QUENCHING AND RECOVERY OF THE PHOTOLUMINESCENCE IN POROUS Si AFTER PULSE IR IRRADIATION

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ABSTRACT

A pulsed, high-power TEA CO_2 laser with lines in the region from 9.2 to 10.6 μm has been used to irradiate luminescent porous Si samples. The visible luminescence quenches and then recovers to its initial value on a time scale of one hour. It is found that the quenching is efficient when the IR wavelength is within the Si-O absorption band. We suggest that the resonant excitation of the Si-O bonds results in a metastable reconfiguration of the oxygen together with the creation of dangling bonds. These non-radiative centers are responsible for the PL quenching.

INTRODUCTION

The origin of photoluminescence (PL) in porous Si (PS) is a subject of intense research. It is now generally accepted that quantum confinement changes the band-gap of the Si nano-particles, and their optical properties. However, the states responsible for the light emission are still not identified. Calcott et al. [1] propose that the luminescence results from recombination of excitons in the volume of the crystallites. Koch et al. [2] argue that the radiative recombination process occurs predominantly via surface states.

Surface defect states are known to play an important role in the non-radiative processes. Rapid thermal oxidation and hydrogen effusion were used to show that the PL properties are strongly related to the density of dangling bonds [3]. There is an anticorrelation between the dangling bond concentration and the intensity of the red luminescence band [4]. The exposure of the PS internal surfaces to organic solvents results in reversible changes in the luminescence intensity [5]. All these results indicate that the chemical and structural conditions of the surface should be considered in the luminescence studies.

In this work we show that CO_2 laser radiation can influence the PL properties, due to the creation of metastable states on the surface of the Si crystallites. The radiation can be tuned to be resonant with the Si-O stretching mode. Such Si-O bonds become strongly excited and can even dissociate. The process results in a decrease of the luminescence intensity which then recovers in a time scale of hours. Here, we focus our attention on the reversible quenching effect. Irreversible quenching of the PL can also be obtained.

SAMPLES AND EXPERIMENTAL SETUP

The samples used in this work are prepared from (100) p-type B-doped, 1Ωcm Si wafers. Before anodization an ohmic back contact is provided by B implantation. Anodization is carried out in a 1:1 vol. mixture of ethanol:HF (49% in water). Etching current density is 30mA/cm^2. The typical sample thickness is in the range of 2 μm. Following anodization samples are removed from the cell, washed with propanol and left to dry under ambient conditions. The freshly prepared samples have very weak luminescence. They are aged for several weeks before the measurements

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in order to form a native oxide [6]. Luminescent H-covered samples (with no oxide) are etched with light assistance.

A TEA CO_2 laser, tunable in the range from 9.2 μm to 10.8 μm (1087-926cm^{-1}) is used as IR radiation source. Maximum radiation intensities used are 6 MW/cm^2, with a pulse duration of 150 ns. The laser light is coupled into the chamber via a thick Ge window, in order to reject visible and near IR light. Calibrated CaF_2 attenuators are used to vary the intensity of the IR light. The intensity of the incident radiation is measured using a fast photon drag detector.

The PL is excited with a He-Cd laser (442nm line) and measured with a photomultiplier. Spectral resolution is achieved using a 22cm Spex monochromator. The PL quenching kinetics on short time scales are recorded with a storage oscilloscope using CW optical excitation (2.8eV). For the long time response a standard lock-in technique is used.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the PL spectrum of one of our samples before and after excitation by one IR pulse. The PL intensity quenches by ~25% following the excitation (λ=9.29μm, I=2.3 MW/cm^2). During this process no change of the spectral shape of the PL is observed.

