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## Reactive Sputtering of Plasmonic Pt/ZnO Films for Decomposition of Gas-Phase Methanol under Visible Light

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The preparation of ZnO films by a versatile and effective facing-target sputtering method under various sputtering pressures is described. The ZnO films are coated with an ultrathin (2 nm) Pt layer through dc diode sputtering to form hybrid Pt/ZnO photocatalytic films. Interestingly, the Pt/ZnO films show an efficient visible-light photoresponse for the decomposition of gas-phase methanol owing to the unique surface plasmon resonance of the Pt film.

Over the past few decades, ZnO has attracted considerable attention as a promising photocatalyst for water and air purification.<sup>[1,2]</sup> ZnO is one of the most suitable materials for the photocatalytic process under illumination with ultraviolet light; the typical electron mobility in ZnO is 10-100 times higher than that in TiO<sub>2</sub>, which leads to a reduced electrical resistance and enhanced electron transfer efficiency.<sup>[3]</sup> ZnO can be prepared through several chemical and physical methods such as sol-gel methods,<sup>[4,5]</sup> ultrasonic spray pyrolysis,<sup>[6]</sup> metal organic chemical vapor deposition,<sup>[7,8]</sup> pulsed laser deposition,<sup>[9,10]</sup> and sputtering methods.<sup>[11-13]</sup> Among them, reactive sputtering deposition has shown more advantages including control of the preferred crystalline orientation, growth at a relatively low temperature, no need for post-calcination, good interfacial adhesion to the substrate, and a high packing density of the grown film.[14,15]

The major disadvantage of ZnO is its high bandgap of 3.2 eV, excited by light in the UV region, which is only about 3-5% of the solar spectrum reaching the earth's surface. For the effective and practical utilization of solar light, it is necessary to modify the ZnO material to obtain a visible-light photoresponse. Many methods have been used to extend its photoresponse region, such as nonmetal species doping,<sup>[16-19]</sup> dye sensitization,<sup>[20,21]</sup> the use of hybrid semiconductors,<sup>[22,23]</sup> and

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so on. Among these methods, noble metal coating is a promising approach because of the excellent chemical and photochemical stability obtained, especially its unique surface plasmon resonance.<sup>[24-26]</sup> However, the amount of noble metal used should be as low as possible in the coating process owing to the scarcity and high cost of these materials.

Recently, some metal oxide films such as  $TiO_{2}$ ,<sup>[27]</sup>  $WO_{3}$ ,<sup>[28]</sup> and Fe<sub>2</sub>O<sub>3</sub><sup>[29]</sup> films have been prepared successfully through the reactive sputtering technique,. In addition, ZnO films under different mixed gas ratios were also prepared, and their photocatalytic activities under UV light illumination were discussed in our previous paper.<sup>[30]</sup> In this study, the reactive sputtering technique is used to deposit ZnO films with two facing Zn metal targets at a fixed gas ratio of Ar/O<sub>2</sub>=6:4 under various sputtering pressures (Ps) of 0.1, 0.5, 1.0, and 3.0 Pa. The prepared ZnO films are coated with an ultrathin Pt layer (thickness 2 nm) to enhance the photocatalytic activity and extend the photoresponse region to visible light. Sputtering at room temperature is a simple and scalable method that allows the circumvention of postannealing or liquid deposition procedures that can induce corrosion of the ZnO, but offers good control of the deposited material quantity, repartition uniformity, and attachment.

Gas-phase methanol is used as the target molecule for photocatalytic decomposition. Methanol is a common indoor air pollutant, and is harmful to human health. In addition, methanol is one of the simplest C–H–O molecules, and with the help of Fourier-transform infrared (FTIR) spectroscopy, the photocatalytic mechanism of methanol decomposition can be analyzed easily. Although the photocatalytic activities of ZnO films have been studied extensively, to the best of our knowledge, there has been no report on sputtering Pt/ZnO films for gas-phase photocatalytic application under visible light illumination.

A schematic diagram of the reactive system is shown in Figure 1. The two Zn metal targets facing each other were separated by a distance of 100 mm, and the substrates were placed at a distance of 50 mm from the middle of a straight line connecting the centers of the target planes. Zn rectangular plates (68 mm long, 48 mm wide, 3 mm thick, purity 99.9%) and glass slides were used as targets and substrates, respectively. After the sputtering chamber was evacuated to a background pressure below  $2 \times 10^{-4}$  Pa, the ZnO films were deposited reactively at a dc input power of 100 W. A series of samples was prepared at various *Ps* values from 0.1 to 3.0 Pa. The ultrathin Pt layer of about 2 nm in thickness was coated on the surface of the as-deposited ZnO films with an auto fine coater



Figure 1. Schematic diagram of the reactive sputtering system.

