Enhancement of gas response of ZnO micro-nano structured layers through plasma treatment

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Abstract. Layers of ZnO micro-nano structures were deposited on quartz substrates and subsequently plasma treated in O₂ and N₂. It was found that exposure to O₂ plasma enhanced gas response to ethanol vapor of the ZnO layers by a factor 8, while exposure to N₂ plasma deteriorated the gas response. This enhancement of the gas response upon O₂ plasma treatment was attributed to the formation of nanocrystallites of ZnO on the original ZnO micro-nano structures which form the gas sensing layers. The surface chemical state of the original sample was found to be not affected by the O₂ plasma while it was modified by the N₂ treatment.

Introduction

Micro and nanostructures of ZnO, a metal oxide semiconductor, have been widely studied due to their ease of fabrication and their potential applications in catalysis [1] (e.g. photocatalytic oxidation of volatile organic compounds), in gas sensing [2,3] and in hydrogen storage [4]. Tetrapods were the first micro-nano structures of ZnO to be synthesized [5], and their gas sensing properties have been recently investigated [2,6,7]. In previous reports [6,7], we have proposed a method to fabricate on a quartz substrate a three dimensional network of tetrapods and demonstrated its potential use in gas sensing of ethanol vapor. In an effort to further improve and control the sensitivity of ZnO micro-nanostructured materials, we proposed to apply surface modification to micro-nano structures of ZnO [8]. We found that, in contrast to N₂ plasma, treatment with O₂ plasma resulted in an enhancement of gas responses. Unfortunately, the mechanism for this enhancement could not be clarified. In this report, we investigate changes in the gas response with the duration of the plasma treatment and discuss the gas response enhancement in reference to surface morphology observed by SEM, microstructure observed by TEM and surface chemical state determined by XPS, with a view to improving our understanding of this gas response enhancement.

Experimental procedure

ZnO micro-nano structured layers are prepared via a thermal oxidation reaction in wet air from Zn powder (Nilaco, 99.999 % purity) placed in a quartz test tube heated in a furnace at 900 °C. The detail of the layer fabrication method is described in previous reports [6-8]. The layers are deposited on quartz substrates (10×10 mm²) using a concentration of water vapor of 10 g/m³ for which micro-nanostructured layers can be formed.

The fabricated layer samples are plasma treated in a Reactive Ion Etching (RIE) system as illustrated in Fig. 1. The RIE system has a parallel-plate type plasma reactor (SAMCO RIE-10NR) and is operated at a RF frequency of 13.56 MHz. The process parameters used in this study are as follows: an applied RF power of 200 W, a gas flow of 100 sccm and a gas pressure of 100 Pa. Our samples are treated in pure O₂ and N₂ plasmas.

The morphologies of the samples prior to and after plasma treatments are investigated using a Scanning Electron Microscope (FE-SEM JEOL JFM-7000F operated at an acceleration voltage of 10
kV). Detailed changes in the microstructure of the plasma treated micro-nano ZnO are analyzed by Transmission Electron Microscope (TEM JEOL 2000EX with an acceleration voltage of 200 kV). The TEM samples are prepared by immersing the layers in alcohol, then detaching some of the ZnO microstructures by using an ultrasonic bath, and finally scooping the ZnO microstructures from suspension by using a Cu mesh covered with a C film.

X-ray Photoelectron Spectroscopy (XPS) data are collected on a Rigaku XPS7000. The XPS system base pressure is $5 \times 10^{-7}$ Pa and the sample surfaces are grounded to minimize charge accumulation at the surface created by the photoemission process. The binding energy scale was calibrated using photoelectron peak of the carbon contamination (C 1s with energy of 285.0 eV).

The gas sensing properties of the samples are characterized by measuring the change in resistance of the samples upon exposure to ethanol vapor. The detailed procedure for gas sensing is described elsewhere [6,7]. In this study, the operating temperature of the measured samples is set at 400 °C and the samples are exposed to a constant gas flow of 0.7 L/min with an ethanol concentration of 130 ppm. Samples are exposed to cycles of pure air, ethanol vapor and pure air during which the sample resistances are monitored. The response to ethanol vapor of the micro-nanostructured films is defined as the ratio between the resistance in air and the resistance in ethanol vapor.

