Photoluminescence peak energy evolution for porous silicon during photo-oxidation and gamma -ray oxidation

Photoluminescence peak energy evolution for porous silicon during photo-oxidation and γ-ray oxidation

L Z Zhang†, B Q Zong†, B R Zhang†, Z H Xu‡, J Q Li§ and G G Qin†

† Department of Physics, Peking University, Beijing 100871, People's Republic of China
‡ Department of Chemistry, Peking University, Beijing 100871, People's Republic of China
§ Department of Technical Physics, Peking University, Beijing 100871, People's Republic of China

Abstract. The evolution of photoluminescence (PL) from a series of as-anodized porous silicon (PS) samples with peaks in a wide energy range has been investigated systematically during oxidation enhanced by either laser illumination or γ-ray irradiation. Under both oxidation conditions, PL spectra initially located in the infrared–red region undergo a blue shift, while those initially located in the orange–yellow region experience a red shift. Eventually, all the peaks are pinned at fixed energies which are in an energy range narrower than that for as-anodized PS samples. These experimental results can be explained by the quantum confinement–luminescence centres model, which argues that photoexcitation proceeds in nanoscale silicon and photoemission through the luminescence centres outside nanoscale silicon, and also by assuming that during oxidation the main luminescence centres change from one kind to another and/or the relative contributions to the PL intensity from various kinds of luminescence centres vary.

1. Introduction

Although efficient visible photoluminescence (PL) from porous silicon (PS) was demonstrated by Canham [1] three years ago and since then both theoretical and experimental studies on PS have been carried out intensively all over the world and there has been a great advance in research, unfortunately the mechanism for the visible light emission from PS is still a subject of controversy. Many models have been suggested, including quantum confinement [1], siloxene [2] or its derivatives, SiH_x complexes [3] or polysilanes [4], hydrogenated amorphous silicon [5], and the surface state mechanism suggested by Koch *et al* [6], which argues that electron–hole pairs are excited in nanoscale-silicon cores and recombine via Si surface states. The quantum confinement–luminescence centres (QCLC) model [7] was recently suggested, which contends that the electron–hole pairs or excitons are excited in nanoscale silicon unites (NSUs), i.e., nanoscale Si quantum dots or wires in PS and then radiatively recombine through luminescence centres outside NSUs. Although these models were proposed according to evidence from a great number of experiments, whether they can account for the evolution of PL from PS during oxidation is a serious challenge, because the evolution processes of the PL peak energy from PS during oxidation is very complicated and seems difficult to explain satisfactorily.

Oxidation processes have been demonstrated to be effective methods for obtaining PS films with stable PL spectra [8–12]. However, with respect to the evolution of PL, many researchers have reported different results. Nakajima *et al* [8], Shih *et al* [9] and Duan *et al* [10] observed a blue shift for PL from the PS under thermal oxidation and photo-oxidation,

respectively. On the other hand, Zhou *et al* [11] and Li *et al* [12] found that oxidation causes a red shift for the PL from PS. In this work, we used two methods of oxidation in air, namely laser illumination and γ-ray irradiation, to investigate the evolution of PL from PS. Detailed results, which are compatible with the work reported previously, are given. The results indicate that the PL peaks in the infrared–red region shift to higher energies and the PL peaks in the orange–yellow region shift to lower energies with oxidation enhancement. Eventually, all the peaks are pinned in an energy range narrower than the original range, where the PL peaks from the as-anodized PS are dispersed. These experimental results can be explained by the QCLC model.

2. Experiments

The samples used in these experiments are 10 Ω cm and 63 Ω cm p-type Si wafers. Before anodization, and Al film was deposited onto the back side of the wafers in a vacuum chamber and then the wafers were annealed at 540 °C for 10 min to obtain good ohmic contact. The wafers were anodized in an anodization system similar to that previously reported [13] with an electrolyte of HF (49 wt%):H_2O:acetone = 1:1:0–4. The current density ranged from 20 to 200 mA cm^{-2} and the anodization was performed with or without light illumination. The above anodizing parameters ensure that the as-anodized samples have PL peak energies distributed in a range from 1.44 to 1.99 eV. Prior to the oxidation experiments, the PL spectra for freshly prepared PS were measured with an HRD-I double-grate spectrometer while under 488.0 nm Ar^+ laser excitation. All measurements of PL spectra of either as-anodized PS or oxidized PS were carried out after a period of laser illumination for 4 min in order to stabilize the PL intensity of PS. A number of as-anodized PS samples with various PL peak energies between 1.44 and 1.99 eV were divided into two groups.