(FESEM, Zeiss SigmaHV) by controlling the sputtering current (20 mA) and time (30 s).

The film thicknesses of all the ZnO films were measured with a DEKTAK surface profiler with different sputtering times (Figure S1 in the Supporting Information). The sputtering time and film thickness showed a linear relation, and the sputtering rates were calculated for different *Ps* values (inset in Figure S1). For comparison of the photocatalytic activities of the ZnO films, they were prepared with the same thickness of 500 nm at different *Ps* by controlling the sputtering time.

The crystal structures of the ZnO films were characterized by grazing incidence X-ray diffraction (GIXRD) using an X-ray diffractometer (Shimadzu XRD-6000) with a CuK<sub> $\alpha$ </sub> source in the range  $2\theta = 20-90^{\circ}$ . Figure 2 shows the GIXRD patterns of ZnO films deposited at different *Ps*. It can be seen that all the peaks of the samples are in good agreement with the wurtzite structure (JCPDS card, No. 36-1451).<sup>[31]</sup> No characteristic peaks are observed for any other impurities. The clear and sharp diffraction peaks also reveal that the deposited ZnO film is of high quality. The preferred orientation does not change with the different part of the structure of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the preferred orientation does not change with the different part of the pa



**Figure 2.** GIXRD patterns of ZnO films prepared at different sputtering pressures. The inset shows the Debye–Scherrer analysis of ZnO crystal size.

ferent Ps values; the (002) diffraction peak is the dominant orientation, and the crystalline intensity depends on Ps. With increasing Ps, both peaks of (002) and (103) increase in intensity and sharpness. The crystal structure of the (002) direction may be explained from the reaction of  $Zn^{2+}$  and  $O^{2-}$ , and the concentrations of Zn<sup>2+</sup> and O<sup>2-</sup> are much higher if high-energy electrons produce O<sup>2-</sup> ions through inelastic collisions, as reported by Shibata.<sup>[32]</sup> The formation of the crystal structure of the (103) pattern is the result of the reaction between neutral Zn and neutral O2. The increase in the (002) peak intensity at high Ps may be explained by the fact that with increasing Ar partial pressure, the ionization of Zn increases and an excess of neutral O<sub>2</sub> is produced. This contributes to the increase in intensity of both the (002) and (103) patterns. For assessment of the quality of the thin films, the full-width at half-maximum (FWHM) values of the (002) peak and the crystallite dimension were estimated according to the Debye-Scherrer equation, as given in Equation (1), in which D is the crystallite dimension,  $\lambda$  is the wavelength of X-ray radiation (CuK<sub>a</sub>=0.15406 nm),  $\theta$  is the diffraction angle, and  $\beta$  is the FWHM.<sup>[33]</sup>

$$D = 0.94\lambda/\beta\cos\theta \tag{1}$$

The relationship between Ps and crystallite dimension is shown in the inset of Figure 2. As Ps increases from 0.1 to 3.0 Pa, the grain size increases. According to Equation (1), the mean crystallite sizes vertical to the *c* axis are 14.01, 15.51, 16.09, and 20.68 nm at Ps values of 0.1, 0.5, 1.0, and 3.0 Pa, respectively.

The surface morphologies of ZnO films were analyzed by field-emission scanning electron microscopy (FE-SEM) (JEOL, FE-SEM 6700). The FE-SEM images presented in Figure 3 allow



Figure 3. FE-SEM images of ZnO film prepared at different sputtering pressures: A) 0.1 Pa, inset is the EDS of Pt/ZnO films, B) 0.5, C) 1.0, and D) 3.0 Pa at low magnification, and a) 0.1, b) 0.5, c) 1.0, and d) 3.0 Pa at high magnification.

the investigation of the effect of different *Ps* values on the ZnO film surface. The FE-SEM images of the ZnO film prepared at higher *Ps* show relatively larger individual grain sizes, and the grain boundaries are clearer. With increasing *Ps*, more Ar atoms attack the Zn metal target, and more  $Zn^{2+}$  is excited, whereas the mobility of  $Zn^{2+}$  is slow at high pressures, causing the slow reaction rate of the  $Zn^{2+}$  and O atom, as shown by the sputtering rate results in Figure S1. The slow reaction rate and high  $Zn^{2+}$  concentration cause the larger grain size. The Pt/ZnO films show the same surface morphology as the ZnO

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films because of the ultrathin thickness of the Pt layer. This result is in good agreement with the analysis of the XRD characteristics. In addition, the ultrathin Pt layer cannot be identified in the SEM images, but the corresponding energy dispersive spectrum (EDS, equipped with FESEM) proves its existence (Figure S2).

