New Phosphor and Material Structures for Displays

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Abstract

We propose a new concept: that of photonic crystal phosphors (PCPs) for display and phosphor related applications. It is well known that microcavities with dimensions comparable to the emitting wavelength strongly enhance light-matter interactions, resulting in a significant increase in spontaneous emission rate, which can be directly translated into enhancement in phosphor efficiency. In recent simulations we have demonstrated that when a microcavity is formed in a nano-phosphor structure, the luminescence band is modified, and can be made spectrally sharp and tunable by engineering the geometry/material properties of the cavity and the surrounding photonic crystal lattice. New phosphor material structures based on photonic crystals are proposed. Applications to thin film EL phosphors and particle phosphors are discussed. Additionally, economic methods of synthesizing and incorporating PCPs into current display applications are proposed.

Keywords: Phosphors, photonic crystals, displays

1. Introduction

Despite the rapid development and introduction of new display technologies into the market place over the last five years (plasma, EL, OLED, etc) there continues to be an ever-increasing demand for higher-performance displays than those currently available. Required display attributes range from compactness and low power to sunlight read-ability and higher resolution. It has long been recognized that because they are ubiquitous to all systems, the development of better phosphors provides a direct and economic way to significantly enhance the performance of all current display systems, and can lead to additional applications. Despite significant successes in the optimization of phosphors for new display applications, revolutionary improvements, for example, in efficiency have not been achieved. Although photonic crystals (PCs) have been shown to offer a way to dramatically improve the performance of devices such as semiconductor lasers, the application of this technology to phosphor particles themselves has not been investigated extensively because of materials limitations.

We propose in this paper the development of photonic crystal phosphors (PCPs) and explore the potential of these structures for display applications and the technologies that must be developed to realize their potential. To investigate these effects we have performed extensive modeling studies and experimental investigations of self-assembly and growth techniques for the formation of PCs. We believe that these techniques can open up new pathways for the economic production of a new class of luminescent materials: PCPs with the potential for low power, brighter, fully saturated color displays, with greater functionality. For example, new output coupling schemes whose non-Lambertian distribution could be used for directed display applications and, for example, easily coupled into the optics for head mounted displays.

2. Results and Discussion
Thin Film Phosphors: 2D PCPs

In a recent paper we presented models of the impact a PC can have on the luminescent properties of a thin film phosphor.[1] A major problem with thin film phosphors is that light is guided within the film rather being projected perpendicular to the film surface. This "light trapping" effect has been overcome in InGaAs LEDs by surrounding the light emitting area with a PC and an increase of 70% was reported.[2] We have, therefore, theoretically studied this effect in thin film EL phosphors. For this, and other studies, we have chosen ZnS as a prototype material. ZnS is a highly efficient luminescent host material, and when doped with a variety of activators, Cu, Ag, Mn, Tb etc, has resulted in its use in many commercial display applications, ranging from CRTs to EL displays. Also, ZnS is transparent in the visible and infrared and has a reasonably large refractive index, and is therefore a good candidate material for studying new effects.

Thin film ZnS:Mn is the most efficient EL phosphor (η = 3 - 6 lm/W) and is used extensively in color-by-white EL displays. However, for tri-color displays its chromaticity is not ideal (CIE, x = 0.5: y = 0.5) and it has been difficult to adjust it by alloying. For example, the addition of Mg moves the CIE coordinates slightly towards the green, but at a considerable loss in efficiency. Thus filters are used to extract either purer red, or green colors. However, if we pattern the thin film so as to produce a 2-dimensional PC then, in principle, considerable control can be obtained over the emission and properties as discussed below.

To compute these effects both the Plane Wave Expansion Method and Finite-Difference Time-Domain Method were used. In the former case, one first obtains an eigenvalue equation from Maxwell's equations, which is then converted to a matrix equation by expanding the H-field with plane waves. Diagonalization then gives the band structure. In the Finite-Difference Time-Domain Method, both time and space are discretized to obtain difference equations that are used to continuously update the E and H fields. Thus this technique is suitable for calculating transmission and reflection coefficients and other time-dependent quantities. Details of the simulations techniques may be found elsewhere.[1] We have used these simulations to both search for the existence of a photonic band gap (PBG) in a given material system, and if one is predicted, to then define the lattice type and dimensions that can lead to optimizing these effects.

