

Optical properties of ZnO loaded in mesoporous silica

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 6265

(<http://iopscience.iop.org/0953-8984/12/28/322>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 05:22

Please note that [terms and conditions apply](#).

Optical properties of ZnO loaded in mesoporous silica

Baodian Yao[†], Huazhong Shi, Huijuan Bi and Lide Zhang

Institute of Solid State Physics, Academia Sinica, PO Box 1129, Hefei 230031,
People's Republic of China

E-mail: nanolab@mail.iissp.ac.cn

Received 30 November 1999, in final form 11 May 2000

Abstract. The optical absorption and photoluminescence (PL) of ZnO loaded in mesoporous silica have been investigated. These ZnO/SiO₂ composites are synthesized by impregnation of mesoporous silica with an aqueous solution of zinc acetate, followed by firing at 550 °C. A significant blue shift of the absorption edge compared to that of bulk ZnO in the absorption spectra is observed, and the band gap luminescence of ZnO is predominant in the emission spectrum, while the defect induced green luminescence, typical of ZnO, does not appear. However, the above sample, after additional annealing at 350 °C in air for three hours, exhibits an absorption edge (365 nm) near to that of the bulk ZnO; the colour of the sample also turns to yellowish from colourless, and green luminescence also appears. Combining the analysis of x-ray photoelectron spectroscopy (XPS), we propose that Zn–O–Si cross linking bonds formed in the interface between ZnO and the pore walls of silica have a great influence on the optical properties of ZnO/SiO₂ before the additional annealing at 350 °C and the corresponding optical properties reflect both those of SiO₂ and ZnO. After annealing, the Zn–O–Si cross linking bonds mentioned above are destroyed, and the optical properties of ZnO are exhibited alone.

1. Introduction

It has been reported that zinc oxide, ZnO, which has been prepared in an appropriate way, shows luminescence spectra with one or several of the following bands: a near UV emission band centred around 380 nm, a green emission band centred around 510 nm, a red emission band centred around 640 nm and an IR emission band centred at 730 nm [1–7]. However, the identities of the recombination centres and mechanisms responsible for the above emission bands are still a matter of controversy. Considering the fact that the luminescence of ZnO is very sensitive to its surface state, while the surface state is largely determined by its preparation method, that is, different preparative methods lead to different optical phenomena, it is not surprising that so much discordance exists in the already published works due to different preparative methods. Here, in the present study, we report an alternative preparative method for ZnO, which is supported in the pores of mesoporous silica by the impregnation method. Since the pores of silica are interconnected and open to the ambient air, it is natural that ZnO within the pores is also in contact with the ambient air. On the other hand, since the pores of silica are nanosized, the second phase, ZnO, imprisoned within these pores, is also very small and chemically active. Therefore, a coupling effect of the interface between pore walls and the second phase, ZnO, within these pores exists, and consequently this effect has an influence over the optical properties of the second phase, as well as the influence of the ambient on the

[†] To whom correspondence should be addressed.

second phase. As a result, the optical properties of ZnO within these silica pores are expected to reflect the features mentioned above. The results of the present study confirm this. There seem to be no reports along the present line, to our best knowledge.

2. Experimental procedures

2.1. Preparation of samples

The monolithic mesoporous silica host was first prepared by the sol–gel technique, as previous described [8], with tetraethyl orthosilicate, deionized water and alcohol (catalysed by nitric acid), followed by ageing, drying and finally annealing at 700 °C. The as-prepared silica host is clear and colourless, typically 2 mm in thickness with a porosity about 50%, a sharply distributed pore diameter at around 3.5 nm and a specific surface area about 650 m² g⁻¹. Supported zinc oxides are prepared by the following impregnation method. Pre-formed silica monoliths are soaked in 1 M zinc acetate solution at 60 °C for about 5 days, which is long enough to soak the sample [9]. These soaked silica monoliths are then washed with deionized water to get rid of the zinc acetate on the surface of silica host, followed by firing at 550 °C in air for 3 hours. These as-prepared samples are called S1, and some of the S1 annealed additionally at 350 °C for three hours are called S2. The heating rate for all samples was 300 °C h⁻¹. All cooled naturally. As-prepared S1 is clear and colourless, while S2 is yellowish.

