Kinetic oscillations of red photoluminescence from nanocrystalline Si/SiO_2 films

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Experimental investigations on the red photoluminescence (PL) from nanocrystalline Si (*nc*-Si) embedded in a SiO_2 matrix, fabricated by plasma-enhanced chemical vapor deposition and a subsequent post-treatment, reveal under certain conditions the occurrence of kinetic oscillations. For the red PL between 1.5 and 1.75 eV, the spectral shift and the peak intensity versus annealing times show temporal oscillations. The spectral variations are explained by the growth and decay kinetics of two oxygen thermal donors (TDs) upon annealing. The oscillatory behavior is a pure kinetic one. It reflects the regrowth of oxygen TDs by an autocatalytic process during their decay. Although the source for the autocatalysis is not clear, this PL oscillation adds more evidence that the red PL observed in our system originates from oxygen TDs-related defect states. © *2000 American Institute of Physics.* [S0003-6951(00)01531-X]

Porous silicon (PS) formed by electrochemical anodization has attracted a lot of interest during the past decade because of its strong visible photoluminescence (PL) at room temperature.[1] Although a great deal of effort has been made to elucidate the origin of the PL, a consensus on PL mechanisms is still lacking due to the difficulty of distinguishing the surface effect and quantum size effect.[2,3]

In addition to PS, nanocrystalline Si (*nc*-Si) synthesized by dry chemical methods has also been investigated in order to understand PL mechanisms.[4–7] The detailed synthesis and PL properties of *nc*-Si/SiO_2 films by plasma-enhanced chemical vapor deposition (CVD) and post-treatment have been reported previously, where oxide-related defect states were suggested to be responsible for the red PL.[8] Afterwards defect studies using electron spin resonance (ESR) in this system demonstrated that Si-NL8-related oxygen thermal donors (TDs) show a strong correlation with the 1.5 eV emission.[9] Recently, we further investigated the dependence of the red PL on annealing temperatures. This investigation further demonstrated that the PL around 1.5 eV is mainly due to Si-NL8-related oxygen TDs whereas the PL around 1.75 eV is mainly connected with another oxygen TDs, i.e., Si-NL10-related oxygen TDs.[10]

In this letter, we report on a spectral oscillatory behavior of the red PL upon annealing at 400 °C. For a PL around 1.75 eV, at shorter annealing times, it red-shifts to ~1.5 eV, accompanied by an increase of the PL intensity. At longer annealing times, it blue-shifts from 1.5 eV back to a higher energy, accompanied by a decrease of the PL intensity. The spectral shift and the peak intensity versus annealing times show temporal oscillations. The spectral variations can be explained by the growth and decay kinetics of Si-NL8 and Si-NL10 defect states upon annealing. The oscillatory behavior is a pure kinetic one. It reflects the regrowth of oxygen TDs by an autocatalytic process during their decay. Although the source for the autocatalysis is not clear, this PL oscillation excludes the variation of *nc*-Si itself as the oscillation element.

One sample used for the demonstration of spectral oscillations was prepared as follows: First, an amorphous Si film was deposited onto a Si (100) wafer from pure silane plasma. Afterwards the film was annealed under 0.03 mbar of hydrogen flow at 660 °C for 40 min. Then the film was preoxidized under a flow of pure oxygen at 350 °C for 4 h. Finally, the preoxidized film was annealed at 870 °C under a forming gas [(FG), 5 mol. % hydrogen in nitrogen] atmosphere for 8 h. The sample gives a weak PL around 1.75 eV. Then the sample was used for the 400 °C annealing experiment.

The excitation source for room temperature steady-state PL spectra was the 325 nm line of a He–Cd laser (Omnichrome Series 56). The pump power density of the laser was $0.4\ W/cm^2$. PL signals were spectrally resolved with a grating spectrometer (Spex Model 1681B) and detected by a Si diode in a lock-in mode. The calibration of the spectral sensitivity of the whole measuring system was performed with a tungsten standard lamp.

Figure 1 shows spectra of the red PL at different annealing times during the first cycle. Figure 2 further displays the spectral shift and intensity variation of the PL versus accumulation annealing times. The sample shows a weak PL around 1.75 eV before annealing at 400 °C. With increasing annealing times (<10 h), the PL gradually red-shifts from 1.75 to 1.46 eV and its intensity increases by a factor of 18. A subsequent 18 h annealing blue-shifts the PL from 1.46 to 1.59 eV and reduces its intensity by a factor of 2.8. From this position, annealing at shorter times (<5 h) leads to a red-shift from 1.59 to 1.49 eV and to an increase of the intensity while annealing at longer times (42 h) results in a blue-shift from 1.49 to 1.63 eV and in a decrease of the intensity. From