One group was oxidized using laser illumination. Exposing the samples to laser illumination in air is a conventional oxidation method and has been discussed in a previous paper [10]. The laser used was a 488.0 nm Ar^+ laser beam with a power density of 1.9 mW mm^{-2}. The PL spectra were measured after various illumination periods, and initial blue shifts or red shifts followed by pinning of the PL peak energies were observed.

Since then γ irradiation has been found to be an effective method for accelerating oxidation of PS and also greatly improving the luminescence stability of PS [14]. The other group of as-anodized PS samples were exposed to air and irradiated by γ-rays. As in the case for laser illumination, initial blue shifts or red shifts followed by pinning of PL peak energies were again observed.

To monitor the extent of oxidation during laser illumination and γ-ray irradiation, the Fourier-transform infrared (FTIR) spectra were measured in these studies. The FTIR spectrometer employed is a Nicolet-7199B instrument, which has a typical frequency resolution of 4 cm^{-1}.

3. Results and discussion

Figure 1 and figure 2 show the evolutions of PL spectra from PS samples 6 and 2, respectively, during laser illumination. From figure 1, it can be seen that the PL spectrum with an initial peak energy of 1.48 eV undergoes a blue shift at first, followed by pinning at 1.65 eV; furthermore, the intensity of PL decreases for about the first hour of laser illumination and then increases slowly. In figure 2, the PL spectrum with an initial energy of 1.85 eV
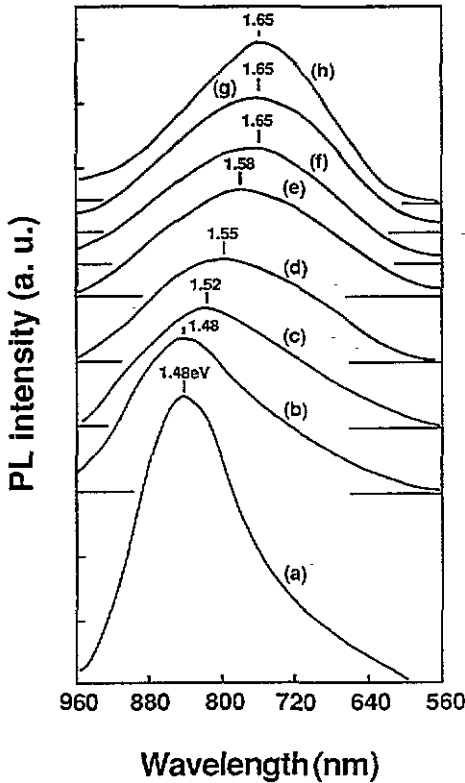
Figure 1. The evolution of PL spectra for PS sample 6 measured after various laser illumination periods (a.u., arbitrary units): curve (a), 4 min; curve (b), 22 min; curve (c), 42 min; curve (d), 67 min; curve (e), 91 min; curve (f), 113 min; curve (g), 150 min; curve (h), 240 min.
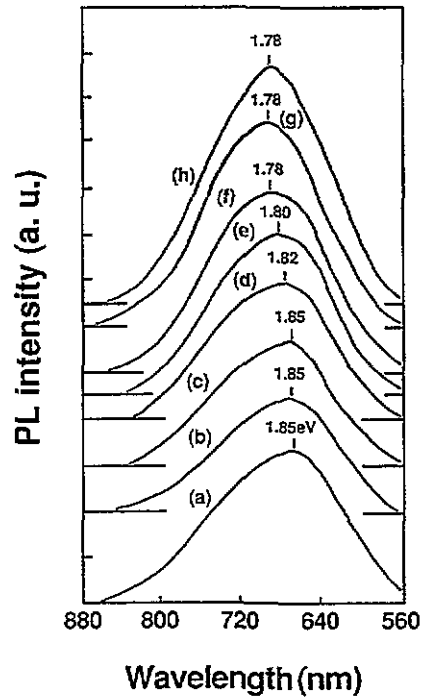
Figure 2. The evolution of PL spectra for PS sample 2 measured after various laser illumination periods (a.u., arbitrary units): curve (a), 4 min; curve (b), 27 min; curve (c), 50 min; curve (d), 73 min; curve (e), 96 min; curve (f), 119 min; curve (g), 179 min; curve (h), 240 min.

