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Hervé Rinnert, Michel Vergnat, G. Marchal, A. Burneau. Intense visible photoluminescence in amorphous SiO_x and SiO_x:H films prepared by evaporation. *Applied Physics Letters*, 1998, 72 (24), pp.3157-3159. 10.1063/1.121578 . hal-02113432

HAL Id: hal-02113432

<https://hal.science/hal-02113432>

Submitted on 28 Apr 2019

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Intense visible photoluminescence in amorphous SiO_x and $\text{SiO}_x\text{:H}$ films prepared by evaporation

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(Received 22 January 1998; accepted for publication 10 April 1998)

Visible photoluminescence (PL) can be observed in $a\text{-SiO}_x$ and $a\text{-SiO}_x\text{:H}$ alloys prepared by evaporation of SiO in ultrahigh vacuum and under a flow of hydrogen ions, respectively. The hydrogen and oxygen bonding is studied by infrared spectrometry. The hydrogen stability is followed by thermal desorption spectrometry experiments. The evolution of the PL with annealing treatments shows that the PL can be attributed to a quantum confinement effect in $a\text{-Si}$ clusters embedded in the matrix of $a\text{-SiO}_x$. Hydrogen does not greatly contribute to the PL efficiency and to the thermal evolution of the $a\text{-Si}$ clusters. © 1998 American Institute of Physics.

[S0003-6951(98)00124-7]

Since the observation of a strong visible photoluminescence (PL) in porous silicon at room temperature,¹ light emission from silicon based devices is an important research area for optoelectronic and display applications. In porous silicon, the visible PL is generally attributed to the presence of silicon nanocrystals, where the band gap is enlarged into visible range, and the quantum confinement effect is thought to be one of the light emission mechanisms. However, the reduction in the non-radiative surface recombinations is a crucial factor in obtaining intense light emission. Hydrogen termination of the surface is known to result in efficient luminescence since thermal effusion of H_2 and SiH_3 entities is correlated to the PL degradation.² Other studies have shown that the surface passivation of porous silicon with good-quality oxide also leads to efficient light emission.^{3,4}

Recently, there was a significant activity to obtain new silicon-based light-emitting materials, specially by techniques compatible with the microelectronics industry technology, and PL has been observed in structures such as Si^+ implanted SiO_2 films,^{5,6} Si/SiO_2 multilayers⁷ or in Si-rich SiO_2 films grown by sputtering or chemical vapor deposition. Amorphous silicon oxygen hydrogen alloys ($a\text{-SiO}_x\text{:H}$) are also candidates for visible PL. They can be prepared by sputtering in water vapor⁸ or by plasma enhanced chemical vapor deposition using a gas mixture of N_2O and SiH_4 .^{9,10}

The purpose of this letter is to show that the evaporation technique also permits to obtain $a\text{-SiO}_x$ thin films which present a very intense PL visible to the naked eye. In order to understand the influence of hydrogen in these materials, hydrogenated alloys were also prepared with the same elaboration technique. The SiO_x alloys were obtained by evaporation of SiO from a tantalum boat onto Si substrates maintained at 100 °C. The background pressure was 10^{-7}

Torr. The deposition rate (1 \AA/s) was controlled by a quartz microbalance system. The theoretical thickness, calculated with the density of SiO, was 2000 Å. The hydrogenated alloys were prepared by the reactive evaporation method, as described elsewhere.¹¹ Energy dispersive x-ray spectroscopy was performed and no tantalum contamination was observed in the films. Photoluminescence measurements were carried out with a multichannel Jobin Yvon T64000 Raman spectrometer equipped with a charge coupled device camera cooled at 140 K. The excitation light source at 488 nm was emitted from a Spectra Physics argon laser with an incident power of around 10 mW/mm^2 . The evolution of the PL was followed during annealing treatments. The oxygen and hydrogen bonding configurations were obtained from Fourier transform infrared (IR) transmission measurements using a Perkin-Elmer 2000 spectrometer with a resolution of 4 cm^{-1} . For thermal desorption spectrometry (TDS) experiments, the films were inserted into an ultrahigh vacuum chamber and were heated at a constant rate of 10 °C/min to 800 °C. The hydrogen atoms desorbing from the surface were detected by a quadrupole mass analyzer. The annealing treatments were made in the TDS chamber with the same heating rate. The samples were cooled down immediately after the annealing temperature T_a was reached.