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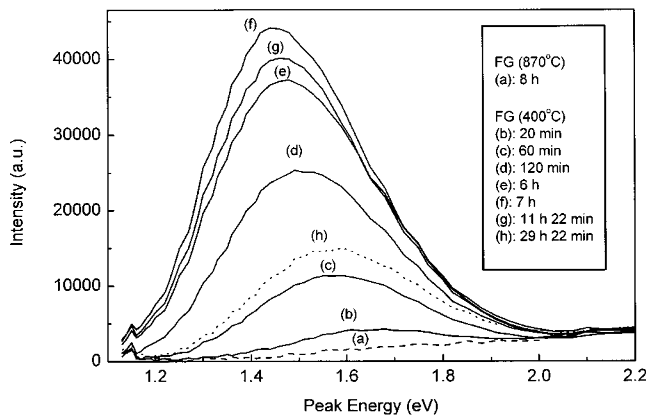

FIG. 1. Evolution of the red PL upon annealing at 400 °C for sample A. Curve (a) is obtained after annealing at 870 °C for 8 h. Other curves are obtained after 400 °C annealing at different times.

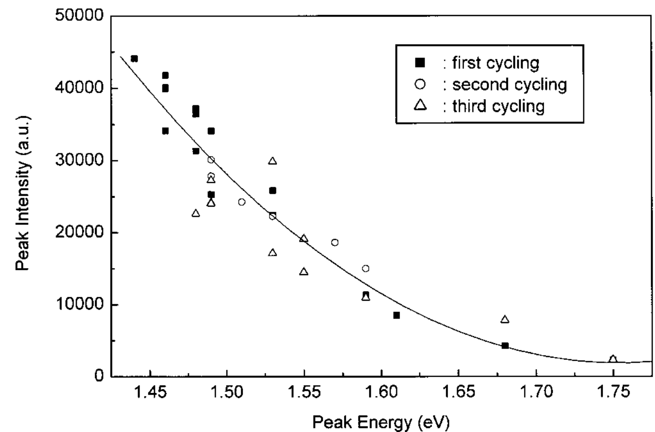

FIG. 3. The peak intensity vs the peak energy for three cycles for sample A. Solid line is used for eye guide.

1.63 eV, again at shorter times (8 h), the PL red-shifts from 1.63 to 1.49 eV with a 3.5 times increase in intensity, whereas at longer times (70 h), it blue-shifts from 1.49 to 1.75 eV with a 11 times decrease in intensity. It can be seen clearly from Fig. 2 that both the spectral shift and the intensity variation versus accumulation annealing times exhibit temporal oscillatory behavior. Each oscillation is composed of two time segments, i.e., a shorter time segment with a red-shift of the peak energy and an increase in intensity and a longer time segment with a blue-shift of the peak energy and a decrease in intensity. FTIR and XRD characterizations show no observable change upon annealing. This means that the macroscopic structure of the nc-Si/SiO_2 film does not change. The peak intensity versus the peak energy for all three cycles is presented in Fig. 3. The PL with lower peak energy is stronger than that with higher peak energy. In addition, the increase in intensity and the degree of red-shift decrease with cycling times.

Oxygen TDs widely exist in oxygen-riched crystalline silicon under low temperature annealing (300–550 °C).[11,12] From ESR measurements mainly two signals (Si-NL8 and Si-NL10) are related to oxygen TDs. The formation process of Si-NL8 states are normally faster than that of Si-NL10 states, but Si-NL8 states are less stable at longer annealing times and at higher temperatures compared with Si-NL10 states.[13] Earlier studies in nc-Si/SiO_2 films have shown that

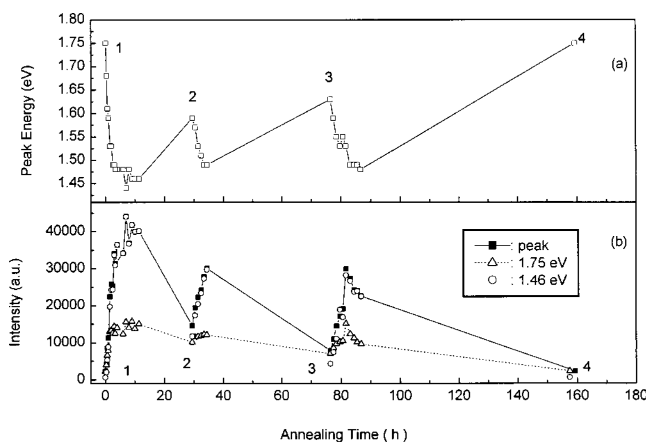

FIG. 2. Temporal oscillations of the peak energy (a) and of the PL intensities at 1.75 eV, at 1.46 eV, and at the peak energy (b) for sample A.

