The photoluminescence of erbium-doped silicon monoxide.

1098

Authors:- S.W. Roberts, G. J. Parker and M. Hempstead.
Dept. Electronics and Computer Science,
Mountbatten Building,
The University,
Southampton, England. SO17 1BJ.

Presented at the 1st International Conference on Materials for Optoelectronics, 21-23/Aug 91
+ Should be published in "Optical Materials"

abstract:- Films of silicon monoxide coevaporated with erbium are shown to produce strong room temperature photoluminescence peaked at 1535nm after annealing at 600°C . Decay measurements show a double exponential function with lifetimes of 0.41ms and 2.12ms, suggesting two distinct optically active erbium sites. Photoluminescence excitation spectroscopy between 700nm and 860nm reveals a monotonic increase in photoluminescence intensity towards shorter wavelengths. This result suggests that the transfer of energy from the pump source to the erbium ions is mainly via the recombination of electron-hole pairs (photocarriers) which are created by absorption within the SiO.

Introduction:- The potential applications of an electrically pumped laser which is integrated with silicon-based microelectronic circuitry are numerous. Currently a major research effort is being directed towards rare-earth doping of silicon [1-3] and silicon-based compounds [4-5] in order to achieve this goal. Erbium-doped crystalline silicon, which immediately suggests itself as a possible laser material, exhibits a strong temperature-dependent quenching effect [3] which greatly reduces the photoluminescence efficiency at room temperature. Oxygen co-doping has been found to reduce this quenching [6], but it is still not clear that active Er^{3+} ions can be incorporated into single crystal silicon at sufficient concentrations to achieve stimulated emission. The required active ion concentration is very optimistically put at $\approx 10^{18}cm^{-3}$[7]. In this paper we present the results of photoluminescence measurements performed upon evaporated layers of erbium-doped silicon monoxide (SiO:Er). Sample layers doped at relatively high concentrations ($\approx 2.7 \times 10^{20}cm^{-3}$) exhibit strong photoluminescence at room temperature which peaks at 1535nm. Most importantly, the luminescence can be excited when the pump wavelength does not directly coincide with an Er^{3+} absorption band. The excitation mechanism in this case is probably via the recombination of electron-hole pairs, or photocarriers, which are generated by absorption in the SiO. Hence it is possible that the luminescence might also be pumped electrically within a forward-biased pn junction within SiO:Er. SiO is an amorphous semiconductor of high resistivity which can be thermally evaporated from a powder source. We believe that layers of this material should be relatively transparent in the 1550nm telecommunications window [8] and hence should form good optical waveguides.

Experimental:- By resistively heating a covered tantalum boat, silicon monoxide was thermally evaporated onto a silicon substrate at a pressure of 5×10^{-4}Pa (5×10^{-6}mBar). A crystal oscillator was used to measure both deposition rate and the final thickness of the film, which were 1.1 – 1.3nm/s and 200nm respectively. Metallic erbium was simultaneously coevaporated from a molybdenum boat using a heating current previously determined to produce a deposition rate of approximately 0.01nm/s. The erbium concentration of the resulting film was then estimated to be $2.7 \times 10^{20}cm^{-3}$. After dicing the wafer with a diamond saw, the samples were annealed for 30 minutes in flowing argon at various temperatures up to 900°C. No visible change in sample appearance was observed on removal from the furnace after any of the anneal cycles.
Photoluminescence spectra were measured using a Perkin-Elmer FTIR spectrometer which was set at $2cm^{-1}$ resolution and fitted with an InGaAs photodiode. Excitation was pro-

vided by an unfocussed 0.8mm diameter beam from an argon ion laser incident on the samples at 45°. The laser was tuned to 488nm with variable power between 100mW and 2.5W. Variation in photoluminescence intensity with pump power was investigated as the beam power was increased up to 2.5W ($\approx 500 W/cm^2$). In this case the photoluminescence was detected by an InGaAs photodiode via a 1530nm narrow band-pass filter and measured by a lock-in amplifier.
For lifetime measurements, the excitation source was chopped at 40Hz. The photoluminescence was filtered and detected as before, averaged on a digital storage oscilloscope and transferred to a computer for analysis.
Photoluminescence excitation spectroscopy was performed by pumping with a Ti : Al_2O_3 laser which was tunable from 700nm to 860nm. The photoluminescence intensity recorded by the lock-in amplifier was normalised to the power output of the Ti : Al_2O_3 laser at each wavelength.