experiences a red shift initially, followed by pinning at 1.78 eV. Figure 2 shows there is a small initial reduction in the PL intensity which is followed by gradual enhancement.

Moreover, from the experimental results for a series of PS samples with different initial PL peak energies, a new characteristic for the evolution of PL spectra during laser illumination is observed, as illustrated in figure 3. The PL peaks within the infrared–red region shift to higher energies and the PL peaks within the orange–yellow region shift to lower energies with oxidation enhancement. Eventually, all peaks are pinned in an energy range narrower than the original energy range, where the PL peaks from the as-anodized PS samples are dispersed.

The evolution of PL spectra from PS samples 12 and 7, which are oxidized under γ-ray irradiation in air, is shown in figure 4 and figure 5, respectively. Figure 4 shows that the PL spectrum with an initial peak energy of 1.45 eV undergoes a blue shift initially, followed by pinning at 1.61 eV; furthermore, the intensity of PL increases continuously. Figure 5 shows that the initial red shift is followed by pinning at 1.89 eV for the PL spectra with an initial peak energy of 1.99 eV, and the PL intensity decreases at first and then remains almost stable as the γ-ray irradiation dose is increased.

Figure 6 shows that for a group of as-anodized PS samples with different initial PL peak
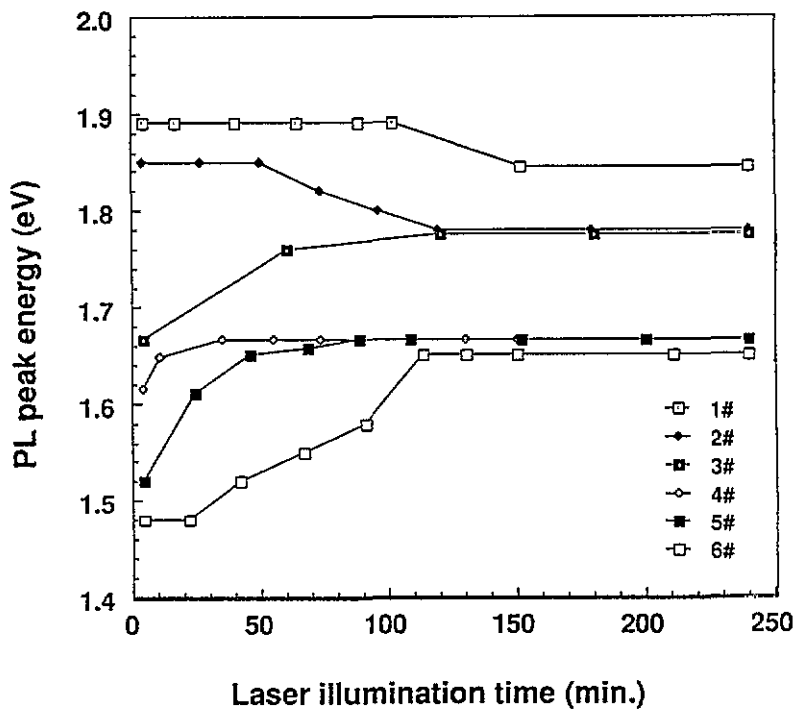
Figure 3. Shift in the PL energies followed by pinning during laser illumination oxidation for a group of samples with different initial PL peak energies.

energies the change in peak energy is a function of the γ-ray irradiation dose. Similar to the case of oxidation enhanced by laser illumination, a red shift occurs in the PL spectra with peak energies higher than about 1.8 eV, while there is a blue shift in the PL spectra with peak energies less than about 1.8 eV during γ-ray irradiation. As the dose of γ-rays increases to higher than 1.6×10^8 rad, the PL peaks for different PS samples are pinned at their corresponding fixed energies, which are located in a range 1.6–1.9 eV which is narrower than the range 1.44–1.99 eV for the as-anodized PS samples.

