Nanostructure Effects in Luminescent Materials

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Abstract

Fabrication of materials with nano features in one (thin and quantum films), two (quantum wires) and three dimensions (nanoparticles and quantum dots) in luminescent materials using thin film deposition techniques is discussed. Examples are given of the effects of these dimensions on the optical properties of semiconductor materials using either band edge or state-to-state recombination processes for optical emission. A detailed discussion is given of the effects of nanoparticles on optical scattering of red light emitted from phosphor thin films of yttrium oxide doped with europium. Brighter emission from Y_2O_3:Eu deposited by pulsed laser ablation was achieved when nanoparticles were created in the thin film by deposition in a high pressure of oxygen. The enhanced brightness was due to forward scattering by anomalous diffraction of the emitted red light.

Introduction

With the ability to grow materials in an atom-by-atom fashion, it has become common to control the dimensions of materials over dimensions of nanometers. Since their mechanical, chemical and physical properties change as their size is reduced, nanostructured materials are expected to open new opportunities for engineered devices. This is particularly true for physical properties since they are based on the electronic structure of solids, and the allowed quantum states for the electrons change as the dimension of solids is reduced below $\approx$10 nm.

Thin films are widely used as nanostructured materials. They are critical to the formation of ohmic contacts to semiconductors,[1] in microelectronic devices using two-dimensional carrier gas such as high electron mobility transistors (HEMTs),[2] and for light confining and/or luminescent layers in light emitting diodes (LEDs) and diode lasers (DLs).[2] Thin films have been reduced in a second direction to produce wires with dimensions of hundreds to tens of nanometers.[3] Finally, dots with dimensions of a few nanometers in three dimensions have been shown to have modified optical and electrical properties which have been predicted by classical and quantum mechanics.[4-15]

Historically thin films, wires and dots have been created using physical vapor and chemical vapor deposition (PVD and CVD) techniques.[16] Production of a device often requires a combination of deposition and lithographic patterning. Rapid progress has recently been made in using scanning probe techniques to control the growth and structure of quantum wires and dots.[17] The more traditional approaches of PVD and CVD complement rather than compete with these scanning probe techniques. Furthermore, nanostructured solids with properties that do not result from quantum size confinement of electronic carrier may be more easily produced using PVD and CVD, as will be illustrated below. While thin films and wires are interesting topics, exciting recent progress has been achieved in nanoparticles. Therefore examples of progress in this area will be the emphasized below.

Nanoparticles

Nanoparticles with equiaxed, cylindrical or platelet geometries can be produced a number of ways. Typical examples include evaporation or sputtering at a high rate in a partial vacuum or atmospheric pressure gas,[4,5,7,13,13] spray pyrolysis of atomized chemical precursors,[5] sol gel and similar chemical synthesis routes,[5-9,11,12] and precipitation, crystallization and grain growth methods.[5,10] The nanoparticles have been dispersed as isolated particles, as agglomerated particles, or as particles constituting a thin film. In many cases, the surfaces of the particles have been "passivated" in order to achieve the desired luminescent properties, presumably to reduce the effects of non-radiative surface recombination of charge carriers. For example, Goldburt, et al.[11,12] used a sol gel route to prepare 4-5 nm nanoparticles of ZnS and Y_2O_3 doped with various transition metals or rare earth ions. Oleic acid or polymethyl-methacrylate was used to passivate the surfaces. Y_2O_3:Tb^{3+} quantum dots deposited near room temperature showed a brightness which was 50% that of traditionally prepared micrometer sized powder.