the PL around 1.5 eV is mainly due to Si-NL8 states and that the PL around 1.75 eV is mainly due to Si-NL10 states.[9,10] The red PL is composed of these two states. The peak energy and the PL intensity are determined by the concentration ratio of these two components. Now we can explain the spectral shift and intensity variation upon annealing times as follows: Low temperature annealing first leads to the growth of oxygen TDs. Since the growth rate of Si-NL8 states are faster than that of Si-NL10 states, the increase of PL intensity in lower energy is larger than that in higher energy. This leads to a red-shift of the peak energy, accompanied by an increase in intensity. After reaching their maximum concentrations, oxygen TDs begin to decay. Since the decay rate of Si-NL8 states is faster than that of Si-NL10 states, the decrease of PL intensity in lower energy is larger than that in higher energy. This leads to a blue-shift of the peak energy, accompanied by a decrease in intensity. In one word, the variance of the growth and decay kinetics of Si-NL8 and Si-NL10 states leads to the observed spectral changes. Thus, the shorter time segment corresponds to the growth process of oxygen TDs while the longer time segment corresponds to the decay process of oxygen TDs.

Apart from the intensity at peak energy, the intensities at 1.75 and 1.46 eV versus annealing times are also displayed in Fig. 2 (b). Both Si-NL8 states and Si-NL10 states exhibit this growth and decay process. Both the growth rate and the decay rate of Si-NL8 states are faster than those of Si-NL10 states.

Figure 4 shows a complete growth and decay process of PL centers for another sample (sample B). The PL variation shows a similar trend to that of sample A, i.e., at shorter annealing times (6.5 h), the PL red-shifts from 1.68 to 1.51 eV, accompanied by an increase in intensity. At longer annealing times (54 h), the PL blue-shift from 1.51 to 1.70 eV, accompanied by a decrease in intensity. However, the details of the variation are different. For example, for sample A from 1.44 to 1.59 eV, the intensities at 1.75 and 1.46 eV decrease by a factor of 1.5 and 2.9, respectively, whereas for sample B from 1.51 to 1.59 eV, the intensities at these two energies decrease by a factor of 1 and 1.4, respectively. The contribution of Si-NL8 states to the whole PL in sample A is larger than that in sample B. This variance is sample dependent.

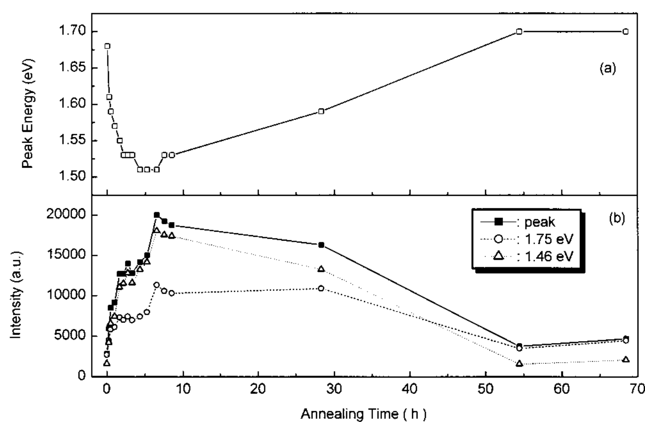

FIG. 4. The peak energy (a) and the PL intensities at 1.75 eV, at 1.46 eV, and at the peak energy (b) vs annealing times for sample B.

Many effects can cause oscillations, such as nonisothermal behavior, transformation of surface structure, mass transfer.[14–16] Since in our case the annealing temperature is kept as a constant, our system can be considered as an isothermal system. Besides, the role of FG is mainly the passivation of nonradiative centers, not a constituent of oxygen TDs, i.e., there is no mass transfer between FG and oxygen TDs. Thus, our system can be considered as a closed system. In a closed system, the concentrations, which vary in an oscillatory way, are those of the intermediates.[14] ESR measurements indicate that the concentrations of oxygen TDs in crystalline Si at a low temperature annealing first increase with annealing times, then reach a maximum, and finally decrease.[13] Both Si-NL8 states and Si-NL10 states are therefore intermediates. They satisfy one of the conditions for oscillations in a closed system. Another vital factor is a "driving force" for oscillations. Some intermediate or product of a series of chemical reactions must be able to influence the rate of earlier steps of the series.[14] Since oxygen TDs have been observed only in crystalline Si in bulk, we think that in our case the oxygen TDs are also around *nc*-Si. In addition, the concentration oscillations of Si-NL8 states and Si-NL10 states have not been observed in crystalline Si in bulk. We think that the spectral oscillations observed in *nc*-Si/SiO_2 film may connect with a limited diffusion space of oxygen TDs in this heterogeneous system. However, the driving force for the oscillations is not clear now.

