Pergamon

Solid State Communications, Vol. 95, No. 7, pp. 443–447, 1995
Elsevier Science Ltd
Printed in Great Britain
0038-1098/95 $9.50+.00

0038-1098(95)00299-5

VISIBLE PHOTOLUMINESCENCE FROM SiO_x FILMS GROWN BY LOW TEMPERATURE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

F. N. Timofeev*+, A. Aydinli, R. Ellialtioglu, K. Turkoglu, M. Gure
Bilkent University, Department of Physics, 06533 Bilkent, Ankara, Turkey

V. N. Mikhailov, O. A. Lavrova
*A.F.Ioffe Physico-Technical Institute, Politeknicheskaya 26,
194021 St. Petersburg, Russian Federation

(Received 3 April 1995 by D. Van Dyck)

a-SiO_x films of varying stoichiometry have been prepared by low temperature plasma enhanced chemical vapor deposition. The majority of films showed photoluminescence (PL) and films prepared in a narrow range of gas flows exhibited much stronger PL after annealing. Peak PL energies ranging from the ultraviolet to the near infrared have been observed. PL, infrared and X-ray diffraction on selected samples indicate formation of Si clusters in the films. The effects of annealing on the PL properties of the films have been found to depend on initial stoichiometry of the films.

Keywords: A. thin films, D. optical properties, E. luminescence

Interest in physical properties of thin films of SiO_x has recently been renewed due to its important applications in device technology. By varying its stochiometry it is possible to obtain semiconductor nanocrystals in these films which are fundamentally important[1]. In addition, recent studies on optical properties of porous silicon have suggested the possibility of lower dimensionality than originally thought. Both TEM and Raman data indicate[2] the presence of quasi-zero dimensional microcrystals responsible for strong photoluminescence at least in some porous silicon samples instead of quasi-one dimensional wire-like structures. In order to clarify the role of dimensionality a natural extension[3] is the study of Si clusters in SiO_x .

Plasma enhanced chemical vapor deposition (PECVD) is currently the most popular technique used for thin dielectric film production since the presence of the ionized reactive gas species enables the substrate temperature to be reduced. The stoichiometry of deposited dielectric film can be changed by varying the PECVD process parameters[4]. For example, at low ratio of the flow rates (or partial pressure p) **R**=**p**{N2O}/**p**{SiH4} in the gas mixture, the silicon suboxide or Si-rich films can be grown[5]. The excess Si in SiO_x matrix at some process conditions can form clusters in the SiO_x matrix[6] . Several authors have found evidence of quantum confinement of free charge carriers in Si-rich SiO_x films prepared by different techniques. In particular, it was reported that Si microcrystals in SiO_2 matrix prepared by Chemical Vapor Deposition (CVD) at 700 °C from nitrous oxide and monosilane show electroluminescence peaks[7]. Analogous films made by magnetron sputtering emitted visible photoluminescence[8] (PL) at 70 K. Room temperature PL was observed from nanoparticles of crystalline Si and SiO_x grown by PECVD from silane and oxygen[9]. Near infrared PL from PECVD grown a-SiO_x for N_2O/ (N_2O+SiH_4) ratios larger than 0.7 grown at 250 °C has also been observed[3].

There exist three main models for the structure of SiO_x . In addition to the Random Mixture Model[10] suggesting mixing of Si and SiO_x at the level of several tetrahedral units and Random Bond Model[10] assuming complete mixing of Si-Si and Si-O bonds, there are also the nonrandom mixture models[11] where Si grains are surrounded by SiO_2 . In the shell model proposed by Bruesch et. al.[1], columnar polycrystalline Si (x=0) evolve first into crystalline Si grains (x=0.12) then into a mixture of amorphous and crystalline Si grains (x=0.23) followed by mostly amorphous Si grains (x=0.58) and finally totally amorphous Si grains (x>0.86). In this model unconnected grains whether

* Permanent Address: Ioffe Physico-Technical Institute, St. Petersburg, Russia

\+ Present Address: Department of Electrical and Electronics Department, University College London, London, England

amorphous or crystalline are embedded into SiO_2 matrix with an intermediate suboxide layer.

In this paper, the properties of room temperature visible PL emission from SiO_x films with different stoichiometries grown by low temperature PECVD are presented. Fourier Transform Infrared Spectroscopy (FTIR), ellipsometry, X-ray diffraction and PL spectroscopy have been used to show that the as-deposited films of SiO_x contain Si clusters, whose size distribution rearranged during annealing treatments. PL emission from near UV to near IR has been observed from these films.