Figure 1 shows that for a ZnS film patterned with a triangular air hole lattice with basis of 200 nm, and an air hole diameter of 120 nm, a stop band can be achieved for the TE mode between 565 - 690 nm. This is wide enough to inhibit the emission at 580 nm from the Mn ion. This has the effect of preventing the emission from propagating along the film and instead projects it perpendicular to the plane, i.e. towards the viewer. Additional modeling studies of this structure show that the introduction of a "defect" (formed by removing a hole) introduces an allowed emission peak within this stop band, which can be tuned from 565 to 608 nm. The effect of this on the CIE coordinates is shown in Figure 2, and allows, in principle, the achievement of highly saturated colors between the red and green. Figure 3 shows the electric field patterns of these same structures, indicating a strong concentration of the field strength around the microcavity and consequent reduction in the decay time. This example illustrates the potential of tuning the color, response time and intensity of the emission from a phosphor, and suggests that new luminescent materials based on photonic crystals (PCs) will exhibit highly saturated colors with enhanced efficiencies. Unfortunately, the fabrication of thin film-PCs requires demanding and expensive patterning technologies. However, the work on the self-assembly of nanoparticles suggests low-cost fabrication routes to obtaining these properties and also for realizing increased functionality. We have therefore examined the applications of 3D PC systems.

3-Dimensional PCPs

To achieve a viable new powder or "particle" phosphor technology the following crucial issues must be addressed.

1. The identification of highly luminescent materials: wide band gap, donor-acceptor, or localized ion-type.
2. The identification, or development, of materials with refractive indexes, n > 3.0 in the visible. These materials must be compatible with, or ideally the same as the phosphor materials.
3. Economic methods of creating opal or inverse opal structures.
4. Obtain the physical characteristics that will allow these new materials to be used and processed in the same way as current phosphors, settled, screened-printed, etc.
5. They should have the same, or a very similar physical form factor as current materials, i.e., approximately spherical with sizes ranging from 20 to 1μm, ideally 5-7μm, as these have the most applications.
6. Achieve material structures that are chemically inert and resistant to UV and electron beam excitation techniques.

New Materials for PCPs

The best 3D structure that creates a photonic bandgap is theoretically shown to be an inverted opal in which the infiltrated material has a refractive index greater then 3.0. Additionally, for phosphor applications the material must provide good host characteristics for luminescent activators. A review of material properties with the characteristics outlined, results in a relatively short list of potential materials. If it is possible to separate the requirements for luminescence and high index properties then it is possible to develop some schemes involving several material schemes.

The direct approach is therefore to choose materials that have these characteristics and then to incorporate them into a phosphor technology. A review of possible materials shows that by far, GaP has the best physical and chemical properties, E_G = 2.25 eV (λ=552 nm) with a refractive index that decreases from 3.6 to 3.2 over the visible region. GaP and related alloys are also highly luminescent materials. Potentially, phosphors of the ZnS genre (i.e. donor-acceptor pair emission) can be developed and their emission characteristic fine-tuned by alloying with In and Al as is currently being done for LEDs. Also "localized-ion" type phosphors can be developed, as for example Mn in ZnS. Also GaP has been developed extensively for many new electronic and opto-electronic applications.

The development of composite materials is completely unexplored, but possible schemes to design a material, which is transparent in the visible has a high dielectric constant and is strongly luminescent are suggested below. The closest materials with these properties is TiO_2 with E_G = 3.2 eV (388nm) and an index of 2.9. A 10% increase in index would therefore give an index ~ 3.2 and provide the required properties. The high index is due to the rutile structure in which the octagonal/triangular structure results in shared O-bonds. This effect strongly polarizes the O atom, which enhances the electronic contribution to the optical index, n; thus alloys which keep the rutile structure are required. We propose that this can be achieved by alloying materials with similar structural properties. The band-bowing factor could lead to a lower band gap and concomitant higher refractive index for an alloy between the two end point materials. An additional requirement is that these materials can be deposited by a technique that allows their infiltration into the (SiO_2) opal lattice and which can be removed by etching without affecting the infiltrate, such that the periodic modulation in the refractive index has the dimensionality to provide the "microcavity" properties. The microcavity would then be formed by incorporating a sphere of the same size as the opal material, but would not be etched.

PC Lattice Fabrication:

It is very complicated and difficult to fabricate 3D periodic structures with the lithographic techniques commonly used in electronics industry because it requires a series of layer-by-layer lithographic patterning, planarization and thin film deposition. On the other hand, the nanoparticle self-assembly technique uses the spontaneous crystallization of colloids to create periodic systems. This method, coupled with a viable infiltration technique, would provide a simpler, faster and more economical way especially well suited for creating 3D PCs in which the fullest effects of photonic band formation are expected. We have therefore studied the synthesis of highly mono-dispersed nanoparticles and phosphors (SiO_2, polystyrene, ZnS and Y_2O_3) with diameters between 140-450nm, and their self-assembly into opals, and the processes of opal infiltration to achieve an infiltrated structure.[1,3] Using a specially designed confinement cell for forced sedimentation, we were able to obtain high quality opals with a large domain size, fewer defects and higher packing density as confirmed by optical characterizations which

showed well-defined stop bands due to Bragg reflections. Most significantly, we have invented a new infiltration technique, which overcomes some of the limitations of previous work.