Figures 7(a) and 7(b) show typical FTIR spectra for the as-prepared PS as well as for the oxidized PS at the beginning of the PL peak pinning and at the end of treatment in air by laser illumination and γ-ray irradiation, respectively. The as-prepared PS samples exhibit a weak absorbance at 1107 cm^{-1}, showing that a small number of Si–O–Si bonds were induced in the short time (less than 30 min) between preparation and the first measurement in air, as well as pronounced infrared absorption features at 2087–2110 cm^{-1} (a doublet, Si–H an Si–H$_2$ stretching modes), 910 cm^{-1} (Si–H$_2$ scissors mode) and 610–670 cm^{-1} (Si–H$_n$ deformation modes), as shown in both figure 7(a) and figure 7(b). However, as the PS is oxidized by either of the two means, the hydrogen content in the samples will decrease or even be eliminated, which is confirmed by the reduction in intensity of the modes at 2087–2110, 910 and 610–670 cm^{-1}; concurrently, the oxygen content rapidly rises and keeps on increasing with increasing laser illumination time or γ-ray irradiation dose. On comparison of curve B with curve C in figure 7(a) as well as curve B with curve C in figure 7(b), it is found that, even after the PL peaks have been pinned, the 1107 cm^{-1} infrared absorption peak increases monotonically during laser illumination and γ-irradiation, showing that oxidation of PS still continues. Figure 7 also shows that γ-ray irradiation has
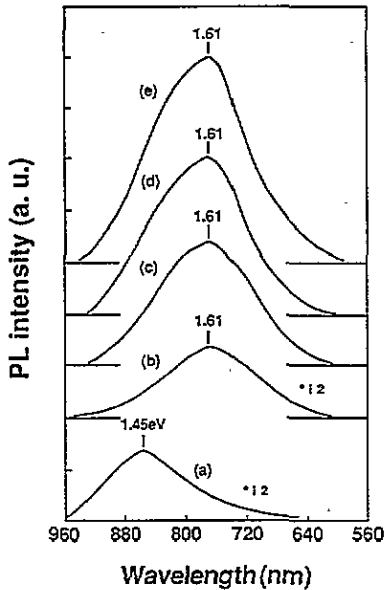
Figure 4. The evolution of PL spectra for PS sample 12 measured after various γ-ray irradiation doses (a.u., arbitrary units): curve (a), 0; curve (b), 1.17×10^8 rad; curve (c), 1.58×10^8 rad; curve (d), 2.80×10^8 rad; curve (e), 3.68×10^8 rad.
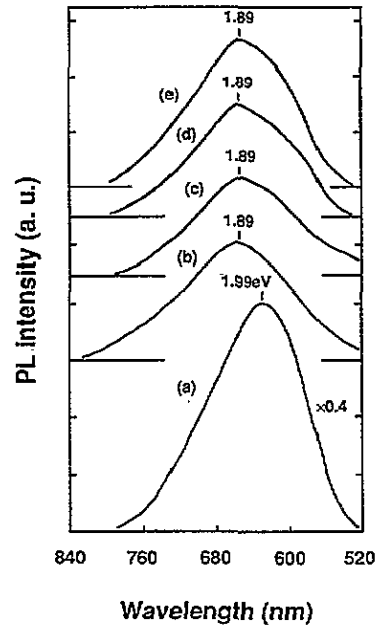
Figure 5. The evolution of PL spectra for PS sample 7 measured after various γ-ray irradiation doses (a.u., arbitrary units): curve (a), 0;, curve (b), 1.17×10^8 rad; curve (c), 1.58×10^8 rad; curve (d), 2.80×10^8 rad; curve (e), 3.68×10^8 rad.

a stronger effect on the H desorption than laser illumination does.