2.2. Characterization of samples

The differential scanning calorimetry (DSC) and thermal gravimetry (TG) analysis of the soaked silica (after fast drying at 110 °C for 2 hours) are conducted in high-purity N₂ with a Perkin–Elmer DSC-2 differential scanning calorimeter and with a Perkin–Elmer TGA-2 thermal gravimeter, respectively. Both measurements are at a heating rate of 10 °C per minute. X-ray photoelectron spectra (XPS) analyses were performed using an Mg K α x-ray source (1253.6 eV) on a VG Escalab mark II spectrometer. Data were acquired with 0.05 eV steps. The pressure in the UHV analysis chamber was below 10⁻⁷ Pa.

2.3. Optical measurement

Photoluminescence is measured on an 850 fluorescence spectrophotometer (Hitachi) at room temperature. Optical absorption is measured on a Cary 5E UV–VisNir photometer over the range from 200 to 800 nm (optical scanning starts from longer wavelength, 800 nm, to short wavelength, 200 nm).

3. Results and discussion

3.1. Thermal analysis

As can be seen from figure 1, the first endothermic peak in DSC curve corresponds to the desorption of physical adsorbed water in silica; the second one centred at 410 °C corresponds to the decomposition of zinc acetate. Corresponding to these two endothermic peaks, two regions of weight loss are observed in the TG curve. The third endothermic peak centred at 510 °C is attributed to the dehydration of chemisorbed water in silica. Based on the above analysis, it is concluded that the decomposition of zinc acetate is complete and no organic residues can remain after the sample has been fired at 550 °C for 3 hours in air. The amount of ZnO in the as-prepared ZnO/SiO₂ is about 3% in weight, calculated according to the method

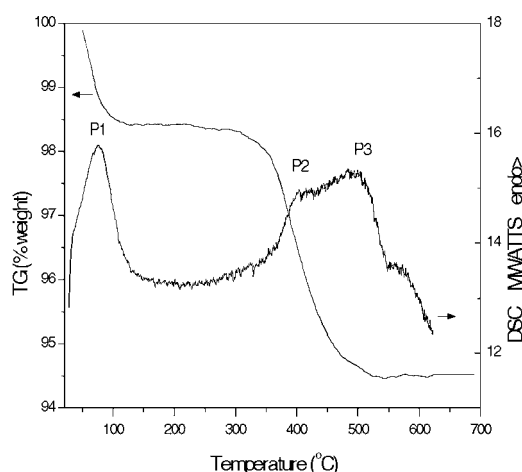


Figure 1. TG and DSC curves of ZnAc/SiO₂, which was dried at 110 °C for 3 hours before measurement.

mentioned in [8], which is also confirmed by the weight loss from the second region of the TG curve in figure 1.

3.2. XPS analysis

Due to the facts that the amount of doped ZnO in silica is small (3 wt%) and crystal ZnO particles formed within silica pores are very small (less than the pore diameter, 3.5 nm) and highly dispersed in the whole silica host [10], x-ray diffraction experiments did not detect the existence of ZnO in as-prepared samples. However, XPS results proved the existence of ZnO in as-prepared samples. The Zn_{2p} photoelectron peak is shown in figure 2. Their shapes showed they belonged to ZnO. The electrostatic charge was assumed to be equal to the difference between the measured C_{1s} (contamination) binding energy and the reference value of 284.6 eV measured for calibration of spectrometer. The binding energies of Zn_{2p} were corrected accordingly and were 1022.7 and 1022.0 eV for sample S1 and S2, respectively. The binding energy of Zn_{2p} for sample S1 increased by 0.6 eV compared to the reported values (1022.1 eV) of bulk ZnO [11], which indicated that the photoelectrons created in S1 were less efficiently screened than those generated in bulk ZnO. Similar to the work of Lassaletta *et al* [12], we proposed that cross-linking bonds of Zn–O–Si were formed at the interface between ZnO particles and the pore walls of SiO₂ which would result in an increase in covalence with respect to bulk ZnO. The changes in electronic structure around zinc must be responsible for the observed shift in Zn_{2p} photoemission. When the as-prepared sample, S1, was additionally annealed at 350 °C for three hours (S2), the binding energy of Zn_{2p} (with error ±0.05 eV) was in agreement with that of bulk ZnO (with error ±0.1 eV) [11]; we thus propose that the additional annealing destroyed the cross-linking bonds of Zn–O–Si existing in S1 in a way which we do not understand so far.

