



Reversible band gap tuning of metal oxide films using hydrogen and oxygen plasmas

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ABSTRACT

We report an approach to the reversible tuning of the band gaps of metal oxide (MO) films. ZnO and CuO, synthesized by hydrothermal methods, were treated with hydrogen and oxygen plasmas. From UV-visible transmittance spectra, we have found that the optical band gaps of MO films blue-shifted with hydrogen plasma treatment, but red-shifted with oxygen plasma treatment. By alternating the treatment sequences of hydrogen and oxygen plasmas, the MO optical band gap values can be reversibly fine-tuned with the tunable ranges of 80 and 550 meV for ZnO and CuO, respectively. The mechanism for reversible tuning of optical band gaps is proposed based on the results of optical emission, X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy characterization. Compared to conventional metal ion doping and high temperature annealing methods, the use of room temperature hydrogen and oxygen plasmas for tuning band gaps is more environmentally friendly.

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1. Introduction

Metal oxides (MOs) have been the hot topics of research and development in recent years [1]. In particular, zinc oxide (ZnO) is a well-known n-type semiconducting and piezoelectric material with wide and tunable direct band gap energy of 3.37 eV and high exciton binding energy (60 meV) [2]. Copper oxide is also an important p-type semiconductor. There are two crystalline forms of copper oxide: cuprous oxide (Cu₂O) with a higher band gap (2.1 eV) and cupric oxide (CuO) with a lower band gap (1.2 eV) [3]. The unique optoelectronic properties, chemical resistance, and thermal stability of MOs have attracted a great deal of interest in the applications such as transparent conductors [4], solar cells [5], chemical and gas sensors [6], and photocatalysts [7].

Device applications of MOs often require the band gaps to be tuned in specific ranges. The commonly used hydrothermal [8–11] and sol-gel synthesis methods [12,13] are effective processes to prepare various nanostructures of MOs. However, in order to achieve specific band gap values, doping process is often used. The conventional chemical doping method for tuning the band gap of MOs often brings pollution issues to the environment and is energy- and time-consuming. Particularly, the scarce-resourced, toxic, and environmentally hazardous rare-earth/transition metals are often used in doping processes [14–18]. Besides, chemical doping is irreversible and has a low precision of tuning optical properties when repeated. MOs doped with other kinds of metals also reflect problems in energy consumption due to high temperature annealing

processes required to improve crystal quality and reach desired band gap values [19–21].

Plasma is a non-equilibrium system composed of various kinds of neutral and charged particles. Due to the mass difference between electrons and molecules, electron temperature T_e ($\sim 10^4$ K) is much higher than gas temperature T_g (300–500 K) of neutral gas molecules at low pressures (0.1–100 Pa). Typical radio-frequency (rf) plasma operated at 100–1000 Pa has relatively low T_g but high T_e [22].

In this work, instead of using conventional metal ion doping and annealing methods, we adopted room temperature plasma treatment as a post-synthesis approach to fine-tune the band gaps of two kinds of MOs (ZnO and CuO) at room temperature. The low temperature plasma method used in this work has the advantages of convenience, less time-consuming, environmentally friendly, with water as the product, repeatability, reversibility, and provides a wide and flexible range for band gap tuning.

2. Experimental details

MOs were synthesized by conventional hydrothermal methods. ZnO was grown by the hydrolysis of zinc nitrate (Zn(NO₃)₂) in water with the addition of hexamethylenetetramine according to the procedures reported by Vernardou et al. [8]. The solution and the Si substrate was placed in Pyrex glass bottles with polypropylene autocleavable screw caps and heated at a constant temperature of 95 °C for 2 h in an oven. The samples were then thoroughly washed with deionized water in order to eliminate residual salts, and dried in air at 95 °C. CuO was synthesized by mixing CuSO₄·5H₂O with NH₄OH aqueous solution following to the method reported by Wang et al. [10]. After being stirred for 15 min, NaOH solution was added into the previous solution. After being stirred for 20 min, the precipitate was heated in an oven at 60 °C

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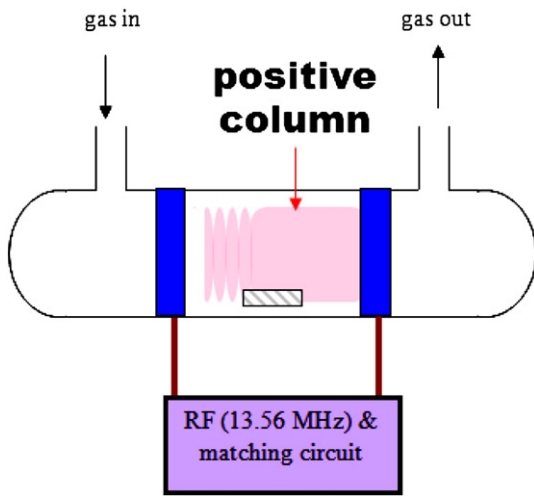


Fig. 1. Experimental setup for the plasma treatment of metal oxides.

for 3 h, and the resulting black-brown CuO nanowires were collected, washed several times using distilled water, filtered, and dried in an oven at 80 °C for 5 h. The synthesized MO nanocrystals were deposited on silicon wafers ($1 \times 1 \text{ cm}^2$).