As presented above, the PL evolution from PS during oxidation is a complicated problem and whether some of the suggested PS luminescence mechanism models can account for the experimental results of the PL evolution from PS during oxidation is a great challenge. First, let us inspect our results using the quantum confinement mode [1], which is the most-cited model on PS luminescence. According to this model, it is predicted that the PL peak positions will show a continuous blue shift when the size of nanoscale silicon in PS shrinks owing to the oxidation process. However, in our studies, not only a blue shift but also a red shift have been observed. Furthermore, in the later stage of oxidation the peaks of PL from PS no longer exhibit a shift and are pinned at fixed energies while oxidation continues. The red shift and pinning of peak energies are difficult to understand in the quantum confinement model.

Koch *et al* [6] also examined the oxidation behaviour of PL from PS using their surface-state mechanism and thought that the red shift of luminescence during thermal oxidation is due to more and deeper surface states resulting from additional disordering and a rise in the surface state density during oxidation. From this reasoning, it is not clear why only PL spectra with initial peak energies in the orange–yellow region undergo a red shift and why only PL spectra with initial peak energies in the infrared–red region experience a blue shift. In addition, the pining phenomenon of PL peaks during oxidation is also not easily explained by the surface-state mechanism. Because Koch *et al* have suggested that the radiative electronic states in the disordered Si of the surface region are 0.3 or 0.6 eV (localization energy) below the core state, if the value of localization energy does not change very much during oxidation, it can be deduced that under oxidation the reduction in size of
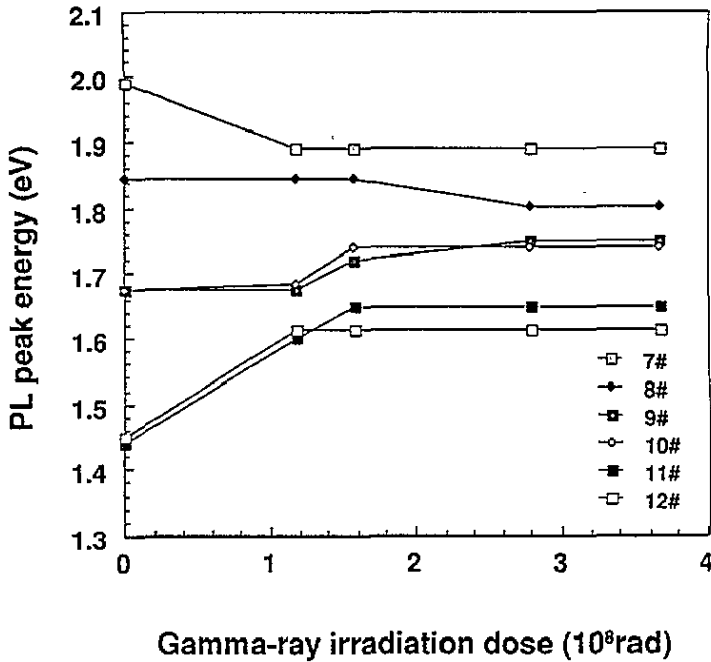
Gamma-ray irradiation dose (10⁸rad)

Figure 6. Shift in the PL peak energies followed by pinning during γ irradiation oxidation for the other group of samples with different initial PL peak energies.
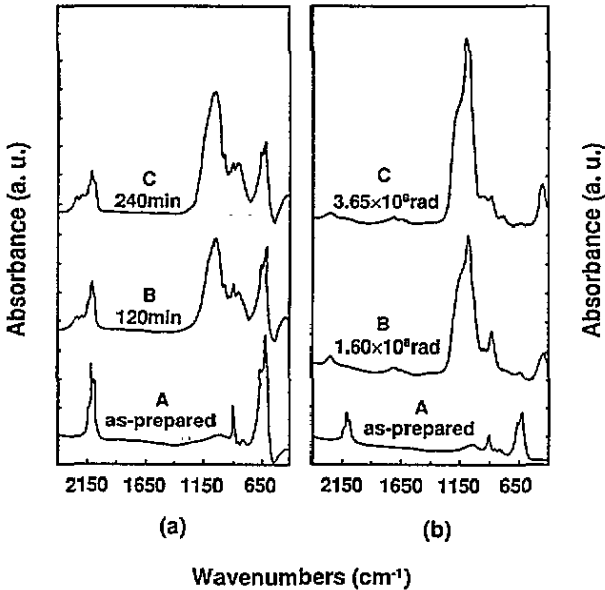