Creation of quantum dots has resulted in shifts in the absorption and emission wavelengths. For example, Koyama, et al.[7] used pulsed laser ablation of a bulk CdS target into Ar at pressures between 10^{-3} and 5 Torr to generate particles between 4 and 10 nm in diameter. The absorption edge shifted higher than the bulk edge by 60 and 80 nm for 10 and 4 nm diameter particles, respectively. Potter and Simmons[10] have sputter deposited amorphous CdS in an amorphous SiO_2 matrix, then heat treated the thin films to produce nanocrystalline CdS precipitates. They showed that for particle diameters <50 nm, the absorption energy increased due to quantum shifts of the bandgap of the II-VI compound semiconductor. The experimental shifts versus particle size were compared with those predicted by Efros and Efros[18], and the observed optical shifts did not match well with the quantum confinement theory. Potter and Simmons attributed this discrepancy to penetration of the electronic wave function well beyond the CdS quantum dot/glass matrix interface. This wave function penetration of the matrix resulted in larger than predicted Bohr orbitals for the excitonic states of CdS. Thus, the interface of nanoparticles do not always match the assumption made in quantum mechanical calculations of confinement.

Hummel and co-workers[15] used a novel spark-discharge approach to produce nanoparticles of Si embedded in a silicon oxynitride matrix. This nanostructured material displayed strong photo, cathodo and electroluminescence. A high voltage discharge against a silicon wafer in air or a controlled ambient resulted in ≈10 nm crystalline Si particles embedded in an amorphous oxynitride matrix. Both the optical emission wavelength and intensity from this structures varied dependent upon the ambient and other conditions. Hummel, et al[15] believe that optical emission results from the formation of a nanoparticle Si/SiO_xN_{1-x} interface, rather than from quantum size shifts of the band structure of silicon. Thus, while quantum size effects are critical to some properties of nanoparticles, other properties simply result from their nanodimensions without quantum confinement.

Optical Scattering in Thin Films

An interesting class of luminescent materials are light emitting semiconductors for LEDs and DLs, or for phosphors for flat panel displays. Molecular beam epitaxy (MBE)[19] and metal organic chemical vapor depositiion (MOCVD)[20] are two common techniques used to grow nanodimension films for LEDs and DLs.[21] Films with thickness <10nm are used to confine the electrons and holes in lower bandgap material which results in enhanced bandedge recombination for optical emission.[2] In contrast, confinement in phosphors is accomplished by doping the materials with "activator" atoms, which create local impurity quantum states within the bandgap. Optical emission results from a transition either from a localized excited state (below the conduction band edge) to a localized ground state (above the valence band maximum), or from very deep donor and acceptor states in the bandgap.[22]

In addition to the differences in luminescent mechanisms, concerns with respect to light scattering are different for phosphors versus LEDs and DLs. In the latter case, MBE and MOCVD growth techniques produce smooth, epitaxial films which internally reflect the luminescence. In fact, "active" layers in DLs are commonly surrounded by optical confinement layers which increase the internal reflection of light in order to result in lasing.[21] Light will be internally reflected when the angle at it strikes the surface is larger than the critical scattering angle defined by:

$$\theta_c = \sin^{-1} (n_a/n_f)$$

where n_f and n_a are the indices of refraction of the film and the surrounding media, respectively. The angle θ is defined to be the angle at which light strikes the surface relative to the normal of the thin film, as shown in Fig. 1. For DLs, it is desirable to confine the light to the active layer, therefore a small θ_c will enhance lasing.

On the other hand, phosphors in flat panel displays, e.g. field emission displays-FEDs, should not internally reflect light.[13,14] Instead, it is desirable for light to escape from the layer in order to be detected perpendicular to the