Our studies show that chemical and photo-chemical techniques, have the potential to realize high infiltration, but that these techniques also induce high porosity and nano-grain boundaries that, respectively, prevent realization of the full refractive index contrast expect from the bulk material characteristics, and quench their photoluminescent properties. To over come this limitation we have discovered that Atomic Layer Deposition (ALD) produces high quality infiltrated material. For these infiltration studies the films were grown under conditions that would normally result in a 70 nm thick film of ZnS:Mn. The schedule included 9 repeats of a cycle that included 100 repeats of a ZnCl pulse and a H_2S pulse, followed by one long MnCl/ZnCl pulse. The initial evaluations show that good infiltration was achieved and that the material has high optical quality and strong luminescent properties. These structures have been shown to be robust enough such that the silica spheres can be etched out (using HF) leaving a free standing inverse opal photonic crystal. However, considerable optimization of these processes is necessary and is in progress, together with further refinements to produce a full 3D-microcavity structure.

As shown by Figure 4, examination of the films by SEM confirmed that the ZnS penetrated the lattice very well. SEM examination showed that the film thickness of the spheres near the surface, was ~ 30 nm. Figure 4 also shows the results of HF etching, resulting in an inverse opal. The PL intensity of this film also equaled, or exceeded that from a simple layer. The peaks shown in Figure 5 correspond to ZnS:Mn and Cl-band emission, respectively.

Doping has also been achieved by directly adding polystyrene nanoparticles to the self-assembly process. We also are working on doping using luminescent nanoparticles. The polystyrene particles will be sintered or dissolved during processing to create void spaces within the opals, which are subsequently infiltrated with luminescent materials by ALD.

Phosphor-Embedded PC Screens for Displays

To apply these concepts for practical display applications, it is important to develop technologies that are compatible with the conventional powder-based techniques used in display manufacturing processes. The holographic filter technology that involves the deposition of MgF_2/metal multilayer filters onto a flexible substrate, and which that is widely used for banknotes shows how this can be accomplished. After deposition the substrate is etched away and the multilayer filter is broken up into small platelets ranging from 2 – 20µm in size by using an ultrasonic agitator. Since the filter thickness is typically 1µm, the platelets align along the surface of the banknote when printed. This technology is already in wide use for US banknotes and thus well developed for mass production. Therefore, this technology can be directly extended for display manufacturing, for which the original mm or cm size phosphor-embedded 3D PCs will be broken into µm size platelets and then screen printed on display screens. One concern regarding this technique is whether the photonic crystal platelets would preserve the original photonic band structure. According to a recent publication, a photonic defect surrounded by 7 unit cell long photonic crystal structure exhibited a very high quality factor.[4] Therefore, photonic crystal platelets 5 – 20µm in size are expected to preserve the original band structure because the nanoparticles constituting the photonic crystals are 150 – 300nm in diameter and thus the PC platelets will contain at least 10 unit cells.

An alternative approach is to use spherical opals which can be fabricated by using surface tension based self-assembly process. Typical phosphor particle sizes used in commercial display

screens are of the order of 2 - 5 microns in diameter. Thus, by using 50 to 100 nano-spheres each 150 - 250 nm in diameter, it should be possible to make spherical opals that are comparable in size with conventional phosphor particles and that contain microcavities infiltrated with phosphor materials. It should be possible to use these phosphor-embedded PC particles in the conventional display manufacturing processes without any significant modification.

Potential Applications

We believe that PCPs will be suitable as direct drop-in replacements for all current display systems using glass phosphor screens, for instance, Plasma, CRT and FED Displays. Additionally there are many more applications for this technology that will lead to enhanced display properties and new schemes for up- and down-conversion, IR to visible conversion, UV to visible and spectral purity and luminescent enhancement, etc.

For example, by making screens from PCPs it should be possible to suppress the "unwanted" infrared emission from the Y_2O_3:Eu phosphor at 710, 630 and 650nm, so as to enhance the intensity of the shortest red emission band at 590 and 611nm. Additionally, higher efficiencies as well as refining the color coordinates of the red emission are possible. In fact the strongest test of this concept will be to design a photonic glass structure that will totally inhibit the red spectra, thereby promoting radiative recombination at shorter wavelengths, for example, at 530 nm from the $^5D_1 - {}^7F_0$ transition of Eu^{3+}. If these effects can be observed then it will unequivocally demonstrate the high potential of this approach to modify the optical properties of many other phosphor systems. These effects are expected to be especially pronounced in the $(Y,Gd)BO_3$:Eu phosphors currently being used in commercial PDPs because they exhibit stronger emission in the longer wavelength region (> 611nm).

Another example is ZnS:Tm^{3+} which emits very strongly in the blue at 487 nm due to the $^1G_4 - {}^3H_6$ transition and also in the red at 645 and 773 nm due to the transitions, $^1G_4 - {}^3F_4$ and $^1G_4 - {}^3H_5$, respectively. By building a photonic crystal structure using the process described above to generate a photonic band gap at the lower frequency range (longer wavelengths) the emission in the red will be suppressed and thus the optical recombination rate equations will changed in favor of the higher frequency (shorter wavelength) transition. Thus, a very efficient blue phosphor can be obtained. Additionally, by designing a structure to create a band gap at the higher frequency the opposite effect can be obtained. Thus we propose to use PCPs to promote one transition with respect to the other, and visa-versa.