Figure 7. (a) The FTIR spectra of sample 3 (a.u., arbitrary units): curve (a), as prepared; curve (b), measured at the beginning of PL peak pinning; curve (c), measured at the end of laser illumination. (b) The FTIR spectra of sample 10 (a.u., arbitrary units): curve (a), as prepared; curve (b), measured at the beginning of PL peak pinning; curve (c), measured at the end of γ-ray irradiation.

the nanoscale Si particles can also result in an energy increase in the radiative bands from surface states. As a result, a continous blue shift rather than pinning for the PL peaks should occur with further oxidation.
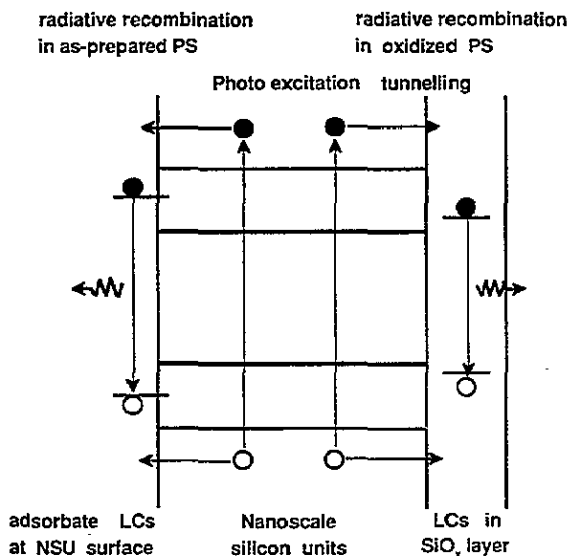
Figure 8. Schematic illustration of electron–hole pairs, excited in the NSUs, recombining to emit visible light through the luminescence centres outside NSUs. On the left is shown an electron–hole pair recombining through an adsorbate luminescence centre at the NSU surface for the as-prepared PS; on the right is shown an electron–hole pair recombining through a luminescent centre in the SiO_x layer for oxidized PS.

As for the QCLC model [7], we can ascribe the blue or red shifts of the PL peaks during oxidation to a change in the main luminescence centres from one kind to another and/or the variation of relative contributions from various kinds of luminescence centres. For the as-anodized PS samples, the main luminescence centres are possibly some adsorbates on the surface of NSUs; Si hydrides are possible candidates for adsorbates, which are introduced or formed during anodization and are different for PS samples prepared by different anodizing conditions. Therefore, as-anodized PS samples can be obtained with different initial PL peak energies which are distributed in a wide wavelength range from near infrared to yellow. However, as the PS is oxidized under laser illumination or γ-ray irradiation, the de-adsorption and the growth of Si oxide will lead to a change in the main luminescence centres which will then be defects and/or impurities and/or self-trapped excitons in SiO_x ($x \simeq 2$) layers covering NSUs. If the luminescence energies of the initial main luminescence centres adsorbed at NSU surfaces are larger than those of the final main luminescence centres in SiO_x, a red shift will be observed; otherwise a blue shift will be observed. Photoexcitation in NSUs, followed by electron and hole tunnelling and photoemission through luminescence centres in SiO_x for the QCLC model, are illustrated in figure 8. In this figure, we suppose that the energy interval between the two energy levels for the adsorbate luminescence centres is larger than that for the luminescence centres in SiO_x layers; then a red shift of PL from PS during oxidation can be explained. Similarly, if we make the opposite supposition about the energy intervals, a blue shift can be explained. Furthermore, because the emitting photon energies for the luminescence centres in SiO_x layers covering the NSUs in PS, which have been fully oxidized, are nearly constant, the pinning of PL peak energies with increasing oxidation can also be explained. In addition, the fact that the final PL peak energies during oxidation are in an energy range instead of at a definite energy is possibly due to the presence of different kinds of luminescence centre in SiO_x layers and/or different stresses in PS samples [7].

