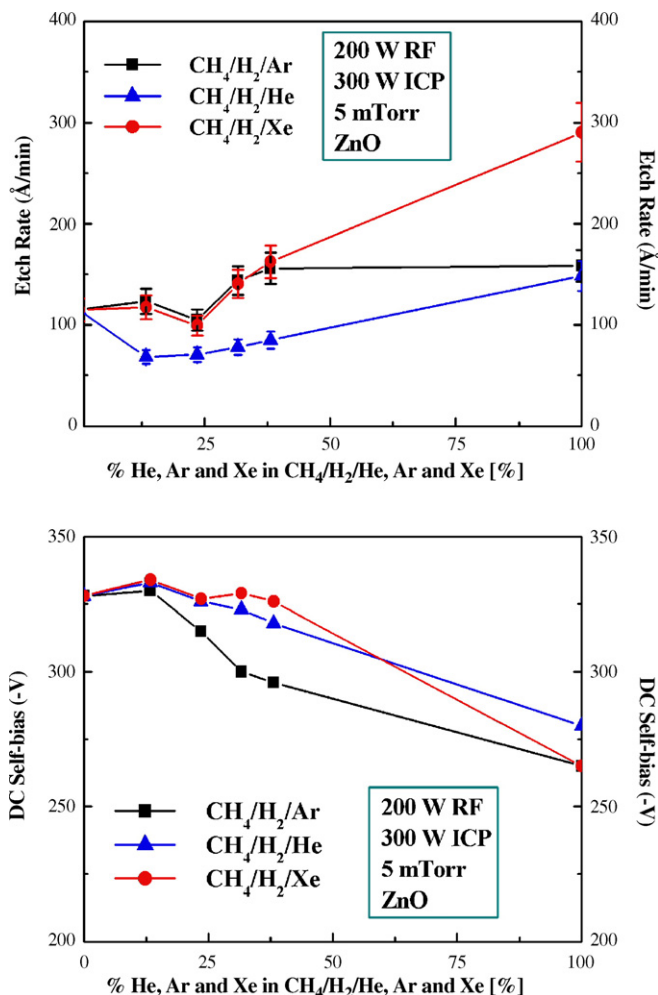


Fig. 1. Etch rate of ZnO (top) and dc self-bias (bottom) as a function of inert gas percentage in the gas flow of CH_4/H_2 discharges.

force microscopy scans shown in Fig. 3, where the root-mean-square roughness of the etched surfaces was comparable to that of the unetched control sample. Thus, the conditions employed here lead to slight Zn enrichment of the surface as determined by chemical profiling discussed below but do not create the extreme condition of Zn droplet formation as is seen in materials such as InP during etching in CH_4/H_2 where In droplets may form due to preferential loss of P [33].

AES surface scans from the ZnO before and after etching in the CH_4/H_2 mixtures with addition of either He, Ar or Xe are shown in Fig. 4. The carbon is adventitious and results from exposure of the sample to atmosphere during transfer to the AES analysis chamber. Table 1 summarizes the near-surface stoichiometry derived from this data. The carbon concentration in all cases falls within the range seen for adventitious exposure and does not result from decomposition of the methane. The clear trend obvious in the data is the decrease in Zn/O ratio as the mass of the inert gas additive increases. This suggests that the preferential loss of oxygen by sputtering by the inert gas ions is the mechanism for the change in surface stoichiometry.

Fig. 5 shows the AES depth profiles obtained from the ZnO before and after etching with the three different mixtures. The preferential loss of oxygen is confined to the top 50 \AA of the

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