This concept can also have very important applications in emission band engineering, such as to develop a totally new concept for a quantum cutter. One of the biggest problems in developing quantum cutter phosphors is the suppression of UV emission, which is in competition with the quantum cutting transition and thus limits the visible quantum efficiency. For conventional phosphors, there are very few means to selectively suppress the unwanted UV emission. However, if the quantum cutter phosphor is embedded in a photonic crystal whose optical bandgap overlaps the UV emission, then the unwanted UV emission can easily be suppressed, maximizing the visible quantum efficiency.

Tunable Properties

It is possible that by incorporating strongly polarizable or electro-optic materials in the photonic crystal structures that electrically tunable emission and steering properties can be obtained. Also optical switches and modulator properties could be incorporated into the material structure. Thus it is expected that these materials could be used to develop electronically or optically driven beam steering devices for scanning displays, and many other applications. These materials will also be combined with active luminescent materials to investigate new

concepts for displays. Also the behavior of liquid crystal infiltrated structures will be studied for tunability and beam steering.

3. Conclusions

A revolutionary proposal, that of developing a photonic crystal phosphor (PCP), has been presented for enhancing and controlling phosphor properties. Simulations performed on 2-D ZnS thin-films have demonstrated what can be achieved. The issue in achieving 3D phosphor structures has been examined and viable pathways discussed for developing this technology. The major challenge to fabricating 3D PCs with a full photonic bandgap that prohibits light propagation in all 3D directions is to obtain high dielectric constant materials, and/or new material structures, that are transparent in the visible. In a direct FCC structure, a full photonic bandgap is not predicted. However, in an inverted FCC structure a full photonic bandgap is possible, but only when the index of the infiltrated material exceeds 3. To overcome the very severe requirement of wide bandgap materials transparent in the visible that exhibit refractive indices we propose the development of metal-coated ZnS nano-particles to fabricate 3D PCs. GaP has also been identified as a material that should be considered and developed further for phosphor applications. It has been discovered that ALD is an excellent tool for achieving high quality inverted opal structures. A review has been given of the potential of PCP for both display and many new applications. Also we have proposed and modeled new luminescent and active opal and inverse opal structures and shown their potential to enhance luminescent properties and to lead to new concepts such as directed light displays.

