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Photoreaction of a ZnO gel film chemically modified with β-diketones

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Chelate formation is confirmed by a red shift of the $n \rightarrow \pi^*$ absorption peak of benzoylacetone (BzAcH) from 309 to 336 nm with its addition to a sol containing Zn^{2+} ions. The chelate bonds between Zn^{2+} and $BzAc^-$ are mostly maintained in the gel film prepared from the sol. Irradiation of the gel film by a Xe lamp with a cut filter ($\lambda_{ex} > 300$ nm) in the presence of H_2O leads to decomposition of the chelate ring. As a result of the photolysis, ZnO–H groups, CH_3CHO and other carbonyl compounds are generated with the lost of CH_3 groups of the $BzAc^-$ ligand and H_2O involved in the film. INDO/S calculations on a model complex (Zn(BzAc)(OEt)) assign the $n \rightarrow \pi^*$ absorption to the electronic transition from a non-bonding molecular orbital (MO) distributed mainly at the phenyl group to an anti-bonding MO localized at the CO bonds. On the basis of these results, a photo-induced hydrolysis mechanism was presented to explain the formation of positive-type patterned ZnO films. *© 2003 Kluwer Academic Publishers*

1. Introduction

Sol-gel methods using metal alkoxides as a starting material are quite useful for preparing various functional thin films at relatively low temperatures. Particularly, chemical modification with β-diketones, which suppresses hydrolysis and condensation of the reactive metal alkoxides, enables one to carry out most of the sol-gel procedures in the atmosphere [1–5]. More interesting is that gel films prepared by the chemically modified sol-gel method give rise to photosensitivity, e.g., their solubility into organic solvents or acidic solutions changes significantly with light irradiation [6, 7]. Taking advantage of this phenomenon, Tohge and coworkers have produced negative-type patterned oxide films such as Al_2O_3 [8], TiO_2 and ZrO_2 [6], i.e., irradiated areas are left after leaching with the solutions. These patterned films are attracting considerable interests for onboard (photo)catalysts [9–12] in addition to optical and electrical applications [6–8]. We have recently found that positive-type ZnO patterned films can be formed using a sol chemically modified with benzoylacetone [13].

The photodecomposition of the chelate bonds between metal ion and β-diketone has so far been shown to occur in the gel films. Although the deep understanding of the mechanism is indispensable to the further development as a nanotechnology, it remains almost unclear. This paper describes the photoreactivity of the ZnO gel films chemically modified with β-diketones and discusses the mechanism on the basis of the spectroscopic and INDO/S calculation results.

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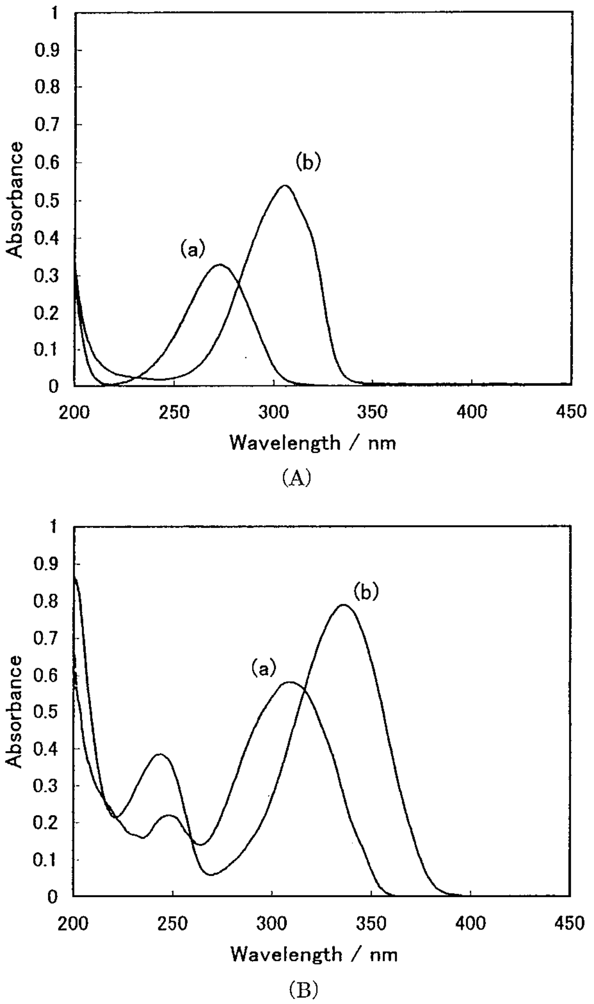
2. Experimental