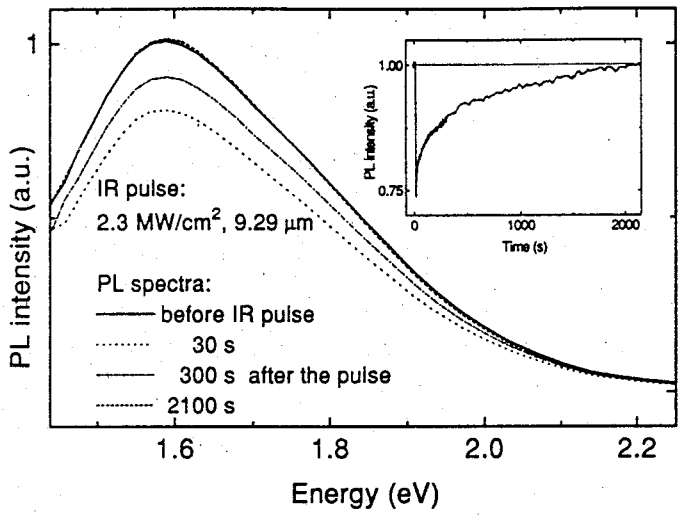

FIG. 1. PL spectra after IR excitation. Insert: PL signal after IR excitation detected at 1.7 eV

The insert in Fig. 1 illustrates the time evolution of the PL, detected at 1.7eV. A fast decrease of the luminescence intensity is observed immediately after the IR pulse, followed by two stages of relaxation. The first is a recovery step that occurs on a time scale shorter than seconds. It will be discussed in detail later. Afterwards, a slow increase of the PL intensity up to its initial value is seen, with a time scale of the order of an hour. For higher IR intensities a higher degree of quenching is achieved, but under these conditions the recovery is incomplete.

The dependence of the PL quenching on the wavelength of the incident IR radiation is shown in fig. 2. The effect is increasing rapidly when the IR wavelength falls within the absorption band of the Si-O stretching mode. Furthermore, no luminescence quenching could be seen for hydrogen

covered samples (which do not contain O). This indicates that the decrease in the PL intensity involves a resonant excitation of the Si-O bonds. We point out that the efficiency of the quenching does not follow the absorption spectrum. In addition, the spectral distribution of the quenching is narrower than the Si-O absorption band. This behavior strongly suggests that the PL quenching is not directly related to the absorbed energy. We might excite selectively one special Si-O configuration. In addition, the excitation process is non-linear and therefore is not expected to follow the absorption spectrum. We point out that similar excitation spectrum is found for the multiphoton excited light emission [7], suggesting a common origin for the two phenomena.

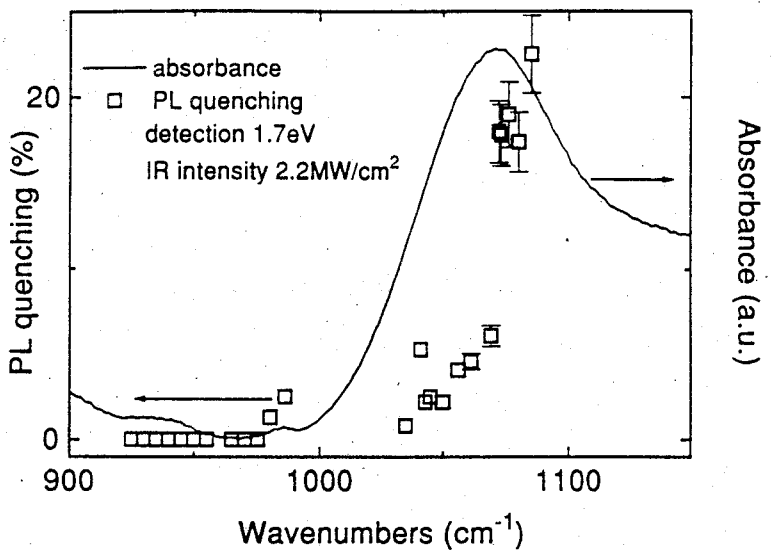

FIG. 2. PL quenching magnitude as a function of the IR excitation wavenumber.