The samples of SiO_x ($0.15 < x < 2.0$) were grown by radio frequency (RF) (13.56 MHz) PECVD on Si(100) substrates using gas sources of nitrous oxide (N_2O) and silane (2% SiH_4 in N_2) in a Plasmalab μP machine[12,13]. The composition of PECVD grown SiO_x films were changed by varying the ratio of the gas flows $\mathbf{R}=p(N_2O)/p(SiH_4{:}N_2)$. All deposition cycles were performed at a low substrate temperature of 100°C for durations of 100-700 s, at a total chamber pressure of 1.0 Torr, low RF power of 7W, fixed flow rate of 180 sccm for $SiH_4{:}N_2$ and differing flow rates of N_2O varying from 1 to 900 sccm ($\mathbf{R}=0.006$-5). Further details of PECVD growth of SiO_x films is described in Ref. {8,9}. The thicknesses of as-deposited films were between 100-1000 nm. The index of refraction measurements were performed on an automatic optical ellipsometer (Rudolph Res. Auto-EL). After the deposition pieces of each sample were annealed for 10 minutes in a Rapid Thermal Processing (RTP) apparatus at different temperatures between 450 °C and 910 °C in ambient air. This resulted in hydrogen and OH desorption from the films and a controlled recrystallization of Si clusters inside SiO_x matrix.

The PL spectra were excited by 457.9 nm line of Ar^+ laser with beam powers between 0.3 and 10 mW at room temperature and measured using double grating monochromator and cooled GaAs photomultiplier. Low temperature PL measurements were performed in a closed-cycle cryostat. Laser beam was focused on the sample into a stripe with size of about 0.25 x 10 mm^2 using a cylindrical lens. The integrated PL intensity was measured by using a Si photodetector with an 480-900 nm optical bandpass filter.

Figure 1 (a-c) shows room temperature PL spectra from the SiO_x samples grown on (001) Si substrate at three different gas flow ratios ($\mathbf{R}=0.006$; 0.15 and 5.0) before and after RTP in air. We first note that as deposited SiO_x grown with R=0.006 shows a broad PL spectrum ranging from 460 to 900 nm with the PL peak position being at approximately 680 nm, Fig. 1a. The full width at half maximum (FWHM) of this peak is around 225 nm. In contrast, films deposited with R > 0.02 show narrower PL spectra centered around 430-510 nm with an exponential type decay towards the long wavelength side, Fig. 1b-c. As-grown SiO_x samples prepared with $0.15 > \mathbf{R} > 0.07$ show the narrowest FWHM of PL spectra (70-90 nm) while width of PL spectra from SiO_x films grown with $\mathbf{R} > 0.15$ are slightly larger (FWHM=100-120 nm).

Fig.2 shows data of integrated (in 480-900 nm spectral range) room temperature PL intensity from SiO_x films (as-grown and annealed) as a function of the gas flow ratio **R**. It can be seen that integrated PL signal intensity for the as-grown film ($\mathbf{R}=0.15$) was slightly

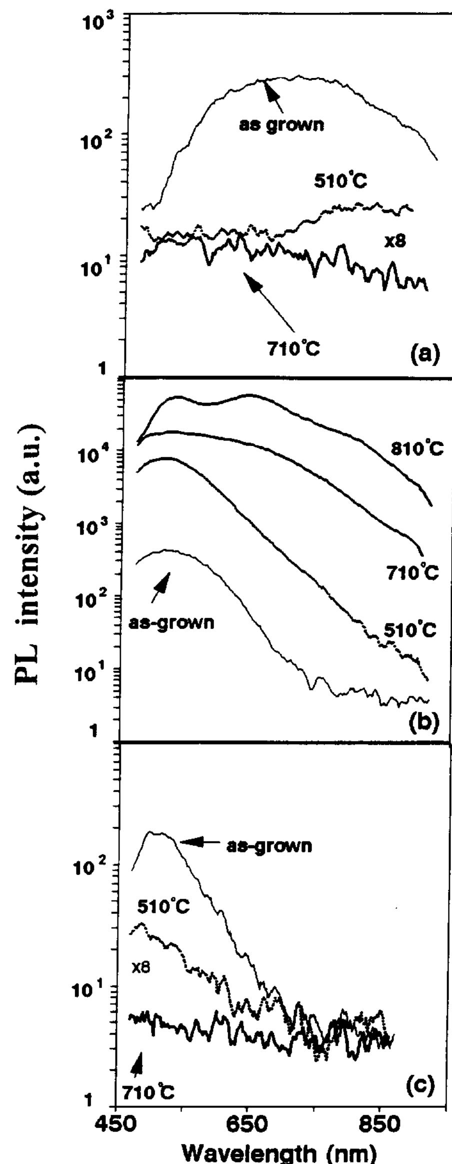

Fig.1: Photoluminescence of as-grown and annealed SiO_x films as a function of luminescence wavelength with a) $\mathbf{R}=0.006$, b) $\mathbf{R}=0.15$, c) $\mathbf{R}=5.0$ at room temperature. The excitation wavelength is $\lambda_i = 457.9$ nm.