Figure 1 shows the IR spectra of the as-deposited $a\text{-SiO}_x$ and $a\text{-SiO}_x\text{:H}$ alloys. The spectrum of the $a\text{-SiO}_x$ sample shows a very intense absorption band at around 1000 cm^{-1} which corresponds to the asymmetric stretching vibration of the oxygen atom in its twofold coordinated bridging bonding site. The absorption band at 650 cm^{-1} is associated to the displacement of oxygen along the bisector of Si-O-Si angle. The spectrum of the hydrogenated sample clearly presents several other absorption peaks in the range 700–875 and 2090–2250 cm^{-1} due to the presence of hydrogen. In pure $a\text{-Si:H}$ films, the absorption bands at 630 and 2000 cm^{-1} are attributed to the bending and stretching vibrations of the Si-H monohydride, respectively. For $a\text{-SiO}_x\text{:H}$ films, oxy-

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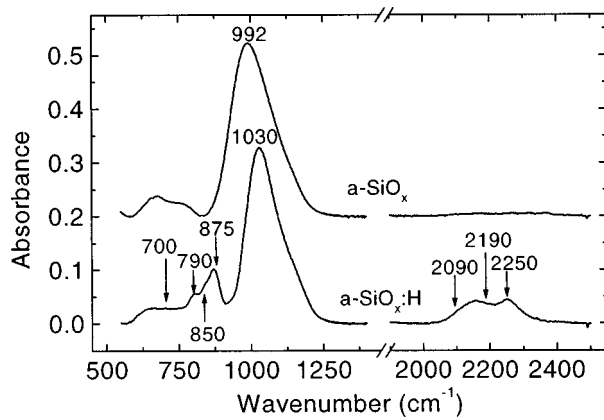


FIG. 1. Infrared absorption spectra of $a\text{-SiO}_x$ and $a\text{-SiO}_x\text{:H}$ samples prepared at 100 °C without postannealing.

gen atoms are back-bonded to the silicon atom of the Si–H bond and the absorption bands frequencies are modified. The absorption bands at 2090, 2190, 2250 cm^{-1} are attributed to the stretching mode of monohydride Si–H bonds with one, two and three oxygen atoms backbonded to the silicon one, respectively. The same shift appears with the bending vibration of the monohydride Si–H bond. Hence the absorption bands at 700, 850, and 875 cm^{-1} are attributed to the bending mode of Si–H bonds with one, two and three oxygen atoms backbonded to the silicon atom.^{12,13} The weak absorption at 700 and 2090 cm^{-1} suggests there are preferentially two or three oxygen atoms backbonded to the Si–H group. The absorption at 790 cm^{-1} is a vibration which strongly couples Si–H and Si–O–Si motions and which appears when oxygen and hydrogen atoms are in the cis bonding geometry.¹² Moreover, we can affirm there is no $\text{Si}_3\text{--Si--H}$ groups since no absorption at 630 and 2000 cm^{-1} is detected. Besides no Si–O–H bonds are present in these films because there is no absorption in the 3000–4000 cm^{-1} range. In conclusion, it can be said that all the hydrogen atoms are bonded in the Si–H monohydride configurations with at least one oxygen atom backbonded to the silicon atom. The vibration at 1000 cm^{-1} gives information about the oxidation degree of the $a\text{-SiO}_x$ and $a\text{-SiO}_x\text{:H}$ alloys. The frequency of this mode is shifted to the higher frequencies as a linear function of x .¹⁴ It is also shifted to the higher frequencies when hydrogen is bonded to a silicon atom (Si–O–Si–H). For an $a\text{-SiO}_x$ film containing a weak number of oxygen atoms, this absorption band shifts from 940 to 980 cm^{-1} when the alloy is hydrogenated.¹² This displacement is comparable to that observed with our samples. Therefore, we can assume that the oxygen concentration x is the same for both samples. Comparing with Lucovsky results¹⁴ which correlate the oxygen content and the absorption band frequencies, x must be equal to 0.8.