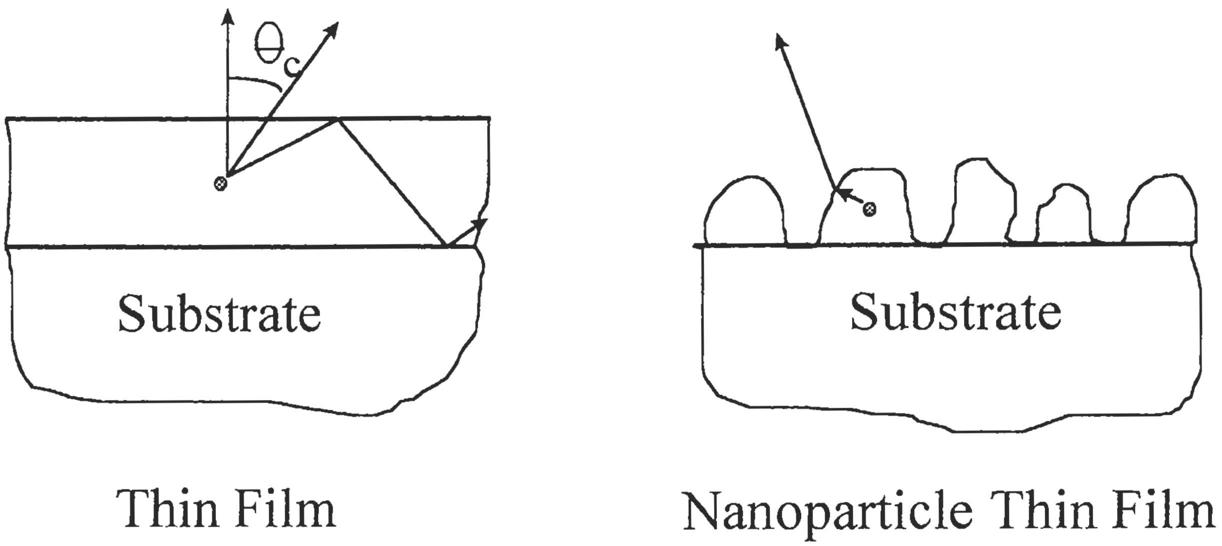


Fig.1 Definition of the critical angle for internal reflection and the effect of film planarity and roughness on optical scattering.

surface, as illustrated in Fig. 1. A large θ_c is desired to minimize internal reflection and enhance the perceived brightness and efficiency of the phosphor. Since θ_c is dependent upon materials properties and is not independently variable, light scattering out of phosphors must be accomplished by material microstructure rather than larger θ_c. As a result, phosphors are most commonly used as powders rather than films. In this case, it is desirable to scatter the light out of the film and avoid internal reflection. We have used pulsed laser deposition of a phosphor, Y_2O_3 doped with Eu, to demonstrate the advantages of a nanostructure to increase optical scattering.[13, 14]

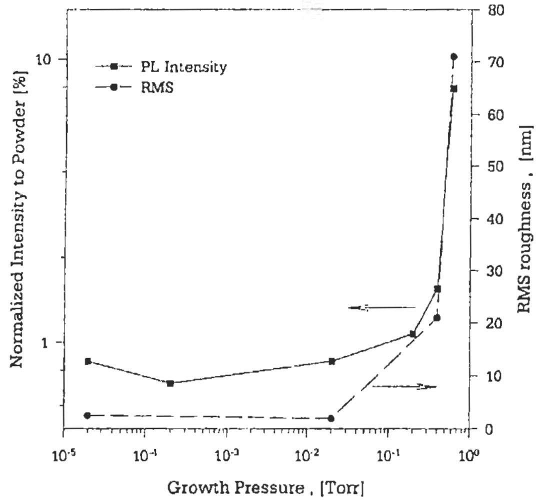


Fig.2 Photoluminescent intensity and root mean square roughness of Y_2O_3:Eu films as a function of oxygen pressure for films deposited at 600℃.

Thin films of the Y_2O_3:Eu were produced using a Lambda Physik Lasertechnik LPX300 KrF laser with a wavelength of 248 nm. A sintered target was ablated with 2J/cm^2 pulses at a 10 Hz repetition rate. The ablated material was deposited onto polished Si wafers heated to temperatures between 250℃ and 800℃. The films were tested for photoluminescence (PL) brightness by exciting them with an ultraviolet lamp operating at a wavelength of 325 nm, with the spectral distribution and brightness measured with a Photo Research Pritchard 650 spectrophotometer. Films deposited at the higher temperatures were brighter.