The optical properties of ZnO films and Pt/ZnO were measured with a Jasco V-550 spectrophotometer at room temperature in the wavelength range 300–900 nm. Figure 4 shows the

![](_page_2_Figure_4.jpeg)

**Figure 4.** a) Optical transmittance spectra of the ZnO and Pt/ZnO films at different sputtering pressures; b) the bandgap determination of ZnO and Pt/ZnO from curves of  $(\alpha h \nu)^2$  versus h $\nu$ .

variation in transmittance of the ZnO and Pt/ZnO films prepared at different *Ps* values of 0.1–3.0 Pa. The Pt/ZnO films show a much lower transmittance at wavelengths of 400– 900 nm than the ZnO films for all the different *Ps* values, which indicates that the ultrathin Pt film enhances the visible-light absorbance of the ZnO films. This result implies the possibility of visible-light photocatalytic applications of Pt/ZnO films.

The optical absorption edge of the ZnO and Pt/ZnO films is around 380 nm. For a direct transition, the optical bandgap ( $E_g$ ) of the ZnO film is determined using Equation (2) in which  $\alpha$  is the absorption coefficient and h $\nu$  is the energy of the incident photon.<sup>[34]</sup>

$$\alpha(h\nu) \propto A(h\nu - E_g)^{1/2}$$
 (2)

According to Equation (2), the bandgap of the as-deposited ZnO film is measured to be about 3.26 eV. All the ZnO samples exhibit nearly the same optical edge, which indicates that the variation in pressure had no significant effect on the optical absorption edge. After Pt deposition, the Pt/ZnO films showed a weak redshift of the optical edge, which agreed well with previous reports that the plasmonic absorption of Pt lies in the UV and blue wavelength region.<sup>[35, 36]</sup>

The photocatalytic decomposition of methanol (5  $\mu$ L) in the gas phase was evaluated by FTIR spectroscopy (JASCO 480 plus), by measuring the concentration decay in a cylindrical cell (9.8 cm length and 3.6 cm width) containing the Pt/ZnO samples of surface area 2.5×6.7 cm. A schematic diagram of the photocatalytic gas cell is shown in Figure 5. The photocata-

![](_page_2_Figure_12.jpeg)

Figure 5. Schematic diagram of the photocatalytic reactor.

lytic degradation of methanol is performed under irradiation by an artificial sunlight simulator of 100 mW cm<sup>-2</sup> (model: SET-140F, Seric LTD, Japan) with filter cutting from 420 to 780 nm for visible light, and from 350 to 780 nm for UV+visible light.

Figure 6a shows the FTIR spectra of methanol decomposition as a function of irradiation time under visible light illumination. The undissociated methanol shows bands at 1015. 1055, 2855, 2972, and 3680  $\text{cm}^{-1}$  at an irradiation time of zero. The double bands at 1015 and 1055 cm<sup>-1</sup> are attributed to the C-O and C-H stretching regions. The bands at 2855 and 2972 cm<sup>-1</sup> correspond to the symmetric and asymmetric vibrations of the methoxy group (CH<sub>3</sub>O<sup>•</sup>), respectively.<sup>[37,38]</sup> The band observed at 3680 cm<sup>-1</sup> could be assigned to the OH stretching mode of intermediate species probably present at room temperature.<sup>[39]</sup> On the basis of the experimental data, we illustrate the variation in the peak heights of bands in Figure 6b. With the increasing irradiation time, the bands at 1015, 1045, 2860, 2950, and 3685 cm<sup>-1</sup> start to decrease in intensity and new peaks appear at 669, 933, 1169, 1456, 1645, 1760, and 2350 cm<sup>-1</sup>. The bands at 1169 and 1760 cm<sup>-1</sup> can be assigned to the C-O and C=O stretching vibration modes, respectively.<sup>[40,41]</sup> The band at 1456 and 1645  $cm^{-1}$  can be assigned to the out-of-plane asymmetric bending of C-H and isolated C= C, respectively.<sup>[42,43]</sup> Notably, the absorption bands at 1015, 1055, and 3680 cm<sup>-1</sup> almost disappear after 3 h of irradiation, whereas the bands at 2855 and 2972 cm<sup>-1</sup> are still present with decreasing intensities. Gaseous CO<sub>2</sub> is a linear molecule with two infrared-active absorption bands at 2350 cm<sup>-1</sup> (antisymmetric stretching mode) and 669  $cm^{-1}$ (bending

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![](_page_3_Figure_2.jpeg)

**Figure 6.** a) Decomposition of methanol on Pt/ZnO films as a function of irradiation time; ZnO films were deposited at 0.1 Pa with a fixed gas ratio of 6:4 under illumination with visible light. b) Variation in peak heights of different bands. c) Variation in peak height at 2350 cm<sup>-1</sup> corresponding to the normal vibration of  $CO_2$  molecules derived from the FTIR transmittance spectra with irradiation time on Pt/ZnO film at different sputtering pressures under illumination of visible light and UV + visible light. d) Histogram of rate constants (*k*) on Pt/ZnO films: A) 0.1 Pa, UV + vis light, B) 0.1 Pa, visible light, C) 0.5 Pa, UV + vis light, G) 3.0 Pa, UV + vis light, H) 3.0 Pa, visible light.

mode).<sup>[44,45]</sup> Hence, one can conclude that the primary two peaks centered at 2350 and 669 cm<sup>-1</sup> imply the formation of CO<sub>2</sub> gas upon methanol decomposition.