For the O$_2$ plasma treatment study, two micro-nano ZnO layers are fabricated under the same conditions and used separately in the gas sensing experiments and in the SEM observations, so as to prevent SEM observation from contaminating the surface of layers used in gas analysis. The XPS data is recorded on the sample used in the gas sensing experiment after gas exposure. Both samples were plasma treated with the total exposure durations of 2, 10, 20, 30 and 60 min. The destructive TEM observation is performed on the sample treated by O$_2$ plasma for 60 min. The same process sequence is used for the N$_2$ plasma treatment.

![Fig. 1: Schematic of the RIE system used to process the samples.](image1)

![Fig. 2: Ethanol response as a function of O$_2$ plasma exposure duration.](image2)
Results and discussion

Fig. 2 shows the variation of the gas response of the fabricated ZnO layer with the exposure duration of the O$_2$ plasma treatment. It is clear from the figure that the response to gas is enhanced by the plasma treatment and the response improvement saturates for a plasma treatment duration of about 30 min. This observed enhancement of the response upon O$_2$ plasma exposure is remarkable as it corresponds to a maximum improvement by a factor 8 of the sensor response. It should be noted that
the opposite effect is observed for the N₂ plasma treatment, namely, the sensor response is deteriorated upon N₂ plasma treatment.

The surface morphological changes induced by the O₂ plasma treatment is seen on the SEM images of Fig. 3. The plasma treatment results in surface roughening, the degree of which increases with the plasma exposure duration. It is also found (images not shown) that the surfaces corresponding to the crystallographic planes {10-10} require a longer plasma treatment to obtain equivalent roughening degree with other surfaces. The {10-10} crystallographic planes are the main surfaces of the ZnO tetrapods which constitute our sensing layers [7]. Thus the effect of the plasma duration on the sensor response can be related to the slow surface roughening of the {10-10} crystallographic planes of the ZnO tetrapods forming our sensing layers.

The TEM images in Fig. 4 reveals the formation upon O₂ plasma treatment of about 10 nm size crystals on the surface of the tetrapod legs, which are known to consist of single crystals [6]. The crystalline state of the observed nanograins on the tetrapod leg of Fig. 4 is inferred from the irregular shape of the grains, which tend to exhibit sharp edges, an indication for the formation of a crystalline phase.

Finally, the analysis of surface chemical states by XPS reported in Fig. 5 shows that the O₂ plasma treatment does not change the surface chemical state of the original ZnO layers, while the N₂ plasma treatment shifts the Zn 2p XPS peaks by 1 eV toward higher binding energies and broadens the peak widths (half-width at half-maximum) by 0.2 eV, both effects providing evidence for an increase in defect density upon N₂ plasma treatment.

Gas response enhancement upon O₂ plasma treatment is also observed on wet chemically grown ZnO layers exhibiting a nanoflower-like structure. This strongly suggests that the reported enhancement is not related to a specific micro-nano ZnO structure (e.g. the tetrapod studied in this report), but rather to the modification of the surface of the ZnO crystals making up the sensing layers.

From the above results, it may be concluded that the enhancement of the sensor response upon O₂ plasma treatment is most likely explained by the formation of a nanostructured surface consisting of ZnO nanocrystals having size of about 10 nm.

Conclusion

It is found that the gas response to ethanol of micro-nano structured ZnO layers is enhanced by a factor 8 upon exposure to an O₂ plasma. Conversely, surface treatment in an N₂ plasma of the same type of layers results in deteriorated gas responses. The gas response enhancement upon O₂ plasma treatment can be correlated to the formation of ZnO nanocrystals on the surface of the original ZnO tetrapod structures. The very small size of the ZnO crystallites, about 10 nm in diameter, is thought to be a major factor in the gas response enhancement, because the formation of nanocrystallites promotes space charge effects and increases the density of surface defects such as kink sites.

References