Oxygen TDs can exist in three charge states: TD^0, TD^+, and TD^{++}. Although a large number of research have been done on oxygen TDs, their core structures are still unclear.[17] Si-NL8 state is considered as a TD^+ state and Si-NL10 state is considered as a TD^0 state,[17] i.e., they have similar core structures. This explains their similar oscillatory behaviors.

As is well known, chemical oscillation normally takes place at special reaction conditions (reactant concentration, temperature, pressure etc.).[14] In our case, annealing temperatures between 200 and 700 °C were investigated. The kinetic oscillation only appeared upon 400 °C annealing. In addition, an oscillation without sustaining eventually will die out, and the system will finally go back to its thermodynamic state. As seen in Fig. 3, the amplitude of oscillations decreases with cycling times. Due to the higher stability of Si-NL10 states at 400 °C, some of them still remain after long annealing times and show a weak PL around 1.75 eV.

As shown in Fig. 2 (b) points 1, 2, and 3, the growth of PL centers can be initiated at different peak energies during the decay of PL centers. Studies on other samples also give similar results. This indicates that the oscillatory behavior observed here is a pure kinetic one. This rules out the structural phase transition or the size variation of *nc*-Si itself as the oscillatory element. However, it supports the concentration changes of Si-NL8 and Si-NL10 states, controlled by pure kinetic reactions, as the oscillatory element.

One disputing focus of visible PL in PS is that the PL originates from *nc*-Si itself or from interfacial defect states.[2,3] Prokes *et al.* have connected the oxygen TDs with nonbridge oxygen hole centers (NBOHs) and suggested that NBOHs are responsible for the visible PL in oxidized PS[18] and the red PL in our *nc*-Si/SiO_2 system.[9] Because the core structure of oxygen TDs is not clear yet, we will not discuss here their possible connections with other oxide-related defect states. But the spectral oscillatory behavior observed here gives support to the view that oxygen TDs-related defect states are responsible for the red PL in this system.

In conclusion, a temporal oscillation of the spectral variations of red PL from *nc*-Si/SiO_2 film has been observed under appropriate annealing conditions. This adds more evidence that oxygen TDs-related defect states, produced in *nc*-Si by annealing, are the most possible candidate for the observed PL in this system. The source for the spectral oscillations, the structure of oxygen TDs in *nc*-Si, and the relation of this red PL to the visible PL in PS need further investigations.

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[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] Y. Kanemitsu, Phys. Rep. **263**, 1 (1995).
[3] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. **82**, 909 (1997).
[4] H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki, and T. Nakagiri, Appl. Phys. Lett. **24**, 2379 (1990).
[5] T. Ito, T. Ohta, and A. Hiraki, Jpn. J. Appl. Phys., Part 2 **31**, L1 (1992).
[6] M. L. Brongersma, A. Polman, K. S. Min, E. Boer, T. Tambo, and H. A. Atwater, Appl. Phys. Lett. **72**, 2577 (1998).
[7] S. Veprek, M. Ruckschloss, B. Landkammer, and O. Ambacher, Mater. Res. Soc. Symp. Proc. **298**, 117 (1993).
[8] S. Veprek and Th. Wirschem, in *Handbook of Optical Properties*, Vol. II: Optics of Small Particles, Interfaces and Surfaces, edited by R. E. Hummel and P. Wissmann (Chemical Rubber, Boca Raton, FL, 1997), p. 129.
[9] S. M. Prokes, W. E. Carlos, S. Veprek, and Ch. Ossadnik, Phys. Rev. B **58**, 15632 (1998).
[10] X. Wu, A. Bek, A. M. Bittner, K. Kern, Ch. Eggs, Ch. Ossadnik, and S. Veprek, Phys. Rev. B (submitted).
[11] W. Goetz and G. Pensl, Phys. Rev. B **46**, 4312 (1992).
[12] P. Deak, L. C. Snyder, and J. W. Corbett, Phys. Rev. B **45**, 11612 (1992).
[13] T. Gregorkiewicz, D. A. van Wezep, H. H. P. Th. Bekman, and C. A. J. Ammerlaan, Phys. Rev. B **35**, 3810 (1987).
[14] *Chemical Oscillations and Instabilities*, edited by Peter Gray and Stephen K. Scott (Clarendon, Oxford, 1990).
[15] R. Imbihl, M. P. Cox, and G. Ertl, J. Chem. Phys. **84**, 3519 (1986).
[16] R. Imbihl, M. P. Cox, G. Ertl, H. Mueller, and W. Brenig, J. Chem. Phys. **83**, 1578 (1985).
[17] *Early Stages of Oxygen Precipitation in Silicon*, edited by R. Jones (Kluwer, Dordrecht, 1996).
[18] S. M. Prokes, W. E. Carlos, and O. J. Glembocki, Phys. Rev. B **50**, 17093 (1994).