Figure 2 shows the hydrogen effusion spectra from the $a\text{-SiO}_x\text{:H}$ film. This spectrum exhibits a very large peak with a maximum at 500 °C and a full width at half maximum (FWHM) equal to 200 °C. In comparison, the effusion peak of an $a\text{-Si:H}$ film prepared with the same experimental conditions presents a maximum at 400 °C with a FWHM equal to 80 °C.¹⁵ The shift of the $a\text{-SiO}_x\text{:H}$ effusion spectrum towards the higher temperatures and the increase of the width can be explained by the fact that hydrogen effuses from dif-

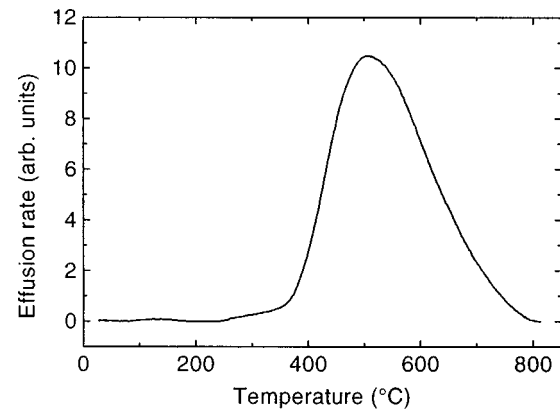


FIG. 2. Hydrogen effusion spectrum from $a\text{-SiO}_x\text{:H}$.

ferent $\text{Si}_{3-n}\text{O}_n\text{--Si--H}$ ($n=1,2,3$) groups which have different desorption energies higher than that of the $\text{Si}_3\text{--Si--H}$ configuration. This is in agreement with the theoretical work of Jing *et al.*¹⁶ who demonstrate that the dissociation energy of the Si–H bond increases from 3.55 eV for $\text{Si}_3\text{--Si--H}$ groups to 4.11 eV for $\text{O}_3\text{--SiH}$ groups, a fact related to the observed increase of SiH stretching frequency with n , i.e., the increase of SiH force constant. Hence the effusion spectrum of the $a\text{-SiO}_x\text{:H}$ film represents the convolution of three desorption peaks corresponding to the three different configurations of $\text{Si}_{3-n}\text{O}_n\text{--Si--H}$ groups. This interpretation is confirmed by the observation of the IR spectra of annealed samples. Indeed the sample annealed at 500 °C presents an integrated absorbance in the 2090–2190 cm^{-1} range two times lower than for the as-deposited sample and the sample annealed at 650 °C presents only an absorbance at 2250 and 875 cm^{-1} characteristic of the Si–H stretching and bending modes of the $\text{O}_3\text{--Si--H}$ configuration.

Figure 3 shows PL spectra of $a\text{-SiO}_x$ films as-deposited at 100 °C or after different annealing temperatures T_a : 350, 500, 650, 800 and 950 °C. From the as-deposited sample to the annealed sample at 650 °C, a strong improvement of the PL intensity by a factor 20 can be observed simultaneously

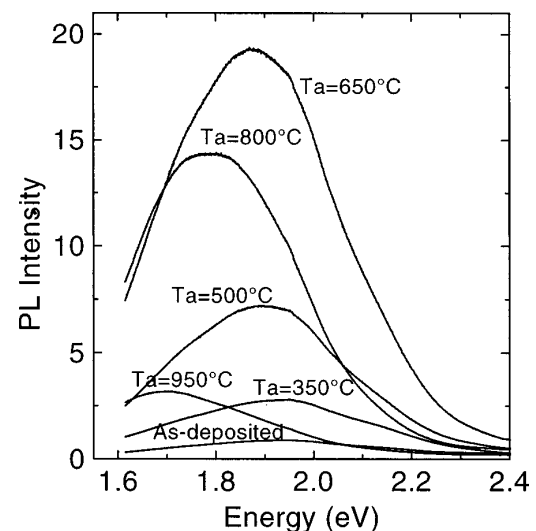


FIG. 3. Photoluminescence spectra of $a\text{-SiO}_x$ films annealed at different temperatures T_a .