3.3. Optical analysis

Figure 3 shows absorption spectra for S1 and S2. The pure silica monolith calcined with the sample S1 at the same time, as a reference, is also measured and shown in figure 3(c). As can be seen, the absorption edge of S1 (250 nm) has a considerable blue shift compared to that of bulk ZnO (370 nm). It is also very interesting that the absorption edge of S2 (365 nm) shifts

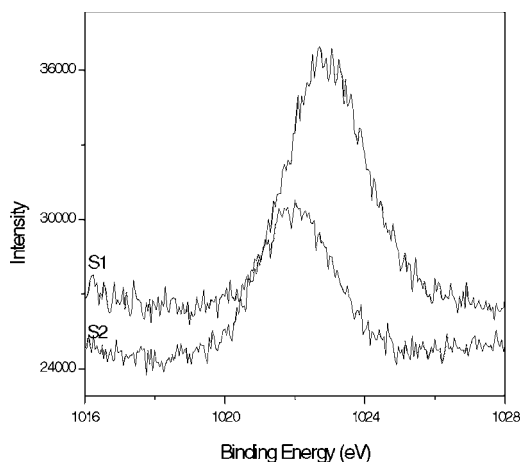


Figure 2. XPS spectra of ZnO: Zn $2p_{3/2}$.

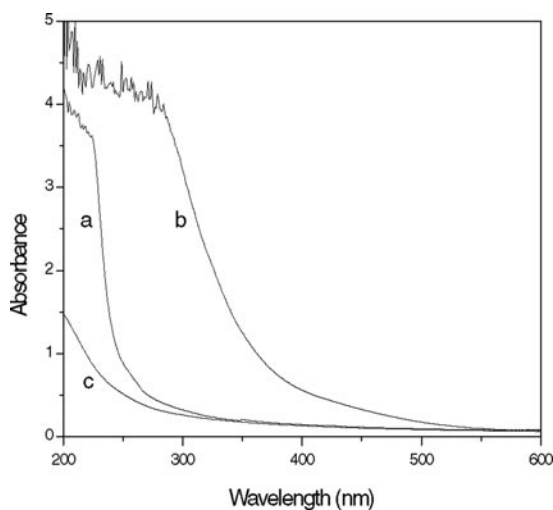


Figure 3. Optical absorption spectra of ZnO/SiO₂ calcined at 550 °C (a); ZnO/SiO₂ annealed additionally at 350 °C (b); SiO₂ (c), heat treated in the same way as (a).

back near to that of bulk ZnO after annealed additionally at 350 °C. Meanwhile, the colour of the sample turns to yellowish (S2) from colourless (S1). According to Srikant and Clarke [7], the yellowish colour originates from the oxygen vacancy in ZnO. If this is true, then it is indicated that there is no oxygen vacancy in S1 and the annealing of S1 leads to the presence of an oxygen vacancy in ZnO. The following photoluminescence emission spectra in figure 4 confirmed this.