Zinc acetate, Dihydrate (3.76 g, >99.0%, Nacalai Tesque) was dissolved into a mixed solution of ethanol (40 ml, >99.5%, Kanto Chemical) and 0.73 ml of monoethanolamine (>99.0%, Kanto Chemical), and then 2.78 g of 1-benzoylacetone (BzAcH, >98.0%, Kanto Chemical) was added. After 10 ml of EtOH and 6.17 ml of water had been added to it, the solution was refluxed at 80°C for 3 h with stirring. The resultant sol served as a coating solution. This sol was coated on quartz or Si substrates (Osaka Titanium, resistivity = $4.5 \pm 1.5\ \Omega$ cm) by a dipping-withdrawing method in an ambient atmosphere. After they had been dried at room temperature for 20 min, the gel-film chemically modified with BzAcH was formed on the substrates. The gel-film chemically modified with acetylacetone (AcAcH, >99.5%, Kanto Chemical) was also prepared in a similar manner. Front-face irradiation of the sample was carried out through a soda-lime glass plate using a 300 W Xe lamp (Wacon, model XDS-301S) at room temperature: the light intensity integrated from 320 to 400 nm was determined to be 8.5 mW cm^{-2} by a digital radiometer (DRC-100X, Spectronics Co.). The light with wavelength shorter than 300 nm was completely cut off by the glass plate under these conditions. Volatile products were analyzed by gas chromatography (Shimadzu GC-9A; f.i.d. column Shimadzu SHINCARBON A (3 mm $\phi \times 3$ m)). The carrier gas was N_2 (0.5 kg cm^{-2}) at an injection temperature of 70°C and a column temperature of 70°C. The film thickness was determined using a surface profilometer (Dektak [3] Surface Profilers). The electronic absorption spectra were recorded in the 200–800 nm range on an ultraviolet-visible spectrophotometer (U-4000, Hitachi) mounted with an integral sphere. Fourier-Transform infrared (FT-IR) spectra were obtained with a FT-IR spectrophotometer (FT/IR-470Plus, JASCO). The spectra were recorded in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with 200 coadded scans. The electronic spectra were calculated by the INDO/S method using a ZINDO program within a CAChe work system (CAChe Scientific) [14].

3. Results and discussion

Fig. 1 shows the electronic absorption spectra of chelating agent (CA) and the ZnO sol chemically modified with the CA: A, CA = AcAcH; B, CA = BzAcH. In spectrum A-a, an absorption peak due to the $n \rightarrow \pi^*$ transition of AcAcH is observed at 273 nm. The absorption peak shifts to 305.5 nm in the spectrum of the sol (A-b). This red shift indicates the chelation between Zn^{2+} and $AcAc^-$. On the other hand, BzAcH has two absorption peaks at 309 and 248 nm (B-a), which could be assigned to the $n \rightarrow \pi^*$ transition and the transition between the molecular orbitals (MO) localized at the phenyl group, respectively, by INDO/S calculations. The former peak is also red shifted by 27 nm with the chelation between Zn^{2+} and $BzAc^-$. INDO/S calculations on Zn(BzAc)(OEt) employed as a model chelate complex also reproduced the red shift of the absorption peak and the enhancement of the $n \rightarrow \pi^*$ absorption intensity with the chelation. The $n \rightarrow \pi^*$ peak for the sol chemically modified with BzAcH is situated at a longer wavelength by ca. 30 nm than that for the AcAcH system.



(A)

(B)

Figure 1 Electronic absorption spectra of chelating agents (a) and the sols chemically modified with the chelating agents (b): A, chelating agent = AcAcH; B, chelating agent = BzAcH.

Fig. 2 shows the electronic absorption spectral change with irradiation ($\lambda_{ex} > 300$ nm) for the gel film prepared from the sol containing AcAcH (A-gel film, A) or BzAcH (B-gel film, B). In spectrum A, at irradiation time $(t_p) = 0$, A-gel film has an absorption peak at 308 nm that is close to the peak position for the corresponding sol (Fig. 1A-b). Apparently, most of the chelate bonds are kept intact in A-gel film. Irradiation leads to a monotonous decrease in the absorption intensity, which indicates that the chelate bond is broken as a result of irradiation. In spectrum B, two broad absorption peaks centered at 336 and 244 nm are present. From the comparison with spectrum 1B-b, it is apparent that the chelate bonds are kept also in B-gel film. Upon irradiation, the absorption due to the chelate ring rapidly weakens to disappear completely at $t_p =$ 60 min, while the change in the absorption intensity of the phenyl group is rather small. Also, the absorption peaks of the CAs (Fig. 1A-a and B-a) are not recovered after the decomposition of the chelate ring. Thus, not only the cleavage of the chelate bonds but also the decomposition of the CA takes place with irradiation.