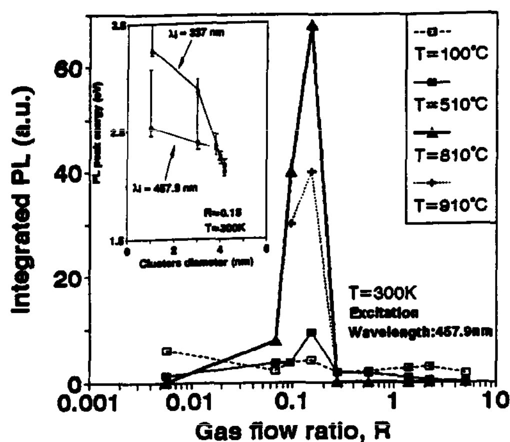

Fig.2: Integrated photoluminescence intensity as a function of gas flow ratio **R**. Photoluminescence peak energy as a function of cluster diameter is shown in the inset.

higher than that for the films grown at larger N_2O gas flow rates (larger **R**) and only the SiO_x film (x=0.15) grown with **R**=0.006 luminesces more. The RTP annealing in air shows different results on PL emission from SiO_x films with different Si concentration. The PL intensity from as grown SiO_x films with **R**>0.18 was reduced significantly and was barely detectable after high temperature treatment at 810 ^oC (Fig 1c,2). The PL peaks for these samples blue shifted further (Fig. 1c). The samples grown with **R**=0.006 also show reduction of PL intensity but maximum of the PL spectra shifted to near IR wavelengths (~780 nm) after RTP at 510 ^oC and disappeared following an RTP at 710°C but a very weak blue band peaked at 480 nm was still observable. For the samples grown with 0.15>**R**>0.07 the integrated PL signal increased (more than 20 times) with annealing in air up to an annealing temperature of about 810 ^oC (Fig 2), reached a maximum and then decreased. Bright photoluminescence from these samples were clearly visible to the eye. The effect of RTP treatment in air on PL from SiO_x films was similar to that observed for RTP in argon atmosphere[13]. The PL spectra of these samples show assymetric broadening (from 70 to 200 nm) towards long wavelengths with annealing temperature and finally the PL peak position also shifted towards low energy (Fig. 1b). The periodic nature of the spectra was found to be due to interference in the SiO_x layer. It is clear from the data that there is a narrow range of **R** values over which RTP annealing causes a large increase in PL efficiency. This may be understood in the framework of a modified shell model which includes the presence of crystalline grains *coated with amorphous Si*. It seems that the narrow range of **R** values where RTP causes a dramatic increase of the PL intensity corresponds to those x values for which amorphous and/or crystalline grains with 1.0-6.0 nm in size exist[1]. RTP causes increase in grain size through (re)crystallization and/or grain reconnection due to H effusion[3]. This is indeed confirmed by x-ray diffraction measurements as will be discussed below. Considering that as x gets larger, more and more of the grains become amorphous[1], it is very likely that (re)crystallization of wholly or partially amorphous grains plays a major role in grain size redistribution during RTP. Outside this range very small grains (small R and x) fully oxidize and large grains (large R and x) are too large to show confinement effects. Finally, we note that PL signal intensity from all as-grown samples degraded in time when samples were excited with high laser power. However, RTP annealed samples show much better stability of PL intensity.

We also performed x-ray diffraction (XRD) measurements on both the as-grown and RTP annealed SiO_x samples, grown with 25 sccm N_2O flow rate (**R**=0.15), which showed the most intensive PL before and after RTP. The average Si cluster size in these SiO_x films were determined from the half width of the (111) Si reflection of XRD spectra[9]. The initial mean size of the clusters in as-grown SiO_x films was estimated to be 1.0-1.4 nm and it increased with RTP temperature up to 4.2 -4.6 nm, accompanied with *red-shift* of PL spectra in annealed samples (inset on Fig.2, dashed line). Further, XRD measurements shows that intensity of the x-ray diffracted signal was increased with increasing annealing temperature, which is most probably due to increase in the volume of Si in the nano-crystalline phase. A study of PL spectra of these samples under UV excitation (pulsed N_2 laser; f=60 Hz; pulse duration 20 ns; average power, 7 mW) was performed. Position of PL spectra maximum for SiO_x sample (R=0.15) before and after RTP where the clusters sizes increase to 4.2-4.6 nm, are also shown on inset of Fig.2 (solid line). It can be seen, that PL peak for as-grown sample (mean diameter of the clusters is about 1.0 nm) is observed at a wavelength of about 3.2 eV but peak PL position for samples containing large Si clusters (after RTP) is the same as in the case of excitation by 457.9 nm laser line suggesting that perhaps yet shorter wavelength excitation source needs to be used in order to determine the actual position of PL maximum from as-grown samples (with Si cluster diameters of ~1.0 nm).