Acknowledgements

4. References

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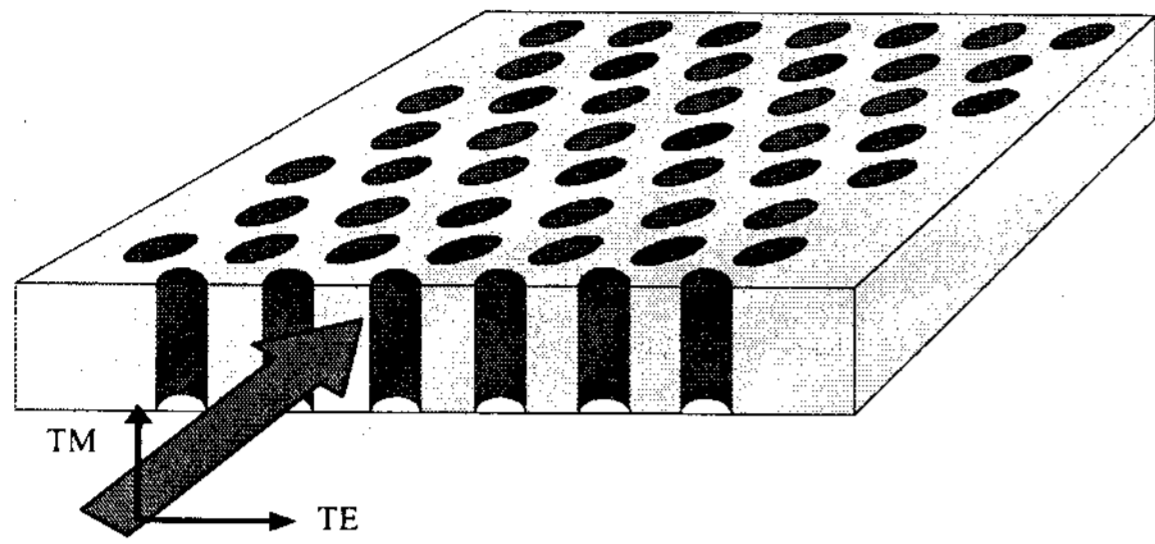
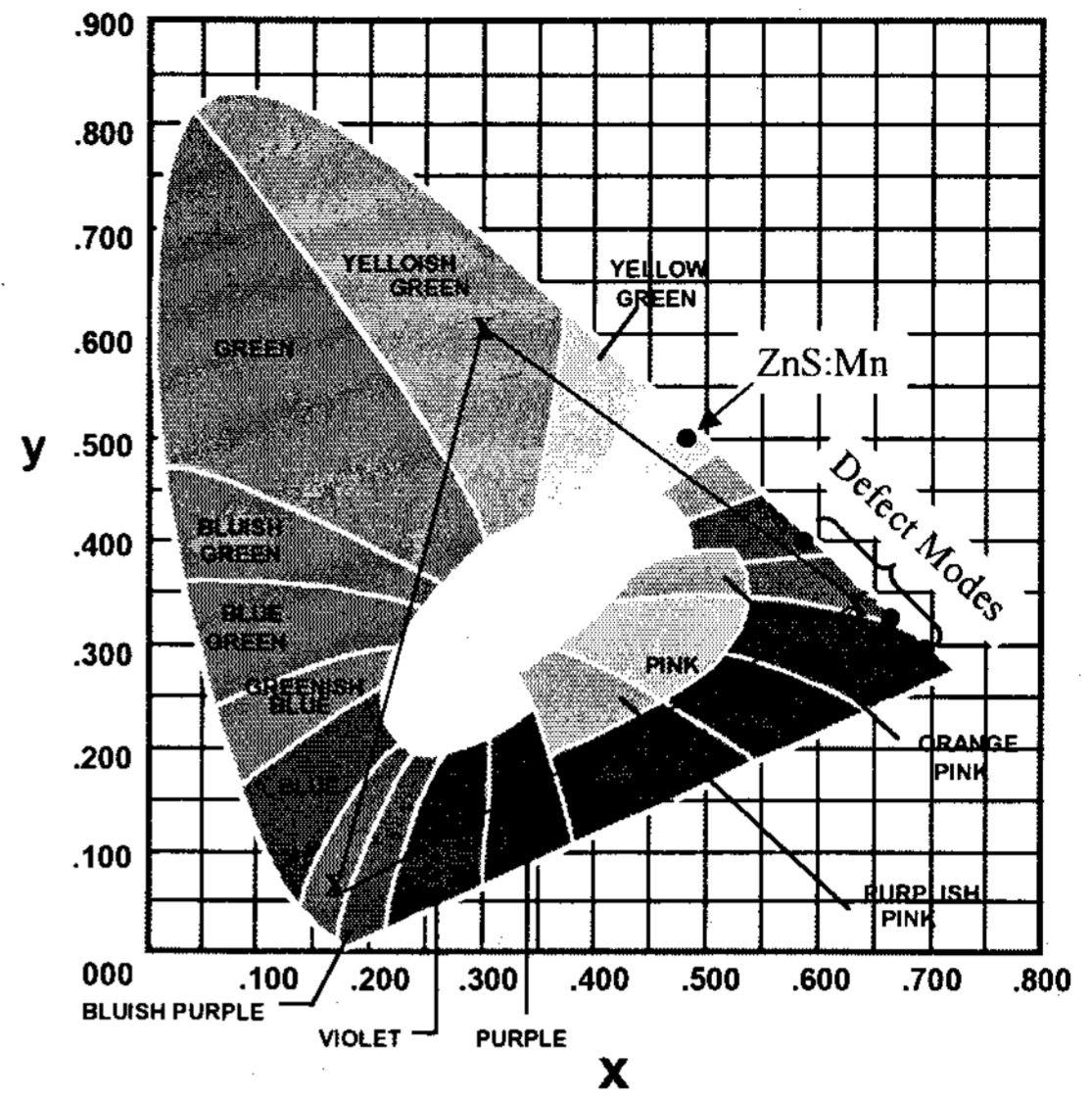Figure 1. Triangluar photonic crystal lattice patterned on a ZnS:Mn thin film