Results and Discussion:- The room temperature photoluminescence spectrum of a sample annealed at 600°C for 30 minutes is shown in Figure 1. The two main peaks are at 1535 nm ($6515cm^{-1}$) and 1549 nm ($6457cm^{-1}$). While the measured full-width-at-half-maximum is 33nm, integrating and normalising the spectrum gives an effective linewidth for gain calculations of 47nm. The spectrum is typical of the intra-4f Er^{3+} transition from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$. The spectrum is also very similar in form to those published for erbium-doped SiO_2 [4,9]. This suggests that the optically active erbium sites within the SiO are similar to those in SiO_2 .
The relative intensity of this photoluminescence is highly dependent upon the temperature of the 30 minute argon anneal, as is shown in Figure 2. Although the emission is detectable immediately after deposition, its intensity increases by over two orders of magnitude following an anneal at 600°C, after which the photoluminescence intensity is maximised. The presence of a maximum in the annealing curve may be explained as follows. Immediately after deposition, much of the evaporated erbium will remain in the metallic form and therefore will be optically inactive. Annealing at increasingly higher temperatures will cause more of this erbium to become oxidised into the optically active Er^{3+} state. Annealing also reduces the density of dangling bonds and other recombination centres which otherwise compete with the erbium population for excitation. Hence, up to 600°C, there is a monotonic increase in the photoluminescence yield. Annealing SiO at higher temperatures is known to cause the formation of silicon nano-grains surrounded by shells of SiO_2 [10]. This structural change is likely to lead to the precipitation and/or segregation of erbium within the silicon grains or at the grain boundaries. Hence, this is most likely to be the cause of the reduction in photoluminescence yield on annealing above 600°C .
The intensity of the photoluminescence was not found to be a linear function of pump intensity, but rather began to saturate at higher powers. This behaviour is shown in Figure 3. If we consider erbium-doped SiO to be a three-level system, then by balancing the rates of excitation and de-excitation of the second (metastable) level we find that its population, N_2, under a pump intensity I is:

$$N_2 = \frac{I}{\frac{hc}{\tau \lambda_{pump} \sigma} + I} N \qquad (1)$$

where h is Plank's constant, c is the velocity of light, τ is the average lifetime of level 2, λ_{pump} is the wavelength of the pump source, N is the concentration of the active Er^{3+} ion population and σ is the absorption cross section of the third (upper) level to the pump. As the observed photoluminescence intensity is proportional to the population N_2, we may fit expression 1 to the curve in Figure 3 to obtain an estimate of the absorption cross-

section, σ. Taking an average lifetime of $\tau = 1$ms (see below) we find $\sigma \approx 10^{-18}$cm^2. For erbium-doped SiO_2 and silicate glasses, absorption cross sections usually peak at around 10^{-20}cm^2 [9].

Using σ it is now possible to find the rate of excitation of Er^{3+} ions and hence the pumping efficiency, η_{pump}:

$$\eta_{pump} = \frac{N\sigma}{\alpha}\frac{\lambda_{pump}}{\lambda_{lum}} \tag{2}$$

Where α is the absorption coefficient of the pump beam in the SiO , and λ_{pump} and λ_{lum} are the pump and photoluminescence wavelengths respectively. Taking $\alpha = 10500$cm^{-1} [8] we find that the pumping efficiency is approximately 1%. Note that this figure is correct assuming 100% activation of the Er^{3+} ions.

