

Effect of laser illumination on the blue-green luminescence from MCM-41 at room temperature

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

2008 J. Phys.: Condens. Matter 20 255217

(<http://iopscience.iop.org/0953-8984/20/25/255217>)

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

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 13:14

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

Effect of laser illumination on the blue-green luminescence from MCM-41 at room temperature

T Y Lin^{1,4}, J Chang¹, G Z Huang¹, H M Lin², Y J Yeah² and J L Shen³

¹ Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 202, Taiwan

² Institute of Bioscience and Biotechnology, National Taiwan Ocean University, Keelung 202, Taiwan

³ Department of Physics, Chung Yuan Christian University, Chung-Li 32023, Taiwan

E-mail: tylin@mail.ntou.edu.tw

Received 20 October 2007, in final form 25 April 2008

Published 21 May 2008

Online at stacks.iop.org/JPhysCM/20/255217

Abstract

The effect of laser illumination on the luminescent properties of MCM-41 was investigated by photoluminescence (PL) measurements. It was found that PL peak energy, PL intensity, and PL degradation of MCM-41 can be manipulated by controlling the laser illumination time. Laser illumination on MCM-41 gave at least a 2.5 times increase in PL intensity and an improvement in PL degrading phenomena. Possible mechanisms were proposed to explain our experimental results in a consistent way. The results presented here are expected to be useful for clarifying the nature of light emission from MCM-41 materials and to be of practical use for its possible applications in optical devices.

(Some figures in this article are in colour only in the electronic version)

Since their discovery by researchers at Mobil Corp. in 1992 [1], mesoporous siliceous materials, which are ordered silica-based molecular sieves, have attracted considerable attention [2]. These materials are synthesized by a liquid-crystal mechanism, and their structures can be formed from molecular aggregates of lyotropic surfactants. The mesoporous materials include the thermally stable MCM (mobile composition of matter)-41 and MCM-48 phases. The structure of MCM-41 can be described as a hexagonal arrangement of parallel cylindrical pores embedded in a matrix of amorphous silica. MCM-8-48 has a complex pore system that consists of two mutually interwoven and branched cubic pore structures. The main properties of the MCM mesoporous materials are their high surface area ($\sim 1000 \text{ m}^2 \text{ g}^{-1}$), a large pore volume ($\sim 1 \text{ cm}^3 \text{ g}^{-1}$) and very narrow pore-size distribution (2–10 nm). A number of important applications have been implemented in these materials, such as catalysis, photocatalysis, adsorption, gas separation, and ion exchange [3–6]. In addition, MCM

mesoporous materials are promising as host materials for assembling nanostructure materials because of their mesopore structures. Various materials, such as semiconductors, magnetic materials, and other nanomaterials, have been encapsulated within the mesopore channels to create advanced composite materials, which may have potential applications in microelectronics, optoelectronics, and magnetic devices [7–9].

An understanding of the optical properties of mesoporous siliceous materials is important for extending their range of applications in optical devices. The photoluminescence (PL) of mesoporous siliceous MCM-41 has been studied recently [10–18]. The red (1.8–2 eV) PL in MCM-41 has been commonly attributed to oxygen-related defects, the non-bridging oxygen hole centers (NBOHCs) [10–12]. However, several models, such as E' centers [10], peroxy radicals [10], twofold-coordinated silicon centers [13, 16–18], Si–OH surface complex [14], hydrogen-related species [12], and self-trapped excitons [15], have been proposed to explain the blue-green (2.4–2.8 eV) PL in MCM-41. Besides, the presence of surface states or surface substances resulting from

⁴ Author to whom any correspondence should be addressed.

electrochemical reactions has been found to play a key role in the luminescence properties of mesoporous materials [19]. Indeed, it was shown that PL properties of porous silicon were essentially changed after laser illumination [19]. Therefore, one can assume that laser stimulated surface processes may themselves influence the spectral features of luminescence of mesoporous materials.

In this paper, we investigate the effect of laser illumination on the blue-green PL of MCM-41 using a 325 nm laser in vacuum. It was found that laser illumination has a different influence on the PL properties of MCM-41 with respect to that of rapid thermal annealing (RTA). MCM-41 samples show the redshifts of PL peak energy with increasing laser illumination time. In addition, laser illumination on MCM-41 gave at least a 2.5 times increase in integrated PL intensity. Besides, PL degradation phenomenon in MCM-41 was found to be highly improved by exposure to laser radiation in vacuum. Our results infer that the blue-green luminescence from MCM-41 can be manipulated by controlling laser illumination time in vacuum.