The PL intensity (on a logarithmic scale) versus pressure during pulsed laser deposition is shown in Fig. 2. The PL intensity was low for films deposited at oxygen pressures of <20 mTorr, but increased dramatically for deposition at 200 or 600 mTorr of oxygen. Films deposited at a vacuum of 1 x 10^{-4} Torr were very smooth as shown in Fig. 3a. However as the oxygen pressure increased above 200 mTorr, the films became increasing granular as shown in Figs. 3b-3d. The surface roughness of the thin films were measured by atomic force microscopy and found to vary from $\approx$3 nm at 0.2 mTorr to 70 nm at 600 mTorr, as shown in Fig. 2. Obviously there is a strong correlation between the surface roughness and the measured PL intensity. The particle size measured after deposition at 600 mTorr was about equal to the roughness of 70 nm. The increased luminescent brightness

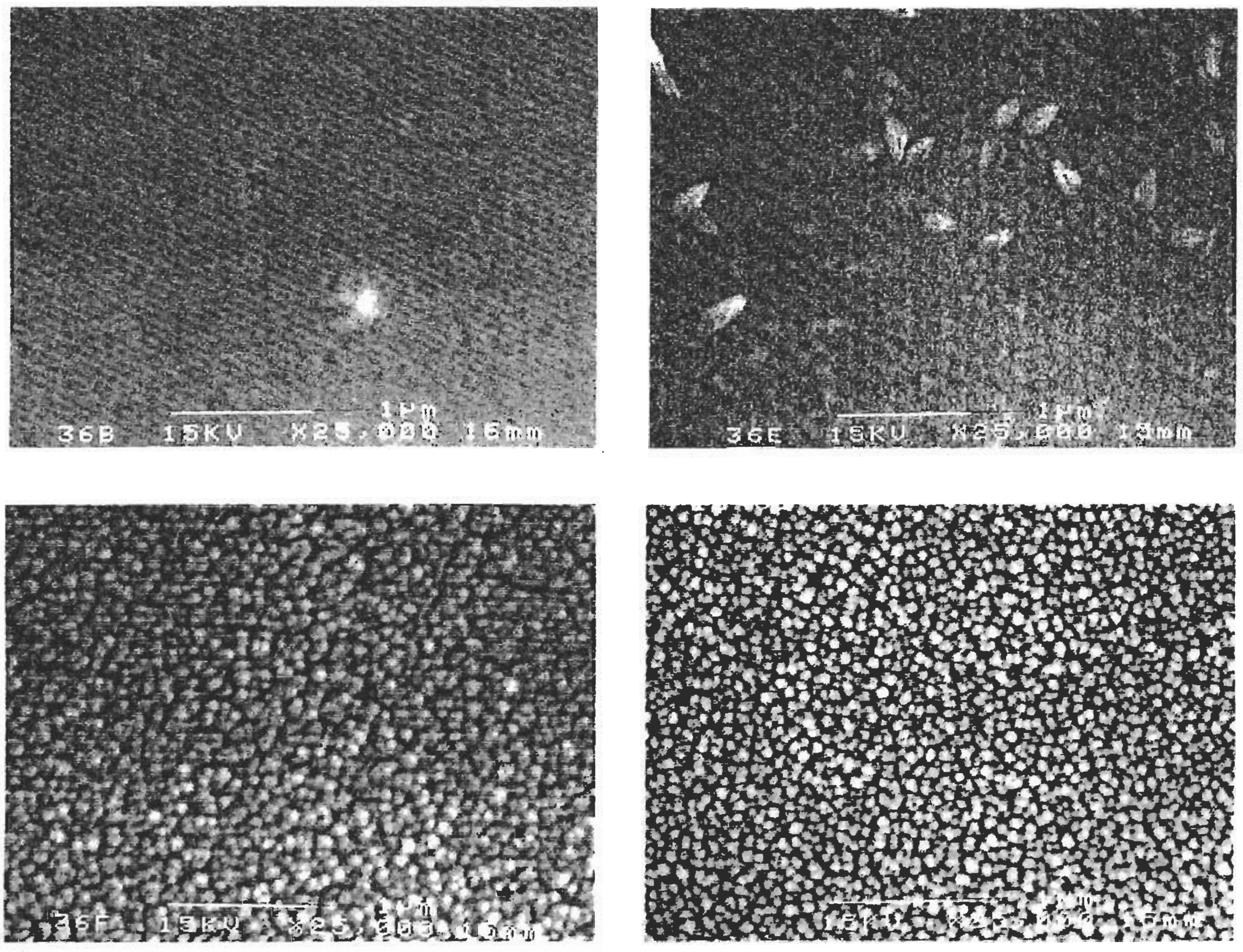
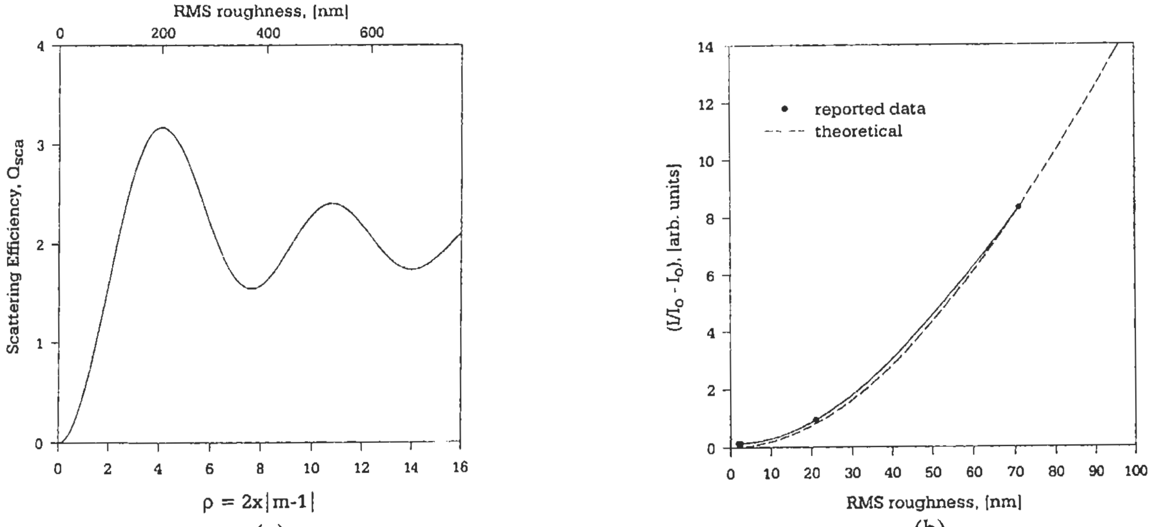