The dependence of the PL quenching on the intensity of the CO_2 laser radiation shows only a slight non-linearity (fig.3). In general, the quenching increases for higher incident intensity, but a finite threshold is observed below which no quenching could be detected. The threshold depends on the atmosphere in which the sample is kept during the measurement. In order to determine whether the quenching results from the increased IR intensity or from the increase of the total energy deposited in the PS layer, we have measured the degree of quenching for a series of pulses. The quenching increases with the number of pulses and then saturates, when the number of IR pulses is beyond a certain limit (fig.3 part2). No dependence on the repetition rate is found in the range investigated (0.1 Hz to 50 Hz). The above results suggest that although the IR intensity is the main factor in determining the PL quenching , there is also an accumulative effect. We would like to add that while an increase of the number of pulses does not lead to further decrease of the PL intensity, the time of recovery becomes longer. However, a comparison between the quenching magnitude for one IR pulse with an intensity of 6 MW/cm^2 (nearly 100%) and for four pulses with an intensity of 1.5 MW/cm^2 each (a decrease of the PL of ~ 20% , see fig.3 part1) shows that the intensity of the IR pulse is the dominating factor in the quenching process. We further point out that for IR intensities larger than 5 MW/cm^2 only a partial recovery is observed on a time scale of hours. The PL signal is then quenched for periods as long as months.

Fig. 4 gives the temporal behavior of the PL quenching. Three processes with different time scales can be distinguished. Immediately after the laser pulse a rapid decrease in the PL intensity is observed (1). A partial recovery occurs on a time scale of the order of 300 ms (2). Afterwards, a much slower recovery process takes place (3). It is known that heating of PS leads to a decrease of the PL intensity [8].

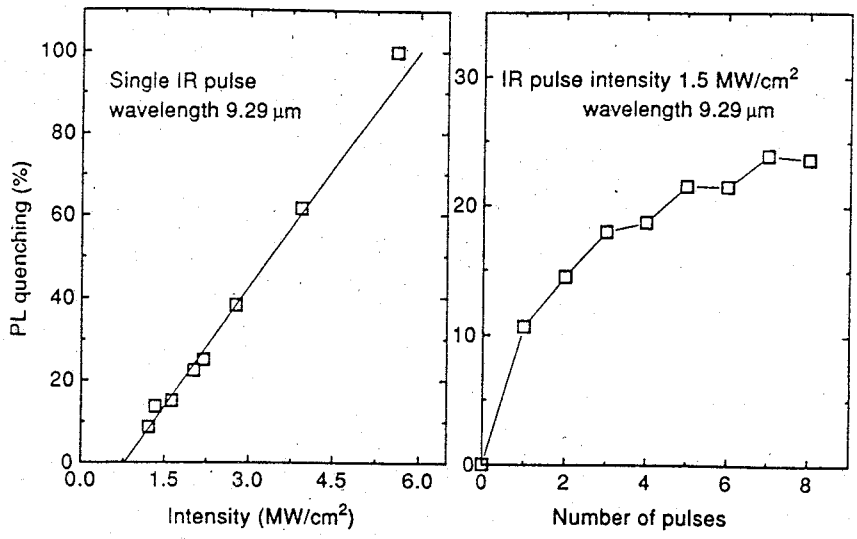

FIG. 3. Part 1: PL quenching as a function of the IR pulse intensity. Part 2: PL quenching as a function of the numbers of IR pulses

It is likely that the first fast stage of the quenching is due to an increase of the PS temperature. This is supported by measurements of induced absorption in the visible range, which also show an increase of the sample's temperature following the IR pulse, with a similar time scale (hundreds of ms). The temperature of the sample at this stage is estimated to be ~100°C [7]. The slower quenching process is most likely due to a chemical or structural change in the PS layer. In this respect, one should notice that this slow process might be cumulative, and therefore the number of pulses should affect the quenching, as we have observed.