The siliceous MCM-41 nanotubes studied here were synthesized using fumed silica (99.8%, metal free, Sigma), cetyltrimethylammonium (CTA) bromide (AR, 99%, Acros) and tetramethylammonium (TMA) hydroxide (25% aqueous solution, Aldrich). The syntheses of the siliceous MCM-41 were made according to the following procedure. (TMA)OH and (CTA)Br were added to deionized water with stirring at 30 °C until the solution became clear. The silica source was added to the solution with stirring for 2 h and then aged for 24 h. Gel mixtures with composition 1.00 SiO₂:0.19 (TMA)OH:0.27 (CTA)Br:40 H₂O were reacted for 48 h at 150 °C in Teflon-lined stainless steel autoclaves. The reaction product was filtered, washed with distilled water and dried in air at 60 °C. Finally, the template was removed by calcination at 550 °C for 8 h. The as-grown sample was characterized by x-ray diffraction (XRD) measurements showing a diffraction pattern within the 2θ range 1.5°–6.5°. The pattern displays four reflection peaks: (100), (110), (200), and (210), typical of a regular hexagonal MCM-41 structure. The lattice parameter of the hexagonal unit cell at about 3.70 nm was determined according to a characteristic strong reflection at low scattering angles 2θ in XRD patterns. The pore-size distribution for the MCM-41 material was investigated by nitrogen adsorption–desorption measurements carried out at 77 K. A reversible type IV nitrogen sorption isotherm indicated the presence of mesopores. A sharp increase in the adsorbed and desorbed volumes at a relative pressure $P/P_0 \sim 0.37$ reflects the uniformity of the pore-size distribution. The average pore diameter calculated using the Barret–Joyner–Halenda (BJH) method was very narrow at 2.9 nm. All these results indicate high quality for the MCM-41 samples studied here.

The as-prepared sample was further treated with RTA in a pure N₂ environment. Annealing treatments were performed at temperatures from 200 to 800 °C with an annealing time of 30 s. Laser illumination of the samples was achieved by diverging the beam of a He–Cd laser (325 nm) into a circular area with a diameter of ~0.5 cm. The power density of this radiation was measured to be 13 mW cm⁻² by a calibrated power meter. The 325 nm line of a He–Cd laser was used

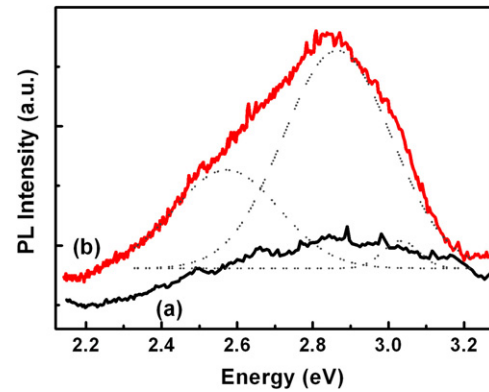


Figure 1. Typical room temperature photoluminescence spectra of as-grown (a) and 600 °C rapid thermal annealing (b) MCM-41 samples.

to generate the PL spectra. The PL signal is dispersed using a monochromator and a photomultiplier tube is used to collect the emitted light. All the PL measurements were carried out at room temperature in atmosphere.

Figure 1 shows the typical PL spectra of as-grown and RTA treated MCM-41 samples. Both spectra have a broad emission with peak energy around 2.5–3.1 eV. For simplicity, we only show the result of the RTA treated sample at 600 °C. As has been shown by a previous report [18], the PL spectrum of the as-grown sample was made prominent by RTA treatment up to an intermediate temperature, for example, 600 °C in this case. But at a higher temperature, the decreased PL intensity with higher RTA temperature, for example, 800 °C here (not shown), is attributed to the collapse of the mesoporous structure of MCM-41, demonstrated by Fourier transform infrared spectroscopy and XRD measurements [20]. The spectrum of the RTA treated sample could be deconvoluted into three Gaussian components peaking at 2.58, 2.88, and 3.04 eV, respectively, as shown in figure 1(b). By adapting the previous result [16], the increased intensity of the 2.58 eV PL is due to the perturbation of the emission from the luminescence centers on the surface by dehydroxylating from the hydrogen-bonded silanol groups and the increased concentration of the twofold-coordinated silicon centers in which the triplet-to-singlet transition is attributed to be responsible for the blue-green luminescence in MCM-41. On the other hand, the PL peaks at 2.88 and 3.04 eV in figure 1(b) are very similar to those obtained in silica nanowires by Chen *et al* [21] and those observed in Si-implanted Si-rich SiO₂ by Lin *et al* [22]. It was revealed that the 2.7 eV band was ascribable to the neutral oxygen vacancy (NOV, ≡Si–Si≡), while the 3.1 eV band corresponded to twofold-coordinated silicon lone-pair centers (O–Si–O) [21]. Lin *et al* have found that the PL intensity of the 2.7 eV emission due to the neutral oxygen vacancy (≡Si–Si≡) increases after the RTA treatment. Thus, the 2.88 and 3.04 eV PL peaks are attributable to the structural defect centers arising from the oxygen deficiency of the MCM-41 sample. Here, our results indicated that RTA treatments could result in pronounced oxygen deficient defects and the collapse of the mesoporous structure in MCM-41.