Photoluminescence decay measurements reveal two simultaneously decaying exponentials, each of which exhibits a different time constant. This result is very strong evidence that there are two distinctly different optically active Er^{3+} sites in the sample. For the measurement made using 2W of 488nm light as the pump source, an extremely good fit to the photoluminescence intensity decay curve was obtained with the formula:

$$\mathrm{I(t)} = 0.43\exp\left(\frac{-\mathrm{t}}{0.41\mathrm{ms}}\right) + 0.57\exp\left(\frac{-\mathrm{t}}{2.12\mathrm{ms}}\right) \tag{3}$$

The respective contributions of the fast and slow decaying sites to the overall observed decay do not represent the actual fractions of fast and slow decaying sites in the Er^{3+} population. This is because it is very unlikely that the emissions are entirely radiative. If we assume that the true radiative lifetime of both of the emitting sites is 10ms (a value representative of the same Er^{3+} transition in pure silica and silicate glasses [9]), then we can calculate the true fraction of the Er^{3+} population which decays at each rate. Considering the radiative efficiencies, we find that only 14% of the active Er^{3+} population decays with the longer lifetime of 2.12ms. The remaining 86% appear to be more heavily quenched and decay at the faster rate.

Figure 4 shows the relative photoluminescence intensity when the pump wavelength is scanned from 700nm to 860nm using a $Ti : Al_2O_3$ laser. The photoluminescence increases monotonically towards shorter wavelengths and corresponds to the increasing SiO absorption coefficient. The existence of this broad-band pumping mechanism is very important and contrasts strongly with the pumping mechanism which operates in erbium-doped insulators such as SiO_2. Optical excitation in erbium-doped SiO_2 results when the energy of a pump photon coincides with the energy of a transition from the erbium ground state to a higher lying 4f level [9]. In this case the insulating host acts merely as a transparent material in which the active Er^{3+} ions are held and is not directly involved in the excitation mechanism. The results presented here show that as a host for Er^{3+} ions, SiO does participate in the excitation mechanism. This process probably involves the creation of electron-hole pairs, or photocarriers, in the SiO band structure which subsequently recombine at erbium sites. This results in excitation of Er^{3+} ions. Note that the Er^{3+} absorption band at $\approx$800nm is not evident in Figure 4 because the direct excitation from this absorption is swamped by the indirect excitation via photocarriers. Similar results have been published for other semiconductors doped with erbium, such as crystalline silicon [1-3], SIPOS material (27% oxygen doped amorphous silicon) [4,5] and semiconducting chalcogenide glasses [11].

At present, we do not have an estimate for the active fraction of the Er^{3+} population, but waveguiding experiments are currently underway to determine this figure from absorption measurements at the 1535nm band. If the active fraction is high and the waveguide losses at 1535nm are low enough, there will be a possibility of demonstrating a waveguide laser optically pumped in a transverse configuration.

Conclusion:- Photoluminescence measurements were performed on evaporated layers of erbium doped silicon monoxide. The maximum photoluminescence yield was obtained after a 30 minute argon anneal at 600°C. Following this anneal treatment, lifetime measurements revealed transients which consist of two simultaneously decaying exponentials with fast and slow time constants of 0.41ms and 2.12ms respectively. A photoluminescence excitation spectrum for pump wavelengths between 700nm and 860nm shows a broad pump band with increasing excitation as the wavelength is shortened. This is probably due to energy transfer from the pump beam to the Er^{3+} ions via photocarriers in the SiO host.