Table I lists the band assignments of the difference FT-IR spectra of B-gel film before and after

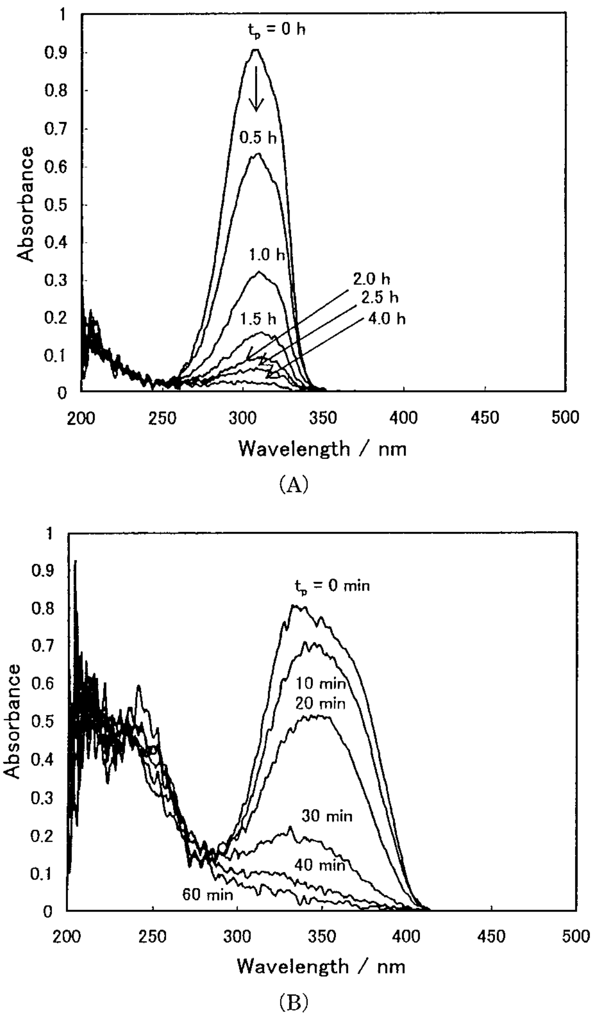


Figure 2 Electronic absorption spectral change with irradiation ($\lambda_{ex} > 300$ nm) in air for the gel film prepared from the sol containing AcAcH (A-gel film, A) of BzAcH (B-gel film, B).

irradiation (Fig. 3). As shown in Fig. 3A, several negative peaks due to the chelate ring in the 1600–1200 cm^{-1} range intensify with increasing t_p [15]. Figs 3B, C and D magnify the difference FT-IR spectra ($t_p = 90$ min) in the ranges of 4000–3000, 3000–2800 and 1900–1400 cm^{-1}, respectively. In Fig. 3B, broad positive and negative bands are observed in the 3700–3500 cm^{-1} and 3500–3000 cm^{-1} ranges, respectively. The former can be attributed to the superposition of the stretching vibrations of ZnO—H (ν(ZnO—H)) [16] and CO—H (ν(CO—H)) groups. The latter is due to the stretching vibration of H_2O (ν(H—O—H)). Evidently, ZnO—H and CO—H groups are generated at the expense of H_2O by irradiation. In Fig. 3C, two negative bands centered at 2960 and 2870 cm^{-1} are assignable to the antisymmetric ($\nu_{as}(CH_3)$) and symmetric ($\nu_s(CH_3)$) stretching vibrations of CH_3 groups, respectively. Irradiation causes the partial lost of the CH_3 groups of BzAc$^-$. Fig. 3D, a broad positive peak appears around 1650 cm^{-1}, suggesting the formation of carbonyl compounds [14]. Also, the generation of CH_3CHO was confirmed by gas chromatography.

TABLE I Assignments of the bands in the difference FT-IR spectra of B-gel film before and after irradiation ($\lambda_{ex} > 300$ nm)

Band position (cm^{-1})	Positive/negative	Assignments
3700–3500	Positive	ν(ZnO—H) + (CO—H)
3500–3000	Negative	ν(H—O—H)
3000–2900	Negative	$\nu_{as}(CH_3)$
2900–2830	Negative	$\nu_s(CH_3)$
1800–1650	Positive	ν(C═O)
1600–1500	Negative	ν(C┅C) + (C┅O)[a]

[a]Dotted lines express the electronic delocalization in the chelate ring.