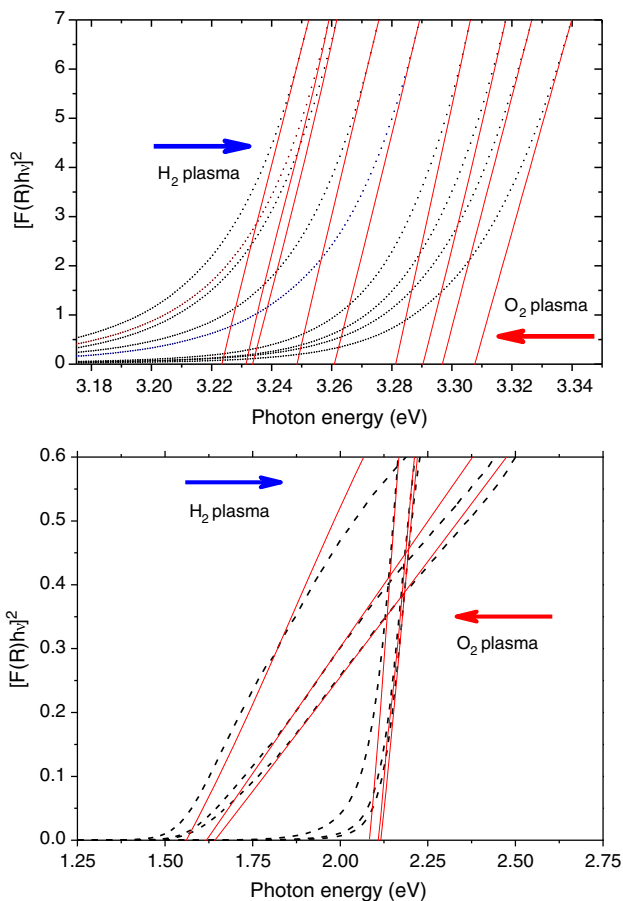


Fig. 2. Typical plots of optical absorption coefficients converted from reflectance spectra of MOs versus photon energy (top: ZnO; bottom: CuO). In general, the curve redshifts with O_2 plasma treatment, but blueshifts with H_2 plasma treatment. The optical band gaps were determined by extrapolating the linear portion of each curve.

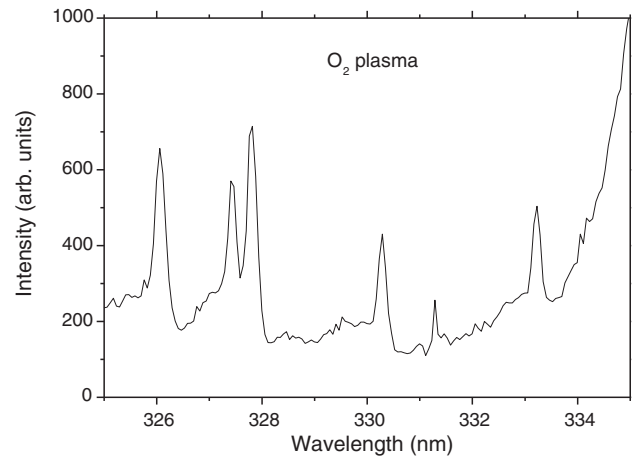
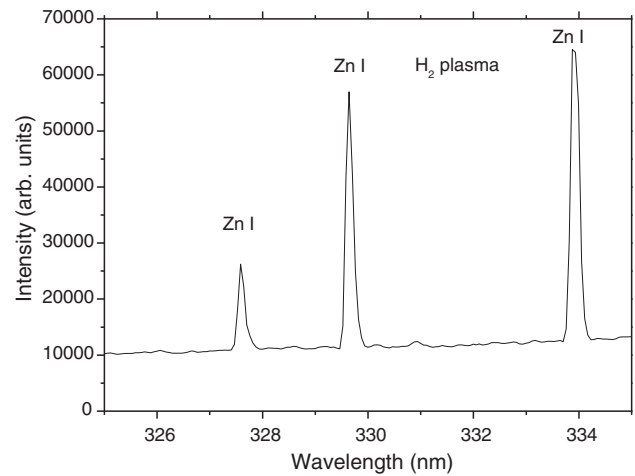


Fig. 3. Top: optical emission spectra of atomic Zn in H_2 plasma; bottom: no atomic Zn emission lines are observed in O_2 plasma. The weak lines are due to O atoms and other impurities.

The MO samples were placed at the center (positive column) inside a Pyrex discharge tube of 1 in. in diameter for plasma treatment (Fig. 1). O_2 and H_2 plasmas were produced using an rf power source (Hüttinger, PFG300RF, 13.56 MHz, 50 W) by mixing carrier gas He (99.995%, flow rate = 100 sccm) with O_2 (10 sccm) or H_2 (10 sccm) at pressure around 100 Pa. Optical emission from the plasma was directed to a scanning monochromator (Jobin Yvon, 600 lines/mm, blazed for 330 nm) by an optical fiber. The slit width was fixed at 0.01 mm. The exposure time of a thermo-electric-cooled CCD (Jobin Yvon) was varied from 500 ms to 10 s to optimize the signal-to-noise ratio. A UV–visible spectrometer (Jasco, V-675) was used to measure the absorption, transmittance, and reflectance of MO films.

X-ray diffraction (XRD) using a PANalytical X'Pert Pro(MRD) PW3040/60 diffractometer, in Bragg–Brentano geometry, with Cu radiation (K_{α} ; $\lambda = 0.154 \text{ nm}$) operated at 40 kV/40 mA and a detector (PANalytical X-celerator) was carried out to characterize the crystalline structures of MO films. Scanning electron microscopy (SEM, Hitachi S4700 II, operating voltage = 15 kV) was used to inspect the surface morphology change of plasma-treated MOs. X-ray photoelectron spectroscopic (XPS) analysis was performed using K-Alpha XPS (Thermo-Fisher scientific). X-ray source are Mg K_{α} ($h\nu = 1253.6 \text{ eV}$) and Al K_{α} ($h\nu = 1286.6 \text{ eV}$). Beam energy and beam current are 10–15 kV and 5–30 mA, respectively. The position of the carbon C 1s peak (284.6 eV) was taken as a reference. Peak fitting was performed with the Origin 8 software.

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