Figure 2. CIE coordinates of the conventional ZnS:Mn phosphor and the defect modes of ZnS:Mn photonic crystals
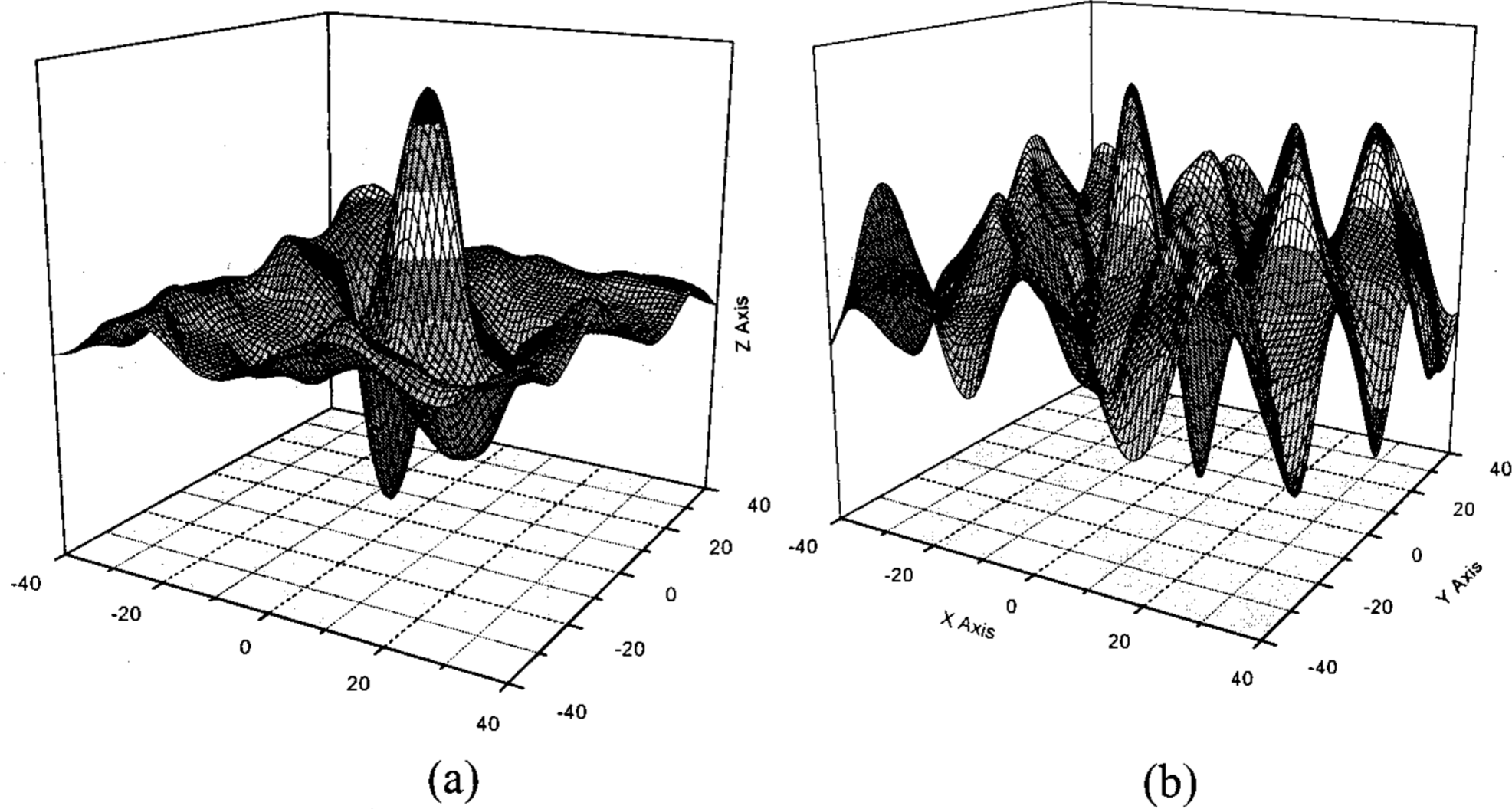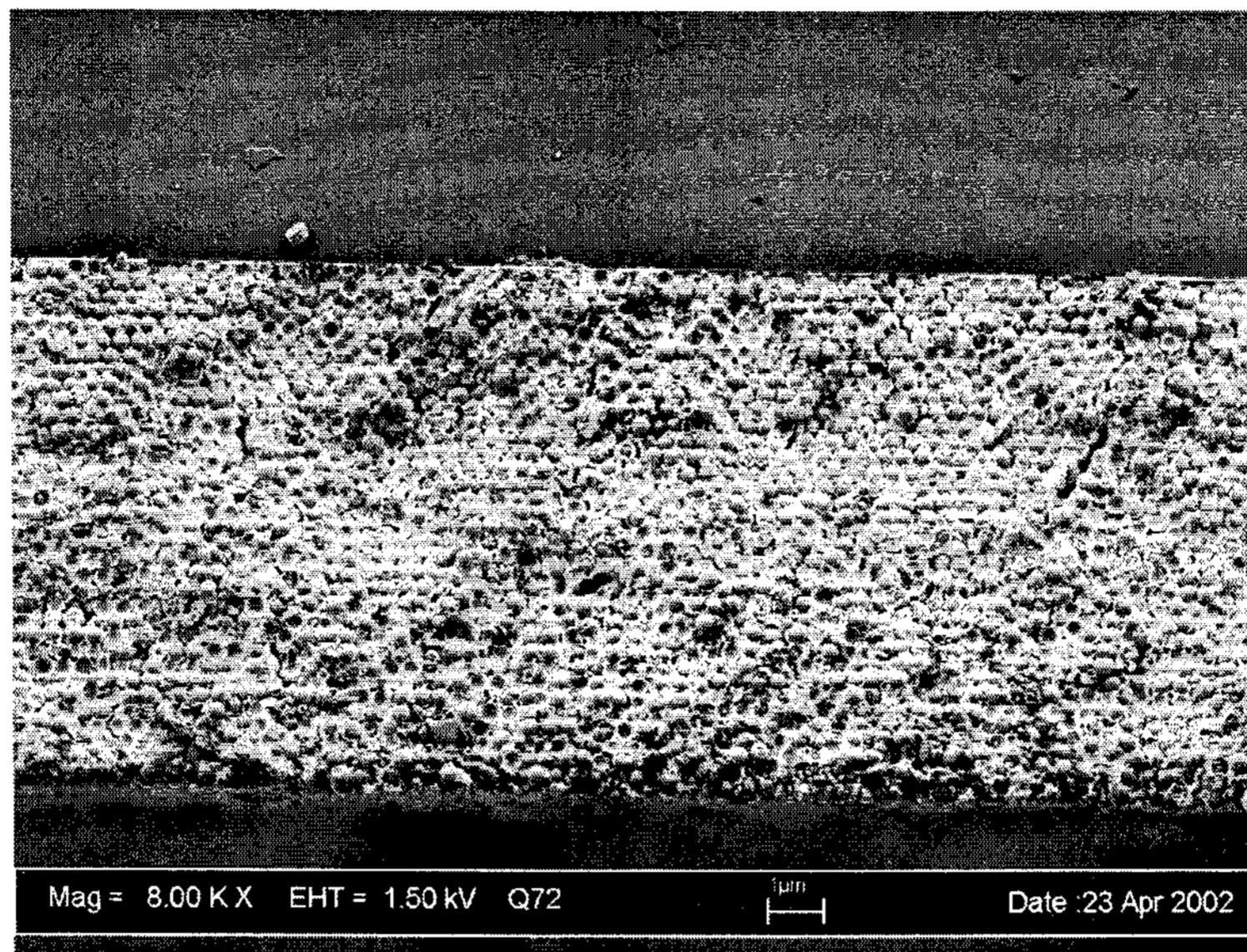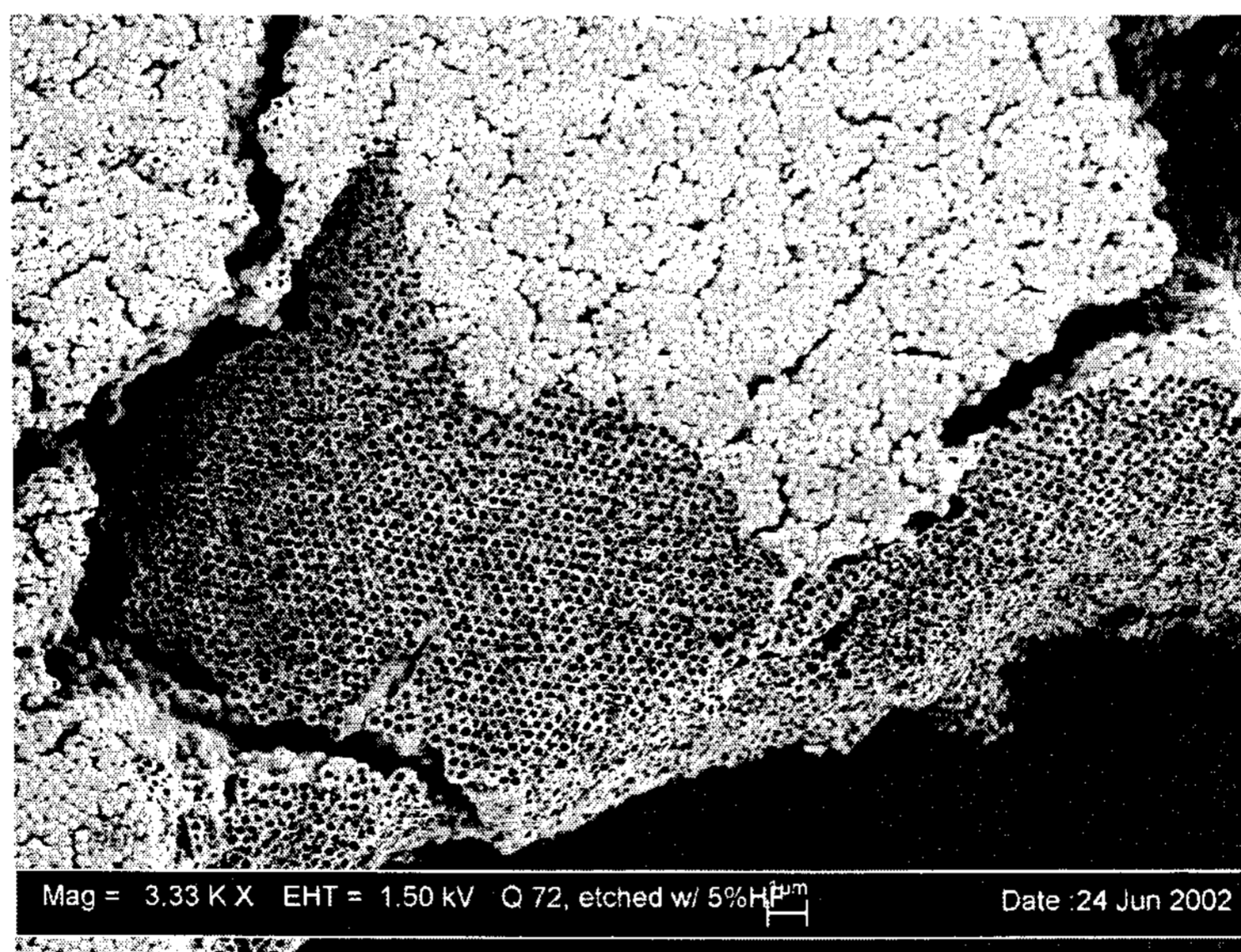