References

[1] H. Ennen, J. Schneider, G. Pomrenke and A. Axmann, "1.54-mm luminescence of erbium-implanted III-V semiconductors and silicon.", Applied Physics Letters, 43, (10), pp. 943-945. (1983)

[2] F. Y. G. Ren, J. Michel, Q. Sun-Paduano, B. Zheng, H. Kitagawa, D. C. Jacobson, J. M. Poate and L. C. Kimerling, "IC compatible processing of Si:Er for optoelectronics.", Materials Research Society Symposium Proceedings, (301), San Francisco, pp. 87-95. (1993)

[3] S. Coffa, G. Franzo, F. Priolo, A. Polman and R.Serna, "Temperature dependence and quenching processes of the intra-4f luminescence of Er in crystalline Si.", Physical Review B, 49, (23), pp. 16313-16320. (1994)

[4] S.Lombardo, S.U.Campisano, G.N.van den Hoven, A.Cacciato and A.Polman. "Room-temperature luminescence from Er-implanted semi-insulating polycrystalline silicon.", Applied Physics Letters, Vol. 14, No. 4, pp. 1942 - 1944. (1993)

[5] S.Lombardo, S.U.Campasano, G.N.van den Hoven and A.Polman,"Erbium in oxygen doped silicon. Electroluminescence." ,Journal of Applied Physics, Vol. 77, No. 12, pp. 6504 - 6510. (1995)

[6] P.N. Favennec, H.L'Haridon, D.Moutonnet, M.Salvi and M.Gauneau,"Optical activation of Er^{3+} implanted in silicon by oxygen impurities." ,Japanese Journal of Applied Physics, Vol. 29, No. 4, pp. L524 - L526. (1990)

[7] Y.H.Xie, E.A.Fitzgerald and Y.J.Mii,"Evaluation of erbium-doped silicon for optoelectronic applications.", Journal of Applied Physics, Vol. 70. No. 6, pp. 3223 - 3228. (1991)

[8] E.D.Palik (Ed.), "Handbook of optical constants of solids.", Orlando : Academic Press. (1984)

[9] Michel J. F. Digonnet (Ed). "Rare earth doped fiber lasers and amplifiers.", Marcel Dekker, Inc. New York. (1993)

[10] G.Hass and C.D.Salzberg,"Optical properties of silicon monoxide in the wavelength region from 0.24 to 14.0 microns." ,Journal of the Optical Society of America, Vol. 44, No. 3, pp. 181 - 187. (1954)

[11] S.Q.Gu, S.Ramachandran, E.E.Reuter, D.A.Turnbull, J.T.Verdeyen and S.G.Bishop, "Novel broad-band excitation of Er^{3+} luminescence in chalcogenide glasses.", Applied Physics Letters, Vol. 66, pp. 670 - 672. (1995)