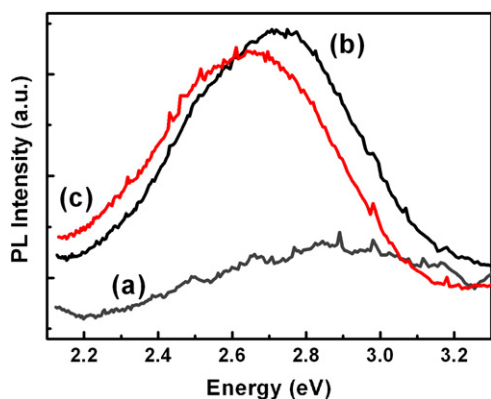
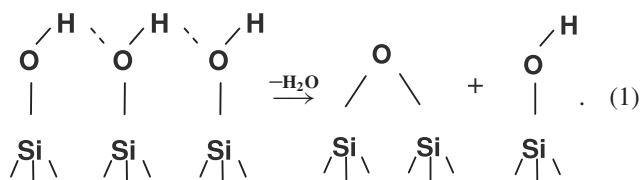


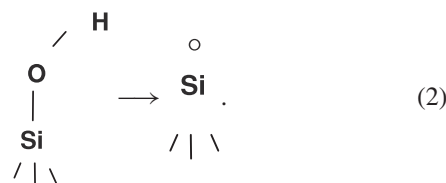
Figure 2. Room temperature photoluminescence spectra of as-grown (a), 1 h (b), and 2 h (c) laser illuminated MCM-41 samples.

In contrast to RTA treatments, laser illumination in vacuum was found to incur redshifts of PL peak energy accompanied by enhancement of the PL integrated intensity from MCM-41 samples. Note that the PL measurement process in atmosphere triggers no significant changes in the PL spectra of MCM-41 samples compared with that caused by illumination under vacuum. In figure 2, we show the room temperature PL spectra of the MCM-41 sample illuminated by a He–Cd laser for 1 h (figure 2(b)) and 2 h (figure 2(c)), respectively. It is clear that the PL intensity of the laser illuminated sample is much stronger than that of the as-grown sample (figure 2(a)), which is a result similar to that observed in the RTA treated samples of figure 1 and of previous reports [11, 16]. The PL intensity of the MCM-41 samples studied here is also found to increase when the pumping laser is less focused. This behavior indicates the surface emission characteristic of MCM-41 materials as described in the previous report [14], because a less focused beam can cover a larger surface area. Accordingly, as equation (1) [23, 24] shows below, the water molecules on the MCM-41 surface could be removed by the absorbed photon energy under laser illumination, which perturbs the emission from the luminescence centers on the surface. The PL intensity is therefore enhanced after laser illumination, as shown in figure 2.