(a)   (b)

Figure 3. Field profile around the defect with (a) r = 0 and (b) r = 0.2a.

(a)

(b)

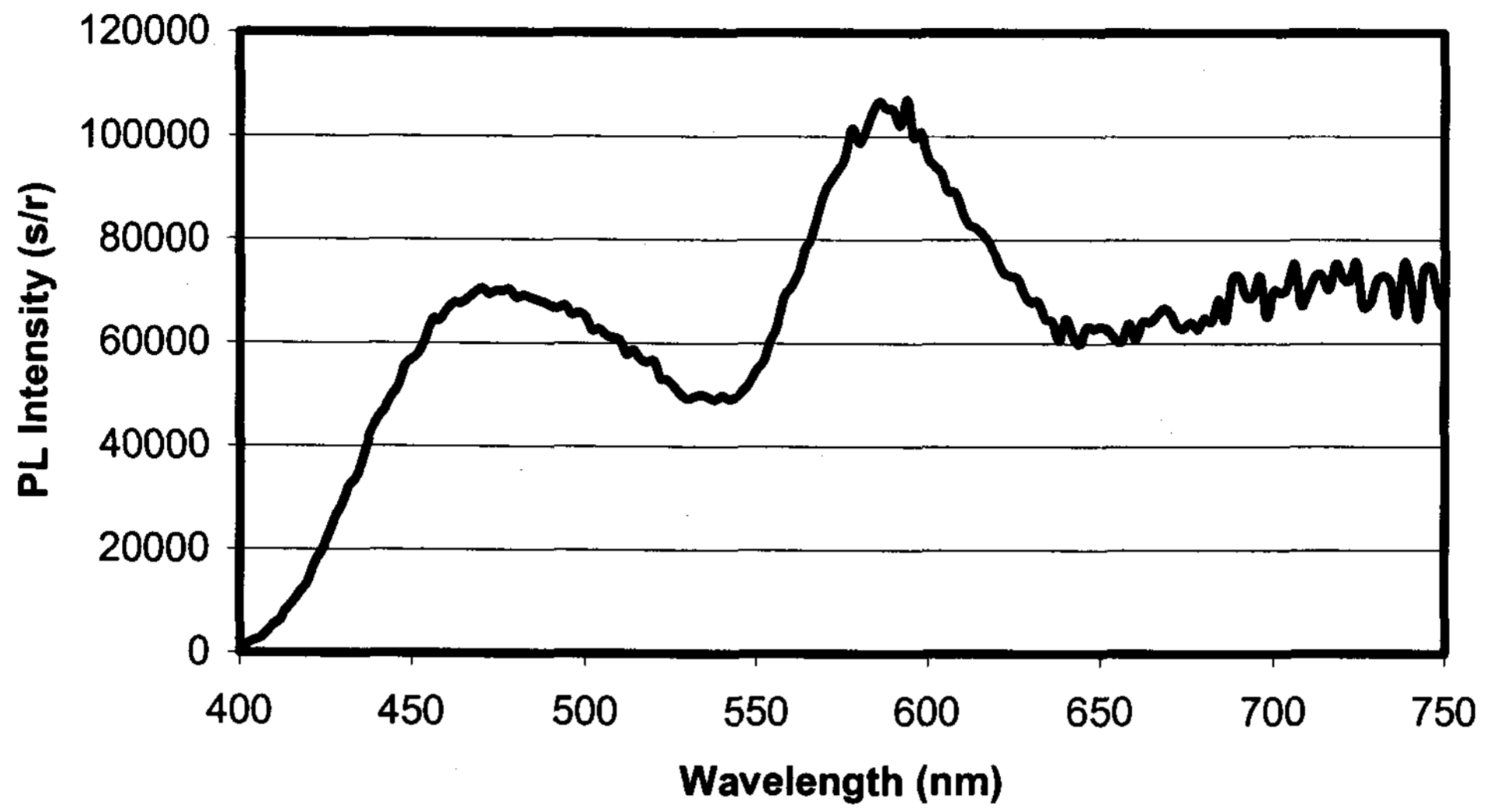Figure 4. SEM's of (a) ALD infiltrated and (b) etched (inverted) 275 nm ZnS:Mn opal.

Q72 PL- 330nm Ex.

Figure 5. Photoluminescence of opal structure formed by ALD.