As can be seen from figure 4, there is only one emission band centred at 370 nm for S1, recorded using excitation wavelength 250 nm, and no luminescence emission when using excitation wavelength 415 nm. The emission at 370 nm is in agreement with the band gap of bulk ZnO (3.35 eV). Therefore, it is the emission that emits luminescence from the recombination of free excitons. The presence of the free exciton emission and the absence of visible luminescence in S1 shows that ZnO in the as-prepared ZnO/SiO₂ composite is characterized by freedom from defects. However, for S2, four PL peaks at 395, 420, 475 and

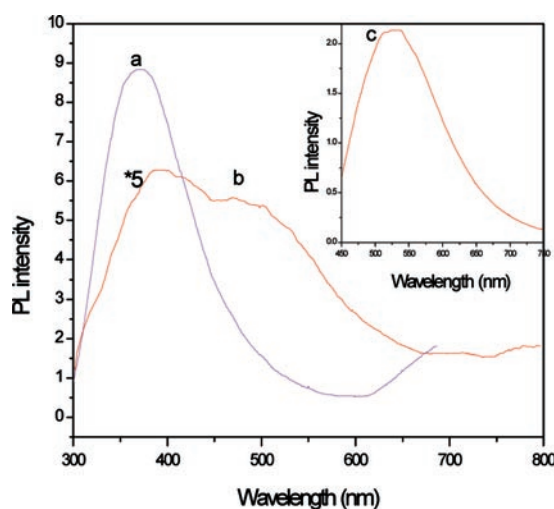
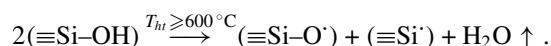


Figure 4. The photoluminescence spectra for (a) ZnO/SiO₂ calcined at 550 °C, (b) and (c) ZnO/SiO₂ annealed additionally at 350 °C. The PL spectra of (a) and (b) were measured under photoexcitation with a wavelength of 250 nm, and a 310 nm shortcut filter was used; the PL spectrum of (c) was measured under photoexcitation with a wavelength of 415 nm, and a 430 nm shortcut filter was used. The curve (b) has been multiplied by a factor of 5.

720 nm can be seen clearly using excitation wavelength 250 nm, and the green emission band centred at 525 nm (figure 4, inset) also appears with the 415 nm excitation. But the intensity of UV emission of S2 is nearly one order of magnitude lower than that of S1. These results indicated that some defects related to oxygen are indeed introduced into S2 by the annealing.

It is well known [13, 14] that the heat treatment of the silica powders in air at $T_{ht} \geq 600$ °C gives rise to the formation of nonbridging oxygen hole centres by the following process:



The absorption band for these nonbridging oxygen hole centres is located at ~ 258 nm [15]. In the present experiment, owing to the small pore diameter, the formation of nonbridging oxygen hole centres on the surface of the pore walls of silica occurs even at a relatively lower heat treatment temperature of 550 °C. The third endothermic peak in the DSC curve in figure 1 corresponds to the dehydration in this process, which in turn confirms that the above process occurred indeed. The absorption edge of the referenced silica at around 260 nm also confirms this. It is obvious that these formed nonbridging oxygen hole centres will readily accept an excess electron from ZnO (which is a typical n-type semiconductor) to form $\equiv\text{Si}-\text{O}-\text{Zn}$ -species at the interface between ZnO and the pore walls of silica, just as the result of XPS. The formation of such species will deplete electrons from ZnO and result in no oxygen being adsorbed on the surface of ZnO from the ambient air. As a result, no defects related to the oxygen exist on the surface of ZnO; no singly ionized oxygen vacancy responsible for green emission can be formed within the ZnO due to the absence of free electrons [3]. Consequently, only the luminescence from the recombination of free excitons can be observed, just as shown in figure 4(a). Considering the facts that the emission of S1 corresponds to that of the band gap of bulk ZnO at 3.35 eV and that the absorption edge of S1 (250 nm) is inconsistent with that of nonbridging oxygen hole centres (258 nm), we suppose that the blue shift of the absorption edge of S1 is not due to the quantum size effect, but to the existence of $\equiv\text{Si}-\text{O}-\text{Zn}$ -species on the interface between ZnO and the pore walls of silica.