Figure 6 c shows the CO<sub>2</sub> transmittance peak height (2350 cm<sup>-1</sup>) of Pt/ZnO films deposited at different Ps under illumination of visible light and UV+vis light. It is observed that the variation in the photocatalytic activities of the Pt/ZnO films depends on the Ps value. With increasing Ps, the photocatalytic activity of the Pt/TiO<sub>2</sub> films decreases under both visible light and UV+vis light. The experimental data in Figure 6c are found to fit approximately a pseudo-first-order kinetic model by the linear transforms  $f(t) = f_{inf}[1 - \exp(-kt)]$  (f is the peak height,  $f_{inf}$  is the peak height at infinite time, and k is the rate constant). The values of the rate constant, k, and regression coefficient are plotted in Figure 6d. The pure ZnO did not show any decomposition of methanol under visible light (Figure S3). The visible light contribution in the photocatalytic processes on the Pt/ZnO is over 50%, which can be ascribed to the surface plasmon resonance effect of Pt on the ZnO films.

As *Ps* decreases, the photocatalytic activity of the Pt/ZnO film is enhanced. The improvement in the photocatalytic activities of Pt/ZnO films deposited at low pressures may be caused by the different surface morphology and crystal structure, as indicated by the results of SEM and XRD analysis. The grain

size increases with increasing *Ps*, which results in a lower active surface area, and prohibits the surface from forming better connections with the Pt thin layer. At high *Ps*, the high concentration of  $Zn^{2+}$  reacts with O atoms, which increases the oxygen vacancies in the formed ZnO film. Similar results have been reported regarding a decrease in photocatalytic activity with an increasing number of oxygen vacancies.<sup>[46,47]</sup>

The photocatalytic decomposition mechanism under visible light is also discussed in this paper. The presence of the ultrathin Pt layer enhances the absorbance of the ZnO film in the visible region and effectively transfers the photogenerated electrons and separates the photoelectrons and photoholes, which restrain the recombination of photogenerated charge carriers, and therefore improve the photocatalytic activity of the as-deposited ZnO films. As indicated in Figure 6a,b, the oxidative pathway of CH<sub>3</sub>OH may undergo the processes shown in Equations (3) to (10) on Pt/ZnO films.

$$e^- + Pt \rightarrow Pt^-$$
 (3)

$$\mathsf{Pt}^- + \mathsf{O}_2 \to \mathbf{O}_2^- \tag{4}$$

$$ZnO + h\nu \rightarrow h^+ + e^- \tag{5}$$

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 $e^- + O_2 \rightarrow {}^{\bullet}O_2^{-} \tag{6}$ 

 $2 \operatorname{CH}_3 \operatorname{OH} + 2 \operatorname{h}^+ \to \operatorname{CH}_2 \operatorname{OH} + \operatorname{CH}_3 + \operatorname{H}_2 \operatorname{O}$ (7)

 $^{\bullet}CH_{2}OH + ^{\bullet}O_{2}^{-} \rightarrow HCHO + ^{\bullet}OOH^{-} \rightarrow HCOOH + OH^{-}$ (8)

 $\mathrm{HCOOH} + 2\,\mathrm{h^+} \rightarrow \mathrm{CO_2} + 2\,\mathrm{H^+} \tag{9}$ 

 $\mathrm{H^{+}} + \mathrm{O}\mathrm{H^{-}} \to \mathrm{H_{2}O} \tag{10}$ 

In summary, the Pt coating, even an ultrathin film, significantly enhances the photocatalytic activity and extends the photoresponse of ZnO films to visible light owing to its unique surface plasmon response. The photocatalytic activity of the Pt/ZnO films is affected by the value of *Ps*. The Pt/ZnO film prepared at the lowest *Ps* shows the highest visible-light photocatalytic activity. FTIR spectra were used not only to evaluate the photocatalytic activity but also to analyze the photocatalytic mechanism. The visible-light contribution in the methanol photocatalytic decomposition processes on Pt/ZnO is over 50%.

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![](_page_5_Figure_4.jpeg)

**Plasmon resonance**: Photocatalytic films of ZnO coated with ultrathin (2 nm) Pt (see figure) are prepared by a sputtering method, and the Pt/ZnO films show an efficient visible-light photoresponse for the decomposition of gas-phase methanol owing to the unique surface plasmon resonance of the Pt film.