The nature of the bonding groups in as grown and RTP annealed SiO_x films has been examined by FTIR measurements. Room temperature IR spectra were recorded from 200 to 4000 cm^{-1} by a Bomem FTIR spectrometer with the reference being the same Si wafer but without the film. IR absorption spectra exhibit three main bands associated with the **Si-O** asymmetric stretching (1050-1079 cm^{-1}), bending (800-810 cm^{-1}) and rocking (450-455 cm^{-1}) modes. The shift of the SiO_x stretching mode towards low frequencies with reduction of N_2O gas flow is displayed in Fig. 2b. (dashed line) demonstrating the fact that the as-grown oxide (SiO_x) moves towards off-stochiometry (from

x=2 to x=0.15) with reduced N_2O flow where the silicon atoms have a higher probability of having one or more Si atom neighbors which shifts the **Si-O-Si** stretching frequency to lower values[2]. The **Si-O-Si** stretching band frequencies for these as-grown SiO_x films shift towards the Si-rich as the FWHM gets broader with decreasing R, demonstrating the presence of suboxides for low $N_2O/(SiH_4:N_2)$ ratio. Fastest increase in Si cluster formation was observed for **R**<0.25. The index of refraction variation of the as-grown SiO_x films with gas flow ratio is also shown in Fig.3 (solid line). As can be seen from this plot, a decrease of N_2O gas flow results in an increase of index of refraction (from n=1.4 to 4.1) due to changes in SiO_x film stoichiometry[14] (from x=2 to x=0.15). The most pronounced changes in the index of refraction was also observed for **R**<0.25 indicating the growth of excess Si concentration inside the oxide matrix. The RTP treatment of the SiO_x films in air resulted in decreasing of refraction index and shifting of **Si-O** stretching mode position toward higher frequencies, Fig.3, indicating a drop in excess Si concentration in silicon oxide matrix. The **Si-O** stretching mode position for the SiO_x films grown at **R**>0.3 after RTP treatment shifted to 1080 cm^{-1} - the value corresponding to SiO_2.

The IR absorption spectra of as-grown SiO_x films (x>0.15; **R**>0.007) show other very weak absorption bands at approximately 3650 and 3350 cm^{-1}, associated with the stretching motion of hydrogen atoms in **Si-O-H** and **Si-H** or **N-H** bonding groups, respectively[4,15], and an absorption band at approximately 935 cm^{-1} that can be attributed to the **Si-O** stretching vibrations of strongly hydrogen-bonded **SiHO** groups. These weak bands disappeared completely after few minutes of annealing at 510 ^{o}C and absorbance of the **Si-O-Si** stretching mode increased indicating increased volume of completely oxidized Si. In contrast, IR spectra of a SiO_x (x=0.15) sample grown at extremely low N_2O flow rates (**R**=0.007) shows strong absorption peak related to **Si-H_n** and **SiOH** bonded groups. Those absorption peaks decreased very slowly in intensity with RTP treatment. Presence of N in the films was not observed since Si-N bending mode may be screened by Si-O mode indicating that N concentration is very small. We also observed that near infrared PL signal from the **R**=0.007 sample decreased with disapperance of those absorption bands, suggesting that the nature of this broad near IR PL emission band may be correlated with the presence of hydrogen and **OH** groups bonded to silicon.

In summary, in addition to the luminescence in the red and near IR wavelengths similiar to previous work on SiO_x and porous silicon we observed blue PL for the first time in SiO_x. Further, we find that there is a narrow range of gas flow ratios that leads to efficient PL after annealing at high temperatures. Thus we conclude that it is possible to grow SiO_x (x<2) films that contain excess Si which have a tendency to form clusters in the oxide matrix. The concentration of Si in as-grown SiO_x films increases rapidly with **R** when PECVD process is performed with **R**<0.2 (Fig. 2b) and larger size clusters form within the film. Some amount of Si within these Si clusters in as-grown SiO_x films show crystalline structure, while majority of the Si is expected to be in the amorphous phase[1], which may coat crystallites embedded into a-SiO_x matrix. Such behavior of Si in SiO_x was previously observed[1,9]. RTP annealing of SiO_x samples in air leads to oxidation of excess Si inside SiO_2 matrix as well as growth of larger Si crystallites inside amorphous Si islands (Fig.2,inset). This process leads to total oxidation of small Si clusters while further crystallization of the larger clusters takes place. In SiOx films grown with high **R** very small Si islands are grown and after RTP in air these clusters completely disappear with corresponding PL signal also decreasing, (Fig.1c,2a) indicating the formation of perfect SiO_2.