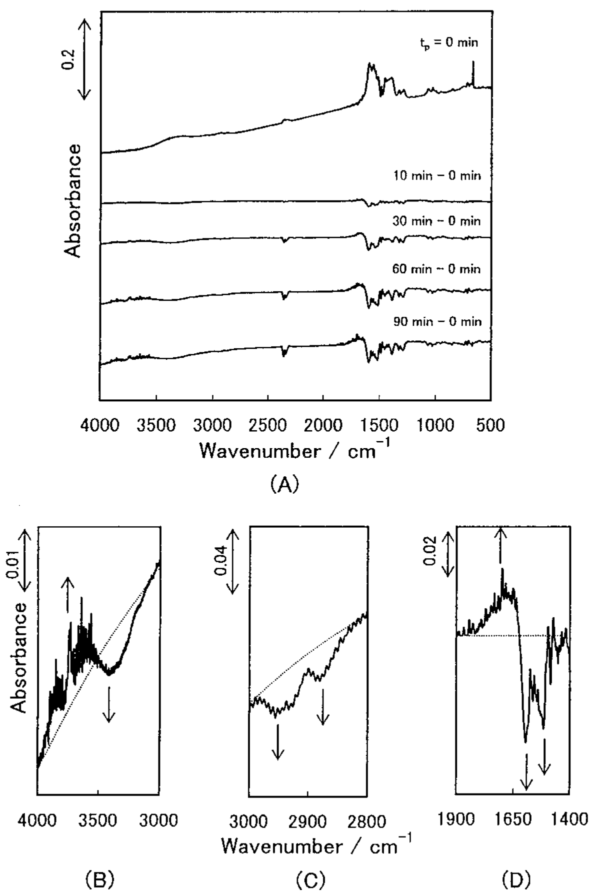


Figure 3 A, Difference FT-IR spectra of B-gel film in the 4000–500 cm^{-1} wavenumber range after irradiation, compared with the spectrum before irradiation ($t = 0$): B, C and D are the magnified spectra (90 min–0 min) in the ranges of 4000–3000, 3000–2800 and 1900–1400 cm^{-1}, respectively.

Fig. 4 shows the time dependences of the absorbance of the n → π^* absorption peaks in A-gel (a) and B-gel (b, c, d) films: A_0 and $A(t)$ are the absorbance at $t_p = 0$

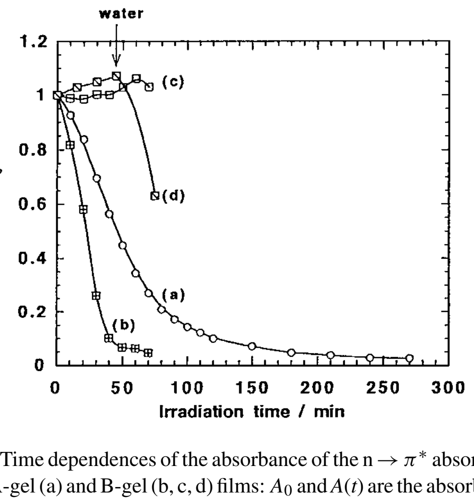


Figure 4 Time dependences of the absorbance of the n → π^* absorption peaks in A-gel (a) and B-gel (b, c, d) films: A_0 and $A(t)$ are the absorbance at $t_p = 0$ and $t_p = t$ min, respectively. (a) and (b), in air; (c) and (d), under vacuum. In curve (d), 0.5 ml of water was injected at $t_p = 45$ min.