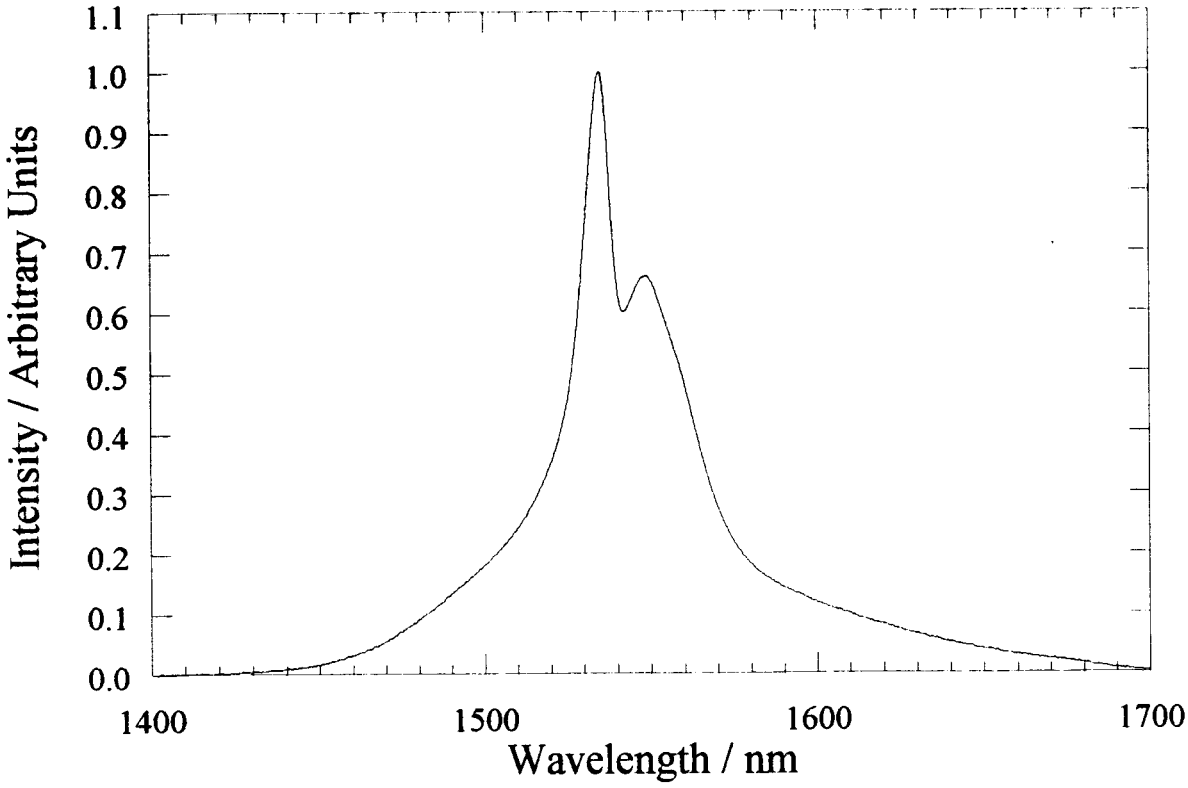

Figure 1: Photoluminescence spectrum of SiO:Er. Annealed at 600°C in argon for 30 minutes.