Fig.3 Scanning electron micrographs of films grown at 600℃ in pressures of (a) 10^{-4} Torr, (b) 200 mTorr, (c) 400 mTorr, and (d) 600 mTorr.



(a)

(b)

Fig.4 Forward scattering efficiency for anomalous diffraction as a function of the scattering parameter ρ (see text for definition) and surface RMS roughness (see Fig. 2). (a) Theoretical curve up to RMS roughness of 700 nm; (b) Theoretical curve and experimental data (dots) over the range of roughness from 2 to 100 nm.

could also be measure using cathodoluminescence for electron beam energies ranging from 0.5 keV to 5 keV.[23]

The increased luminescence results from the development of the nanodimension surface morphology. Optical scattering in thin films can be analyzed in terms of Rayleigh, Rayleigh-Gans, or intermediate scattering or anomalous diffraction, dependent upon the wavelength of light, optical constants, and the surface morphology.[24,25] The applicable scattering is defined by two scattering parameters x and ρ , where $x = 2\Pi a/\lambda$ and $\rho = 2x[n-1]$. In these expressions, a is the size of the particles causing scattering, λ is the wavelength of the light being scattered, n is the optical index of the scattering material, and scattering is assumed to occur into air or vacuum. For the case of Y_2O_3:Eu, the value of x is 0.73 and ρ is 1.36,[23] therefore anomalous diffraction is the appropriate mechanism to describe the increased brightness.[24,25] Based on the theory of anomalous diffraction, the light should be forward scattered to the detector used in these experiments. A plot of the intensity of the forward scattering versus x or the surface roughness (which in this case is equal to the nanoparticle size) is shown in Fig. 4. As shown in Fig. 4a, the scattered intensity increased as the roughness increased from zero to a value of about 200 nm, with an oscillatory intensity observed above this value. The curve of intensity versus roughness between 0 and 100 nm is expanded in Fig. 4b and compared to the experimental data. Note that the fit is excellent. Thus, development of nanoparticles on the surface by pulsed laser deposition of the phosphor thin film has increased the outcoupling of light and increased the effective brightness and efficiency of the phosphor.