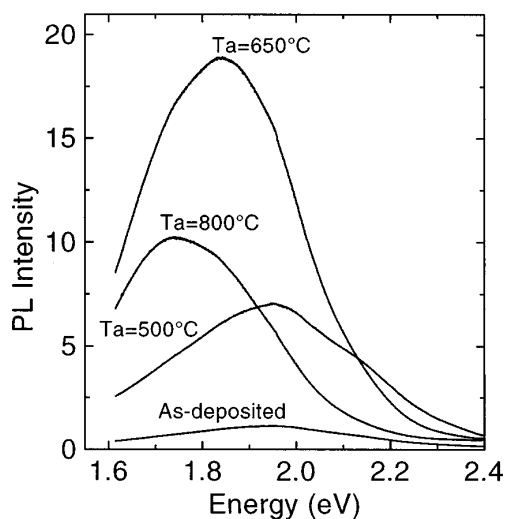


FIG. 4. Photoluminescence spectra of $a\text{-SiO}_x\text{:H}$ films annealed at different temperatures T_a .

with a redshift. The PL is visible to the naked eye. After subsequent annealing a strong decrease of the PL appears mainly in the green range. Such an evolution is characteristic of a PL mechanism with a quantum confinement origin which can be explained by the formation of Si clusters embedded in the matrix of $a\text{-SiO}_x$. As nanocrystals are not visible by transmission electron microscopy, these clusters can be considered to be amorphous. When T_a increases, oxygen atoms diffuse to form oxygen-rich regions and the number of oxygen-free clusters increases. The redshift of the PL signal is assumed to originate from the increase of the cluster size. In a first step, for $T_a < 650^\circ\text{C}$, annealing the films contributes to create new clusters and to increase the size of already existing clusters. For $T_a > 650^\circ\text{C}$, there is a coalescence phenomenon due to the growth of the clusters. The small clusters disappear, involving a decrease of the PL signal at high energy and finally, the clusters become too large to show the quantum confinement effect. The PL signal disappears. Another proof of this evolution is the shift of the IR absorption peak from 992 cm^{-1} to 1052 cm^{-1} and the formation of a shoulder at 1200 cm^{-1} with increasing T_a . This shift to the higher frequencies attests the presence of very oxidized areas in the films, originating from the diffusion of oxygen atoms.

The evolution of the PL in the $a\text{-SiO}_x\text{:H}$ samples (Fig. 4) is the same as for unhydrogenated films. When T_a increases, the PL continuously shifts to weaker energies with an intensity which increases for $T_a < 650^\circ\text{C}$ and then de-

creases for higher T_a . The main conclusion is that hydrogen does not greatly contribute to the PL efficiency of $a\text{-Si}$ clusters. Lin *et al.*¹⁷ explained a similar evolution of PL in their samples by a model based on the diffusion of hydrogen. They claimed that the effusion of hydrogen allows the growth of clusters by creating new Si-Si bonds between silicon atoms previously bonded to hydrogen atom. It is here demonstrated that the effusion of hydrogen is responsible neither of the coalescence of $a\text{-Si}$ clusters nor of the shift of the PL range. We believe that $a\text{-Si}$ clusters confined in an $a\text{-SiO}$ environment form quantum wells which grow by the diffusion of the oxygen atoms.

In conclusion, visible to the naked eye PL can be observed in $a\text{-SiO}_x$ and $a\text{-SiO}_x\text{:H}$ alloys prepared by evaporation of SiO in ultrahigh vacuum and under a flow of hydrogen ions, respectively. The evolution of the PL with annealing treatments shows that the PL could be attributed to a quantum confinement effect in $a\text{-Si}$ clusters embedded in the matrix of $a\text{-SiO}_x$. Hydrogen, which is always bonded to silicon having oxygen neighbors, does not greatly contribute to the PL efficiency and to the thermal evolution of the $a\text{-Si}$ clusters.

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