Recently, some research work has emphasized the importance of the luminescence from SiO_x layers surrounding NSUs in the light emission of PS. For example, Prokes [15] has examined the luminescence behaviour of thermally oxidized PS at various temperatures for different times and suggested that the oxide-related luminescence centre are a possible source

of the luminescence from oxidized PS. Although the continued presence of the same energy PL with increasing oxide growth has been attributed to oxide-related luminescence centres, he has not explained the intial blue shift. Cullis *et al* [16] claimed that 750 nm luminescence can be accounted for by crystalline nanostructures and luminescence properties of silicon oxides are of paramount importance in interpreting the many additional (shorter-wavelength) emission bands observed.

4. Conclusions

In conclusion, the energy evolution of the PL peaks from PS during both laser illumination and γ-ray irradiation has been investigated. In both cases, experimental results have shown that, if the initial values of the peak energies for the PL are in the infrared–red region, the PL peaks will undergo a blue shift while, if the initial peak energies are in the orange–yellow region, the PL peaks will experience a red shift. In the later stage of oxidation, all the PL peaks are pinned and localized within a narrower energy range than the initial range of PL peak energies. These results do not agree with the quantum confinement model or the surface state mechanism suggested by Koch *et al* but seems to be in accord with the QCLC model.

Acknowledgment

References

[1]   Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
[2]   Brandt M S, Fuchs H D, Stutzmann M, Weber J and Cardoma M 1992 *Solid State Commun.* **81** 307
[3]   Tsai C, Li K H, Kinosky D S, Qian R Z, Hsu T C, Tsn T-C, Banerjee K, Haance B K and White J M 1992 *Appl. Phys. Lett.* **60** 1700
[4]   Prokes S M, Glembocki O J, Bermudez V M, Kapian R, Friedersdorf L E and Searson P C 1992 *Phys. Rev.* B **45** 13788
[5]   Pickering C, Beale M I J, Robbins D J, Pearton P J and Breef R 1984 *J. Phys. C: Solid State Phys.* **17** 6535
[6]   Koch F, Petrova-Koch V, Muschik T, Nikolov A and Garrilenko V 1993 *Mater. Res. Soc. Symp. Proc.* vol 283 (Pittsburgh, PA: Materials Research Society) p 197
[7]   Qin G G and Jia Y Q 1993 *Solid State Commun.* **86** 559
[8]   Nakajima A, Itakura T, Watanabe S and Nakayama N 1992 *Appl. Phys. Lett.* **61** 46
[9]   Shih S, Tsai C, Li K H, Jung K H, Campbell J C and Kwong D L 1992 *Appl. Phys. Lett.* **60** 633
[10] Duan J Q, Zhang L Z, Zhang B R, Mao J C and Qin G G 1993 *Mater. Res. Bull.* **28** 407
[11] Zhou W, Shen H, Harvey J F, Lux R A, Dutta M, Lu F, Perry C H, Tsu R, Kalkhoran N M and Namavar F 1992 *Appl. Phys. Lett.* **61** 1435
[12] Li K H, Tsai C, Campbell J C, Meyer B K, Koch F and Lehmann V 1992 *Appl. Phys. Lett.* **62** 3501
[13] Turner D R 1958 *J. Electrochem. Soc.* **105** 402
[14] Fu J S, Mao J C, Wu E, Jia Y Q, Zhang B R, Zhang L Z and Qin G G 1993 *Appl. Phys. Lett.* **63** 1830
[15] Prokes S M 1993 *Appl. Phys. Lett.* **62** 3244
[16] Cullis A G, Canham L T, Williams G M, Smith P W and Dosser O D 1994 *J. Appl. Phys.* **75** 493