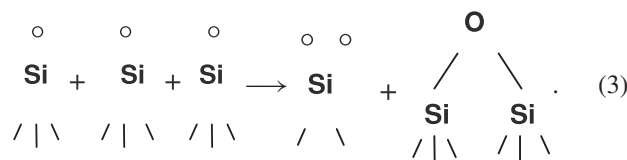


In addition, as shown by figures 2(b) and (c), a two-staged redshift of PL peak energy was observed in the laser illuminated samples. The PL peak energy is first redshifted to 2.75 eV, and then to 2.58 eV after laser illumination for 1 and 2 h, respectively. This result infers the changes in the mechanism of emission from MCM-41 materials as a result of the accumulation effect of laser irradiation. Based on the surface chemistry of mesoporous materials, we analyze the blue-green PL with laser illumination time as follows. With

He–Cd laser excitation, the photon energy was absorbed by the MCM-41 sample. According to previous reports [10, 16], the E' center could be the defect responsible for the PL band at 2.75 eV. Thus, at the first stage (figure 2(b)), we suggest the generation of E' centers by direct dissociation of the single silanol groups with the absorbed photon energy under laser illumination according to:



As the time of laser illumination increases, the concentration of E' centers on the sample surface increases, as described by equation (2). Shen *et al* [16] and Zhang *et al* [13] have reported that the twofold-coordinated silicon centers can emit 2.58 eV luminescence in a triplet-to-singlet transition. Based on the above two reports and the similar process in [25], we suggest that the surface E' centers can combine and produce twofold-coordinated silicon centers according to the following process:



Thus, the observation of redshift of PL peak energy from 2.75 to 2.58 eV in MCM-41 with 2 h laser illumination could be understood in a consistent way.

In order to further understand the effect of laser illumination on the blue-green PL in the MCM-41 sample, we performed persistent PL measurements. The PL peak intensity in MCM-41 and/or in MCM-48 has been found to degrade with time during photoexcitation [26]. The formation of an adsorption complex between the adsorbed molecules and the active emitting sites, leading to the reduction of the number of active emitting sites associated with luminescence, is attributed to the dominant mechanism of PL degradation in M41S. Figures 3(a)–(c) show the PL peak intensity of MCM-41 as a function of irradiation time for as-grown, 1 h, and 2 h laser illuminated samples. The PL peak intensity of as-grown, 1 h, and 2 h laser illuminated samples dropped by 82%, 35%, and 14%, respectively, after illumination of about 2 min. As shown in figure 3, the PL degradation is ameliorated with laser illumination time, in sharp contrast to the extensively observed PL decay in as-grown MCM-41 after laser exposure. These results could be in line with the increase in the number of active emitting sites by laser illumination. When the MCM-41 sample is illuminated by an He–Cd laser, the number of single silanol groups increases by dehydroxylation of hydrogen-bonded silanol groups. The absorbed photon energy can lead to the generation of E' centers by direct dissociation of single silanol groups, simultaneously increasing the intensity of the 2.75 eV PL. The laser illumination induced reaction, denoted by equation (2), increases the concentration of E' centers at the sample surface. With the increase of laser illumination

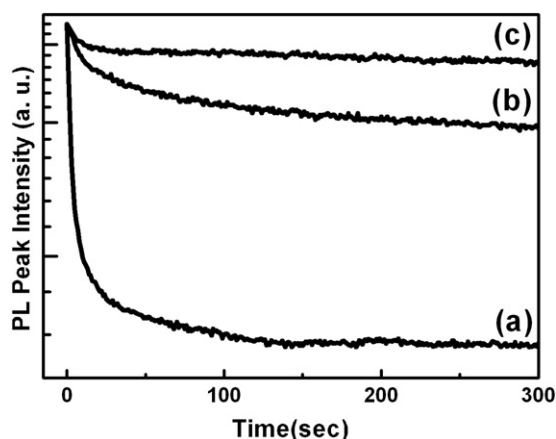


Figure 3. Photoluminescence degradation of MCM-41 as a function of irradiation time for as-grown (a), 1 h (b), and 2 h (c) laser illuminated MCM-41 samples.

time, more E' centers can combine and produce the twofold-coordinated silicon centers, which increase the PL intensity of the 2.58 eV luminescence. Accordingly, for both the 2.75 and 2.58 eV luminescence, the increase in the number of corresponding active emitting sites with laser illumination time leads to the mending of PL degradation phenomena. Thus, the two-staged redshift of PL peak energy and the improvement of PL degradation phenomena could be unambiguously explained in a consistent way.

In conclusion, the effect of laser illumination on the PL properties of MCM-41 was investigated. The emission wavelengths and PL integrated intensities of MCM-41 can be manipulated by controlling the laser illumination time. Besides, the PL degradation in MCM-41 was highly improved after laser illumination on the samples. Possible mechanisms were proposed according to previous reports to account for our experimental results in a consistent way. We suggest that the mechanisms of generating blue-green PL in MCM-41 can be manipulated by controlling laser illumination time. An interesting task for future work is to explore the transformation of the species of surface complexes responsible for the PL in MCM-41 materials with the accumulation effect of laser illumination to correlate them with the observations of this study. The results presented here are expected to be of practical use for possible applications of MCM-41 in optical devices.