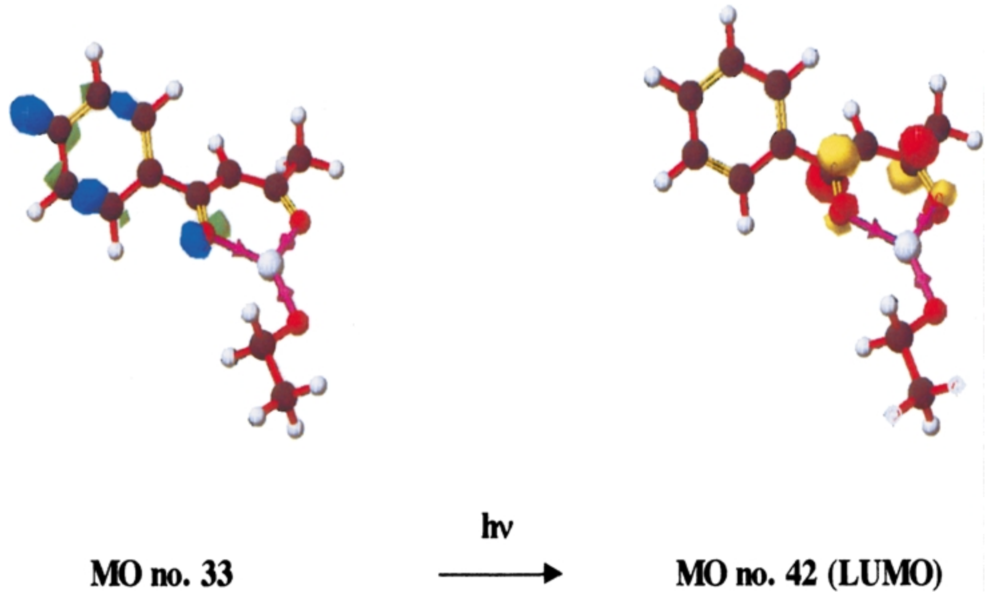
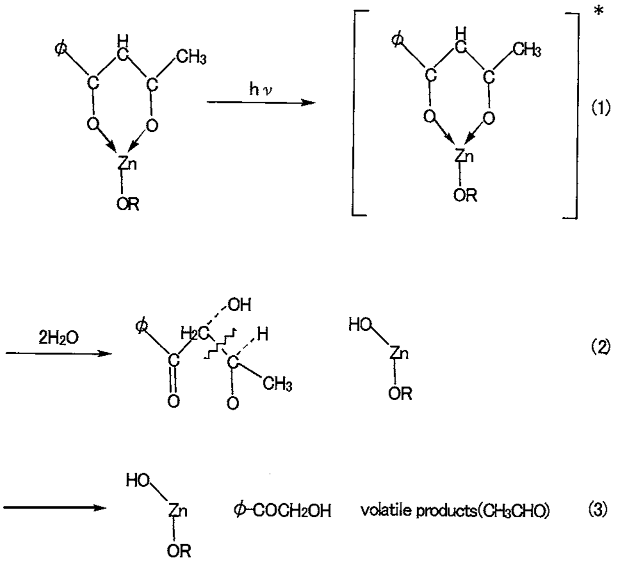


Figure 5 Contour maps for the molecular orbitals taking part in the n → π^* excitation of Zn(BzAc)(OEt): black, carbon; red, oxygen; white (large), zinc; white (small), hydrogen.

and $t_p = t$ min, respectively. In air (a and b), the absorption intensity decreases monotonically with increasing t_p in each gel film. The chelate ring decomposition in B-gel film is significantly faster than that in A-gel film. This result is consistent with the fact that B-gel film is more fitted to produce a patterned ZnO film within a shorter period of time [13]. *It should be noted that under vacuum* (c), *no decomposition of the chelate ring occurs in B-gel film even after 70-min irradiation.* When H_2O (0.5 mL) is injected into the reaction vessel (0.64 L) under vacuum at $t_p = 45$ min (d), the decomposition begins to proceed. These findings suggest that both irradiation and H_2O are necessary for the decomposition to proceed.

Fig. 5 depicts the MOs taking part in the n → π^* excitation of Zn(BzAc)(OEt). This photoabsorption corresponds to the electronic transition from a non-bonding MO mainly distributed over the phenyl group of $BzAc^-$ (MO 33) to an anti-bonding MO localized at the CO bonds (MO 42, LUMO).



Scheme 1 A proposed mechanism of the photolysis of the ZnO gel film chemically modified with BzAcH.

The mechanism of the present solid-phase photoreaction was proposed as shown in Scheme 1. When Zn(BzAc)(OEt) in B-gel film absorbs the light ($\lambda_{ex} > 300$ nm), the electron is excited from MO 33 to MO 42 (LUMO). Since electron is partially distributed on the oxygen atom in MO 33 (Fig. 5), the excitation may reduce the coordination strength of the $BzAc^-$(Equation 1). Photoinduced hydrolysis of the cheleate ring yields Zn(OH)(OEt), CH_3CHO and other carbonyl compounds such as ϕ-$COCH_2OH$ (Equations 2 and 3). The generation of ϕ-$COCH_2OH$ is presumed on the basis of the facts that the IR peaks of ν(C=O) and ν(CO–H) appear with most of the phenyl groups survived after irradiation. These products are more hydrophilic than the original chelate complex (Zn(BzAc)(OEt)). Thus, only irradiated parts would be easily leached out with an aqueous solution of HNO_3. In this manner, this photo-induced hydrolysis mechanism explains the formation of the positive-type patterned ZnO film [13].

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