When S1 is annealed in air at 350 °C additionally, because these $\equiv\text{Si-O-Zn-}$ species at the interface between ZnO and the pore walls of silica are destroyed, the surface pair of $[\text{Zn}^{2+}\text{-O}^{2-}]$ could be formed from the oxygen which was chemisorbed on the surface of ZnO from outer ambient air, according to the work of Kokes [16]. Accordingly, the emission around 395 nm in figure 4(b) could be concluded to arise from the annihilation of bound excitons, i.e., electron-hole pairs, from the excited state, $[\text{Zn}^+\text{-O}^-]$, to the initial state, $[\text{Zn}^{2+}\text{-O}^{2-}]$ [17]. Meanwhile, the singly ionized oxygen vacancy also appears, which, on the one hand, gives rise to the yellowish colour for S2, and on the other hand, results in the visible green emission around 525 nm in figure 4 (inset). The luminescence emissions at 420 and 475 nm also arise from the surface state of ZnO instead of SiO_2 , based on the fact that these emissions do not appear when the nonbridging oxygen hole centres predominate the optical properties of ZnO/SiO_2 composites. Mahamuni *et al* [1] also observed similar features at 420 and 485 nm and proposed that the oxygen vacancy and interstitial oxygen are responsible for the two features, alone or together. Because these $\equiv\text{Si-O-Zn-}$ species do not exist in S2, the optical absorption edge of S2 reflects that of ZnO particles alone.

In summary, ZnO/SiO_2 composites with highly dispersed ZnO within silica pores can be obtained by the impregnation method, followed by calcination at 550 °C. The optical properties of such composites are governed by the interaction existing between the interface of ZnO and silica. For these as-prepared ZnO/SiO_2 composites, optical absorption reflects the absorption of these $\equiv\text{Si-O-Zn-}$ species formed between the interface of ZnO and silica, and only the photoluminescence emission corresponding to the band gap of ZnO is observed. After the additional annealing at 350 °C, the interaction between the interface of ZnO and the pore walls of silica are destroyed. Consequently, the optical absorption of ZnO is predominant in the absorption spectrum; visible green luminescence, typical of ZnO, also appears.

Acknowledgments

We thank the Chinese Climbing Programme for support of this research. Dr Yao is grateful to Professor Junhui Jia, Institute of Solid State Physics, for help with the optical absorption measurements.

References

- [1] Mahamuni Shailaja, Borgohain Kavita, Bendre B S, Leppert V J and Risbud Subhash H 1999 *J. Appl. Phys.* **85** 2861
- [2] Koch U, Fojtik A, Weller H and Henglein A 1985 *Chem. Phys. Lett.* **122** 507
- [3] Vanheusden K, Warren W L, Seager C H, Tallant D R, Voigt J A and Gnade B E 1996 *J. Appl. Phys.* **79** 7983
- [4] Mo C M, Li Y H, Liu Y S, Zhang Y and Zhang L D 1998 *J. Appl. Phys.* **83** 4389
- [5] Wong E M and Searson P C 1999 *Appl. Phys. Lett.* **74** 2939
- [6] Monticone S, Tufeu R and Kanaev A V 1998 *J. Phys. Chem. B* **102** 2854
- [7] Srikant V and Clarke D R 1998 *J. Appl. Phys.* **83** 5447
- [8] Weiping Cai and Lide Zhang 1997 *J. Phys.: Condens. Matter* **9** 7257
- [9] Koone N D and Zerda T W 1995 *J. Non-Cryst. Solids* **183** 243
- [10] Anpo M, Aikawa N, Kubokawa Y, Che M, Louis C and Giamello E 1985 *J. Phys. Chem.* **89** 5017
- [11] Deroubaix G and Marcus P 1992 *Surf. Interface Anal.* **18** 39
- [12] Lassaletta G, Fernández A, Espinós J P and González-Elipe A R 1995 *J. Phys. Chem.* **99** 1484
- [13] Glinka Y D, Jaroniec C R and Jaroniec M 1998 *J. Colloid Interface Sci.* **194** 210
- [14] Glinka Y D, Lin Sheng-Hsien and Chen Yit-Tsong 1999 *Appl. Phys. Lett.* **75** 778
- [15] Skuja L, Tanimura K and Itoh N 1996 *J. Appl. Phys.* **80** 3518
- [16] Kokes R J 1962 *J. Phys. Chem.* **66** 99
- [17] Anpo M and Kubokawa Y 1984 *J. Phys. Chem.* **88** 5556