Conclusions

Nanostructured luminescent materials may be produced by a number of techniques, including physical vapor and chemical vapor deposition. Using optical scattering and electronic carrier confinement, both the intensity and wavelength of emission may be affected. Examples of this were given with respect to anomalous diffraction of light from thin film phosphors with a nanostructure ranging from 2 to 70 nm in size. Examples of quantum dot affects upon optical emission were discussed using specific examples of CdS in glass and spark processed silicon.

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References

1. T-J. Kim and P.H. Holloway, Crit. Rev. Solid State Materials Sciences, **22**, 239-273 (1997).
2. K-N. Tu, J.W. Mayer and L.C. Feldman, *Electronic Thin Film Science for Electrical Engineers and Materials Scientists* (Macmillan Publishing Co, NY, 1992.
3. P.M. Petroff, A.C. Gossard and W. Wiegmann, Appl. Phys. Lett. **45**, 620 (1984).
4. A. Matsunawa, S. Katayama, A. Susuki and T. Ariyasu, Trans. JWRI **15**, 61 (1986).
5. L.E. Brus, Appl. Phys. **A53**, 465 (1991).
6. Y. Wang and N. Herron, J. Phys. Chem. **95**, 525 (1991).
7. T. Koyama, S. Ohtsuka, H. Nagata and S. Tanaka, J. Crystal Growth **117**, 156 (1992).
8. S.H. Tolbert and A.P. Alivisatos, Science **265**, 373 (1994).
9. B.O. Dabbousi, M.G. Bawendi, O. Onitsuka and M.F. Rubner, Appl. Phys. Lett. **66**, 1316 (1995).
10. B. G. Potter, Jr. and J. H. Simmons, Phys. Rev. **B37**, 838 (1988).
11. E.T. Goldburt and R.N Bhargava, J. SID **4**, 365 (1996).
12. E.T. Goldburt, B. Kulkarni, R.N. Bhargava, J. Taylor and M. Libera, Mat. Res. Soc. Symp. Proc. Vol. 424, p. 441 (1997).
13. S. L. Jones, D. Kumar, Rajiv. K. Singh and P.H. Holloway, Appl. Phys. Lett.,**71**, 404-406 (1997).
14. K.G. Cho, D. Kumar, S.L. Jones, P.H. Holloway and R.K. Singh, Appl. Phys. Lett, **71**, 1-3 (1997).
15. M.H. Ludwig, Crit. Rev. Solid State Materials Sciences, **21**, 265 (1996).
16. R.F. Bunshah, Editor, *Deposition Technologies for Films and Coatings* (Noyes Publications, Park Ridge, NJ, 1982).
17. K. Birkelund, E.V. Thomsen, J.P. Rsamussen, O. Hansen, P.T. Tang, P. Moller and F. Grey, J. Vac. Sci. Technol. **B15**, 2912 (1997).

18. Al.L. Efros and A.L. Efros, Sov. Phys. Semicond. **16**, 772 (1982).
19. G.W. Wicks, Crit. Rev. Solid State Materials Sciences **18**, 239 (1993).
20. Y.-M. Huong, Crit. Rev. Solid State Materials Sciences **17**, 277 (1992).
21. P. Zory, Editor, *Quantum Well Lasers* (Academic Press, New York, 1993).
22. G. Blasse and B.C. Grabmaier, *Luminescent Materials* (Springer-Verlag, New York, 1994).
23. Sean L. Jones, "Enhanced Luminescence form Europium Doped Yttrium Oxide Thin Films Grown via Pulsed Laser Deposition", Ph.D. Dissertation, University of Florida, 1997.
24. H.C. van de Hulst, *Light Scattering by Small Particles* (Dover Publications, New York, 1981).
25. F.A. Jenkins and H.E. White, *Fundamentals of Optics, Ed.* by R.A. Fry and A.T. Vinninicombe (McGraw-Hill, New York, 1976).