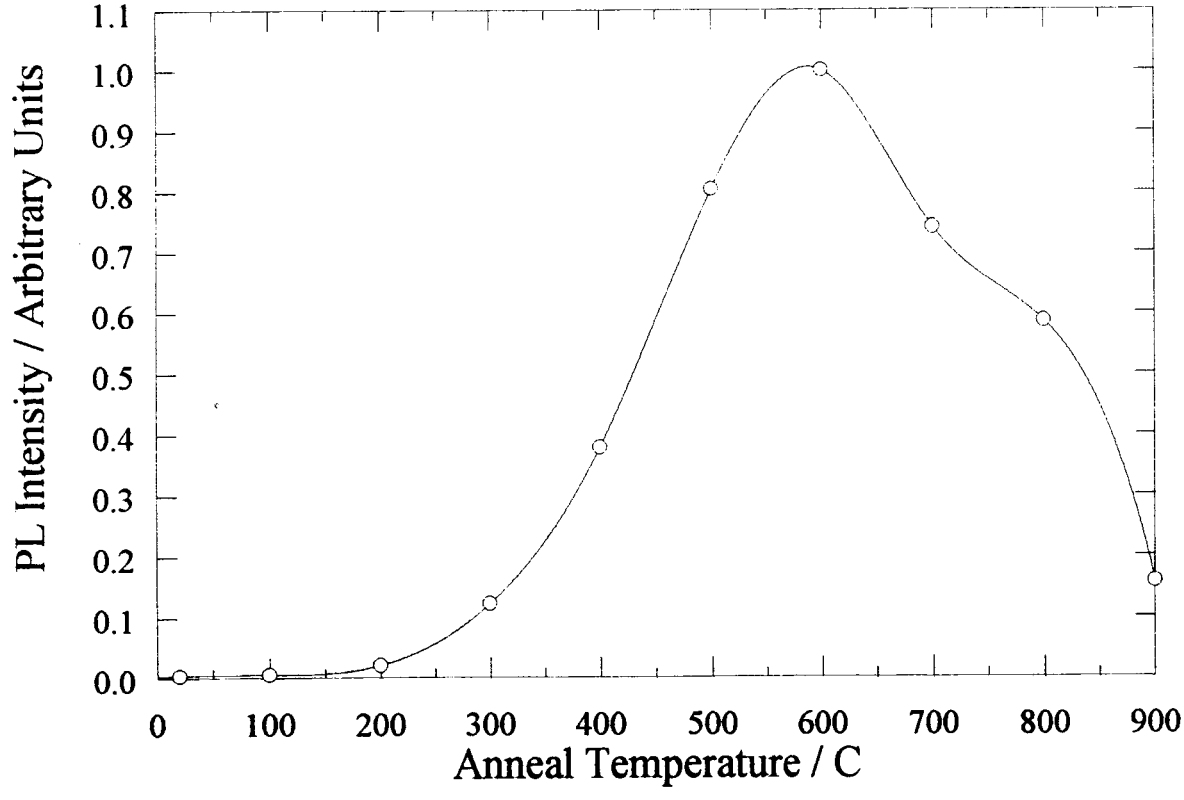

Figure 2: Relative photoluminescence intensity for various anneal temperatures in argon for 30 minutes.