We now discuss the origin of the quenching process. As stated before, the quenching is efficient for excitation wavelengths within the Si-O stretching band. The absorption in this vibration mode would result in strong oscillation of the Si-O atoms. The amplitude of the oscillation will increase with the absorption. Since the vibration energy of the Si-O bond is much above the optical phonon of the Si skeleton, the coupling to the Si core is poor and only a slow relaxation occurs. Under these conditions, there is a possibility that the bond will acquire high enough energy to dissociate. As a result, part of the oxygen atoms can change their configuration in space, moving to another metastable position. This metastable state is accompanied by the creation of dangling bonds, which will disapear following relaxation to the equilibrium configuration. An increase of the dangling bond density is observed in EPR after the sample is exposed to the high intensity IR pulse. The importance of the oxygen reconfiguration process that we have suggested, is supported by another experiment. We have measured the degree of

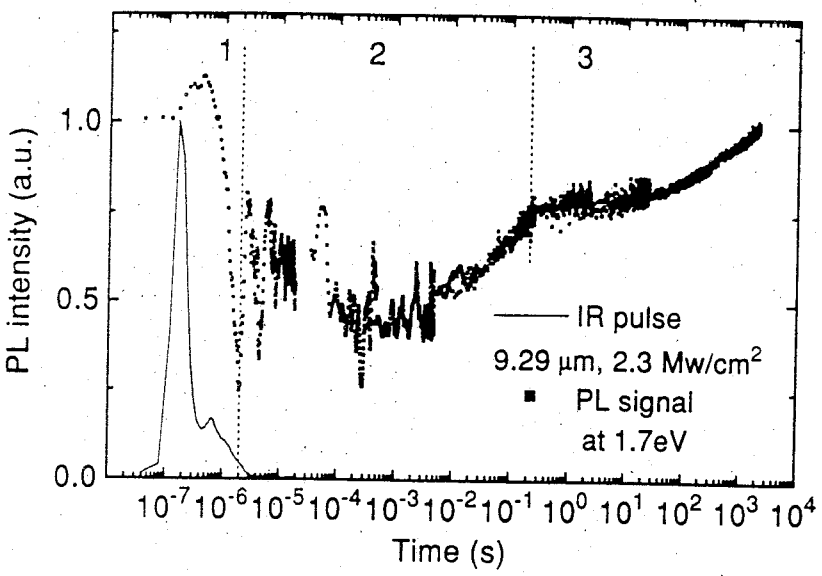

FIG. 4. Time dependence of the PL quenching level.

quenching, while the sample is exposed to different gases. In oxygen, a fast recovery is observed. A full but slower recovery is seen for a forming gas environment. For a sample kept in vacuum or N_2, no recovery is observed. Since H or O can passivate the dangling bonds, the PL can be fully recovered. However, when O is inserted into the cell after the sample was exposed to the IR pulse, a fast recovery is not observed. This suggests that not only the chemical reaction, but also the kinetics of the creation of the dangling bonds are affected by the ambient.

Since the absorption of the IR pulse results in local heating, effusion of hydrogen might be also a possible reason for a creation of dangling bonds. Quenching of the PL, accompanied by a drastic increase of the density of dangling bonds, have been observed in RTO treated samples [3]. This was attributed to removal of H, which passivates the surface Si. In that case, the IR absorption spectrum shows a decrease in the Si-H bond density. However, in our samples, the IR absorption does not show any change in the chemical composition of the layer following the IR pulse. This observation is an indication that PL quenching by the IR light is not related to H-effusion. The temperature at the first stage of the quenching (marked 2 in fig. 4) is of the order of 100°C and H-effusion is not expected.

We point out a possible similarity between our results and those reported for STM studies of PS and a-Si:H surfaces [9,10]. It was found that it is possible to modify the PS surface by current from an STM tip. When the electrons had only low kinetic energy the "STM-written" structures would fade after a few hours. However, for energetic electrons the modification of the surface remains for a long period of time. In a similar manner, low IR intensities quenched the luminescence for minutes, while under high intensity excitation the luminescence would not recover for months.

We believe that this phenomenon and our observation are related. Unlike the creation of dangling bonds by RTO, for which the recovery takes years, for the IR and the STM excitation

the recovery of the PL is achieved within minutes. It seems that a passivation of the dangling bonds and reconstruction of the surface is easier for low density of these centers. We are unable to determine at this stage what is the mechanism of the dangling bonds formation by the IR radiation and whether the dangling bond has the same nature as that formed by hydrogen effusion. Further investigations are needed to clarify these questions.

Acknowledgements

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