Acknowledgments

This work was supported in part by the National Science Council of Taiwan, Republic of China, under research

grant NSC 95-2112-M-019-007-MY3 and by National Taiwan Ocean University under grant NTOU-RD941-05-04-07-02.

References

- [1] Kresge C T, Leonowics M E, Roth W J, Vartuli J C and Beck J S 1992 *Nature* **359** 710
- [2] Anpo M, Suzuki T, Giamello E and Che M 1990 *New Development in Selective Oxidation* (Amsterdam: Elsevier) p 683
- [3] Polarz S and Smarsly B 2002 *Nanopor. Mater. J. Nanosci. Nanotechnol.* **2** 581
- [4] Ciesla U and Schuth F 1999 *Ordered Mesopor. Mater. Micropor. Mesopor.* **27** 131
- [5] Sayari A and Liu P 1997 Non-silica period *Mesostruct. Mater. Recen. Prog. Micropor. Mater.* **12** 149
- [6] Selvam P, Bhatia S K and Sonwane C G 2001 *Ind. Eng. Chem. Res.* **40** 3237
- [7] Chen L, Klar P J, Heimbrodt W, Brieler F J, Froba M, von Krug H-A N, Kurz T and Loidl A 2003 *J. Appl. Phys.* **93** 1326
- [8] Tang Y S, Cai S, Jin G, Duan J, Wang K L, Soyoz H M and Dunn B S 1997 *Appl. Phys. Lett.* **71** 2448
- [9] Govindaaraj A, Nath M and Eswaremoorthy M 2000 *Chem. Phys. Lett.* **317** 35
- [10] Gimón-Kinsel M E, Groothuis K and Balkus K J Jr 1998 *Micropor. Mesopor. Mater.* **20** 67
- [11] Shen J L, Chen P N, Lee Y C, Cheng P W and Cheng C F 2002 *Solid State Commun.* **122** 65
- [12] Glinka Y D, Zyubin A S, Mebel A M, Lin S H, Hwang L P and Chen Y T 2002 *Chem. Phys. Lett.* **358** 180
- [13] Zhang Y, Phillip F, Meng G W, Zhang L D and Ye C H 2000 *J. Appl. Phys.* **88** 2196
- [14] Chang H J, Chen Y F, Lin H P and Mou C Y 2001 *Appl. Phys. Lett.* **78** 3791
- [15] Glinka Y D, Lin S H, Hwang L P and Chen Y T 2000 *J. Phys. Chem. B* **104** 8652
- [16] Shen J L, Lee Y C, Lui Y L, Cheng P W and Cheng C F 2003 *J. Phys.: Condens. Matter* **15** L297
- [17] Lee Y C, Liu Y L, Lee W Z, Wang C K, Shen J L, Cheng P W, Cheng C F and Lin T Y 2004 *Phys. Status Solidi a* **201** 3188
- [18] Lee Y C, Liu Y L, Wang C K, Shen J L, Cheng P W, Cheng C F, Ko C H and Lin T Y 2005 *J. Lumin.* **113** 258
- [19] Shih S, Jung K H, Yan J, Kwong D L, Kovar M, White J M, George T and Kim S 1993 *Appl. Phys. Lett.* **63** 3306
- [20] Gu G, Ong P P and Chu C 1999 *J. Phys. Chem. Solids* **60** 943
- [21] Chen Y, Zhou Q, Jiang H, Xiao H, Zhu L and Xu L 2006 *Nanotechnology* **17** 1022
- [22] Lin G R, Lin C J, Lin C K, Chou L J and Chueh Y L 2005 *J. Appl. Phys.* **97** 094306
- [23] Zhao X S, Lu G Q, Whittaker A K, Millar G J and Zhu H Z 1997 *J. Phys. Chem. B* **101** 6525
- [24] Inaki Y, Yoshida H, Yoshida T and Hattori T 2002 *J. Phys. Chem. B* **106** 9098
- [25] Skuja L 1998 *J. Non-Cryst. Solids* **239** 16
- [26] Shen J L, Lee Y C, Liu Y L, Yu C C, Cheng P W and Cheng C F 2003 *Micropor. Mesopor. Mater.* **64** 135