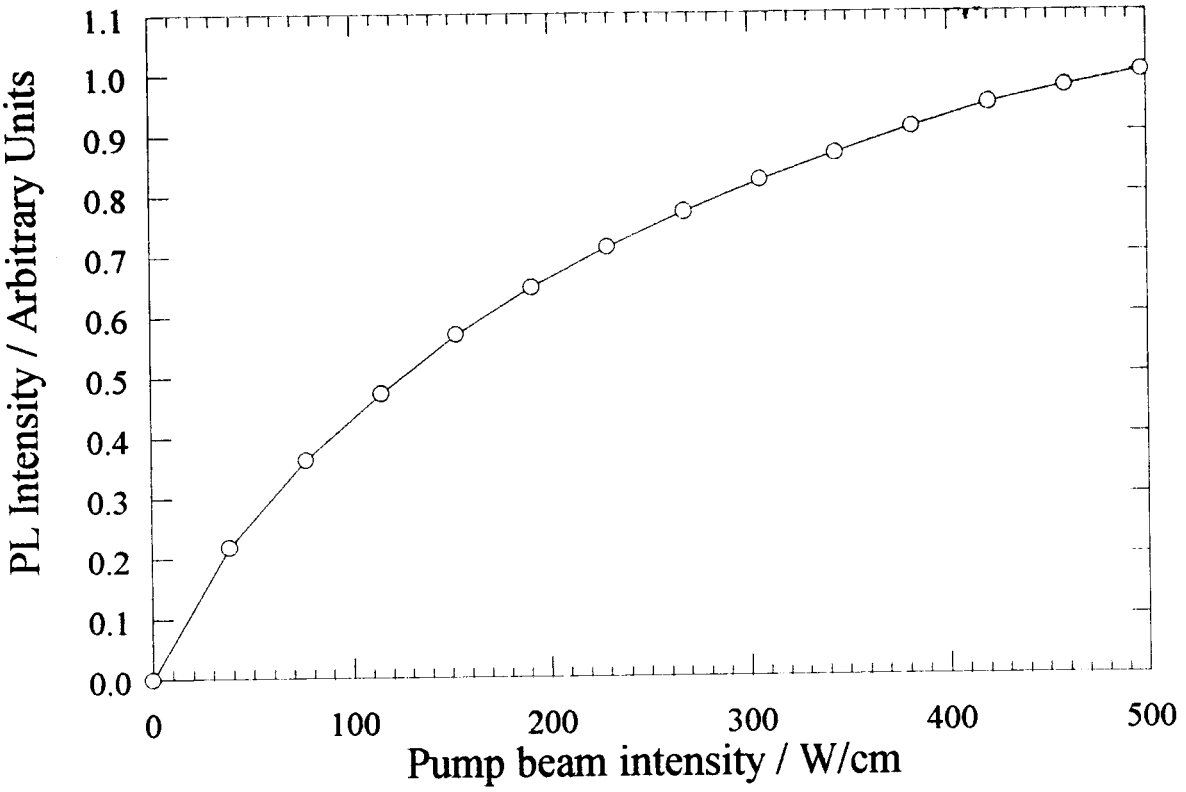

Figure 3: Relative photoluminescence intensity for various pump beam intensities. The pump excitation wavelength was 488nm with a beam diameter of approximately 0.8mm.

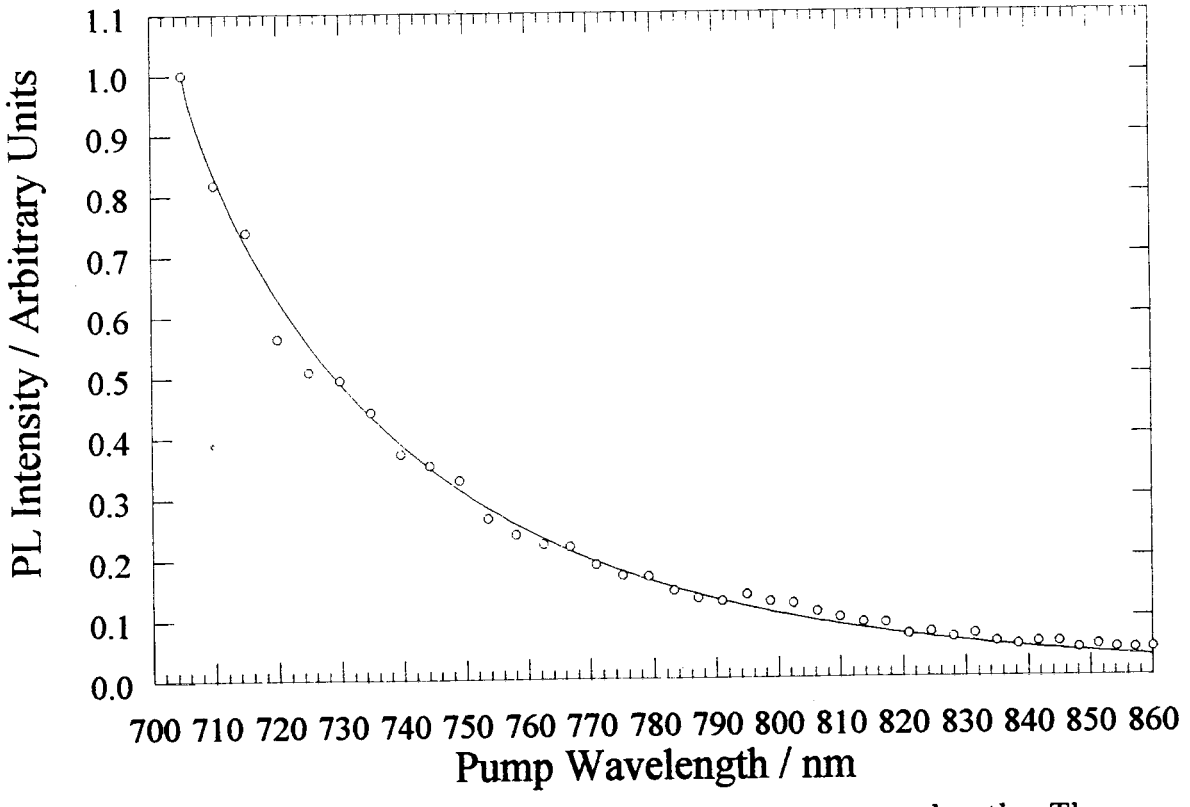

Figure 4: Relative photoluminescence intensity for various pump wavelengths. The pump excitation source was a Ti : Al_2O_3 laser.