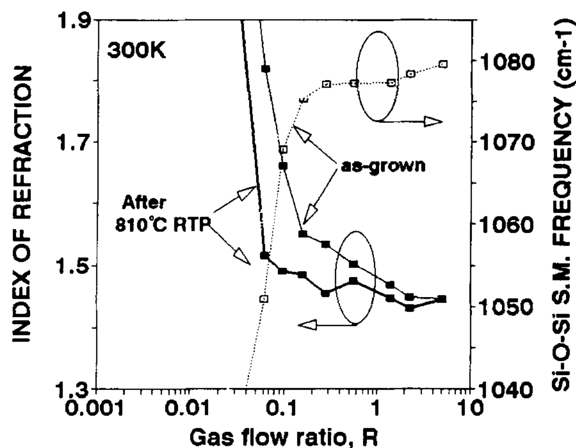

Fig.3: Both the index of refraction and the Si-O-Si stretching frequency shifts as a function of gas flow ratio **R**.

We would like to thank Prof. S. Suzer for FTIR and Dr. N.N.Faleev for XRD measurements, Dr. B.V.Egorov for support during experiments and two of us (T.F.N. and V.N.M.) would like to thank Prof. Zh. I. Alferov and S. A. Gurevich for their encouragement throughout this work. Partial financial support of this work by Turkish Scientific and Technical Research Council (TUBITAK) is gratefully acknowledged (Grant No: TBAG -1244). T.F.N. would like to thank TUBITAK for a financial support.

References

1. P.Bruesch, Th.Stockmeier, F.Stucki, P.A.Buffat, J. K. N. Linder, J. of Appl. Phys.**73**, 7677 (1993).
2. Y.Kanemitsu, H. Uto, Y. Masumoto, T. Matsumoto, T. Futagi, H. Mimura, Phys. Rev. B. **48**, 2827 (1993).
3. Chi-Huei Lin, Si-Chen Lee, Yang-Fang Yen, Appl. Phys. Lett. **63**, 902 (1993).
4. G. Lucovsky and D. V. Tsu, J. Vac. Sci. Technol A **5**, 2231 (1987).
5. P. G. Pai, S. S. Chao, Y.Takagi, G. Lucovsky, J. Vac. Sci. Technol. A **4**, 689 (1986).
6. T. Shimizu-Iwayama, M. Ohshima, T. Niimi, S. Nakao, K. Saitoh, T. Fujima, N. Itoh, J. Phys. Condens. Matter. **5**, L375 (1993).
7. D. J. DiMaria, J. R. Kirtley, E. J. Pakulis, D. W. Dong, T. S. Kuan, F. L. Pesavento, T. N. Theis, J. A. Cutro and S. D. Brorson, J. Appl. Phys. **56**, 401 (1984).
8. Y. Osaka, K. Tsunetomo, F. F. Toyomura, H. Myoren and K. Kohno, Jpn. J. Appl. Phys. **31**, L365 (1992).
9. P. D. Milewski, D. J. Lichtenwalner, P. Mehta, A. I. Kingon, D. Zhang and R. M .Kolbas, J. of Electronic Materials, **23**, 57 (1994).
10. W. Y. Ching , Phys. Rev. **B26**, 6610 (1982).
11. J. Ni and E. Arnold, Appl. Phys. Lett. **39**, 554 (1981).
12. F. N. Timofeev, K. Bozkurt, M. Gure, A. Aydinli, R. Ellialtioglu, S. Suzer, K. Turkoglu, Sov. Phys. Lett. **14**, 79 (1994).
13. F. N. Timofeev, A. Aydinli, R. Ellialtioglu, S. Suzer, M. Gure, K. Turkoglu, V. N. Mikhailov, and I. N. Timofeev, Sov. Tech. Phys. Lett., **14**, 51 (1994).
14. A. L. Shabalov, M. S. Feldman, Thin Solid Films, **151**, 317 (1987).
15. G. A. Ruggles, R. Koba, R. E. Tressler, J. of Electrochem. Soc. 133, 2549 (1986)