

Silicon dots/clusters in silicon nitride: photoluminescence and electron spin resonance

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Abstract

Photoluminescence (PL) properties of SiN_x ($0.51 < x < 1.3$) films are studied. A visible luminescence near the UV region is observed and the PL intensity and peak positions are found to be governed by the excess silicon composition. A large scale potential fluctuation due to the spatial variation of chemical composition in SiN_x is proposed to explain these observations. In addition, non-radiative recombination centers (N_3Si -, N_2SiSi -, NSi_2Si -, or Si_3Si -), which have prominent effect on the luminescence intensity, are also studied using electron spin resonance (ESR) measurement. The ESR results suggest that the excess silicon content should not be too high in order to have a strong PL. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently, a lot of investigations on the luminescence properties of silicon-based structures, including porous silicon (PS) [1], silicon nanoclusters (SNC) in amorphous SiO_2 [2–4], have been conducted in a search for the origin of luminescence and possible applications in silicon devices. A wide range of luminescence, including the red–orange band (luminescence peak with energy 1.6–2.0 eV) and blue band (2.6–2.8 eV) in these structures was observed [5,6]. A green line was also found by making use of the silicon nitride (Si_3N_4) structure [7,8] which provides the possibility for fabricating full-color devices based on silicon technology.

Although some researchers suggested that the luminescence of PS and SNC/ SiO_2 systems is due to the defects at the Si– SiO_2 interface or in the SiO_2 [6,9], we are inclined to believe that the luminescence is due to the confinement of electrons and holes in the silicon dots/nanoclusters (SNC) [1]. Instead of considering the quantum confinement in silicon nanoclusters, a more general case for the carrier confinement due to the large scale potential fluctuations

was proposed [10]. It was suggested that the SiO_x film consists of five different tetrahedral $\text{SiSi}_\nu\text{O}_{4-\nu}$, ($\nu = 0, 1, 2, 3, 4$). That is, the SiO_x may appear in the following phases: SiO_2 , Si_2O_3 , SiO , Si_2O , and Si . As a result, the band gap may vary from 1.1 eV (Si) to 8.0 eV (SiO_2). The spatial fluctuation of chemical composition in SiO_x leads to the formation of potential wells where carrier confinement occurs. This model had been used in Ref. [11] to explain the weak temperature dependence of the luminescence intensity in porous silicon.

However, the field strength needed for electroluminescence in SiO_x will be larger than 6 MV/cm for electron injection and more than 10 MV/cm for hole injection from Si into SiO_2 [12,13]. This field strength is very close to the breakdown field of silicon dioxide. This constraint can be resolved by employing the SiN_x structure which has several potential advantages over SiO_x . It is well known that the band gap of Si_3N_4 is 4.6 eV [8]. The barriers at the Si– Si_3N_4 interface are 2.0 eV and 1.5 eV for electrons and holes, respectively. Hence for double (electron and hole) injection, a field strength of 2–4 MV/cm is enough in Si_3N_4 [14]. This field strength is much lower than the breakdown field (~ 9 MV/cm) of Si_3N_4 [15]. Silicon nitride also contains a high density of electron and hole traps which will result in a strong trapping of electrons and holes. Conse-

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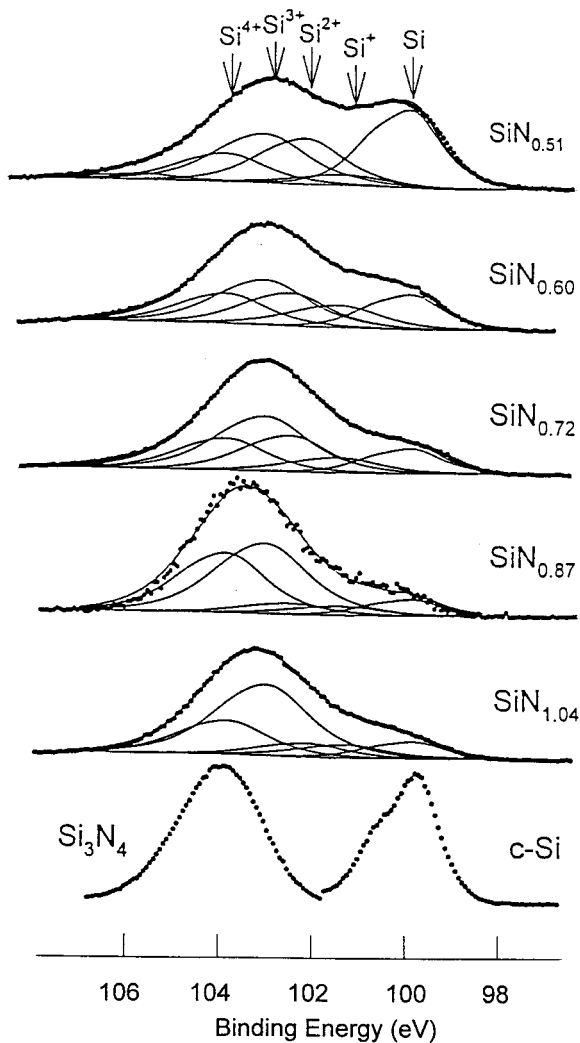


Fig. 1. XPS spectra of Si 2p level for SiN_x samples with different compositions. Markers represent the experimental data and curves are their deconvoluted results using the five-tetrahedron model. Spectra for Si_3N_4 and crystalline Si are also shown for comparison.

quently, the injection current of Si_3N_4 is 5–8 orders of magnitude larger than that of SiO_2 [15]. Hence the electroluminescence intensity in SiN_x should be larger than that in SiO_x because of the larger injection current. Of course, the actual luminescence intensity in these structures will be governed by the density of non-radiative defects. On the other hand, since the refractive index of SiN_x ($n > 1.96$) is larger than that of SiO_2 ($n = 1.46$), light localization in SiN_x or waveguide effect is possible with the SiO_2 – SiN_x – SiO_2 structures; that is, the luminescence in SiN_x can be observed in both the normal direction of the surface and the direction along the surface. SiN_x therefore has several potential applications in optical devices in the future. However, detailed investigation must be conducted before these applications come to light.

This work explores the possibility of application of SiN_x structure in a light-emitting device. Photoluminescence (PL) properties of the SiN_x film with x in the range of

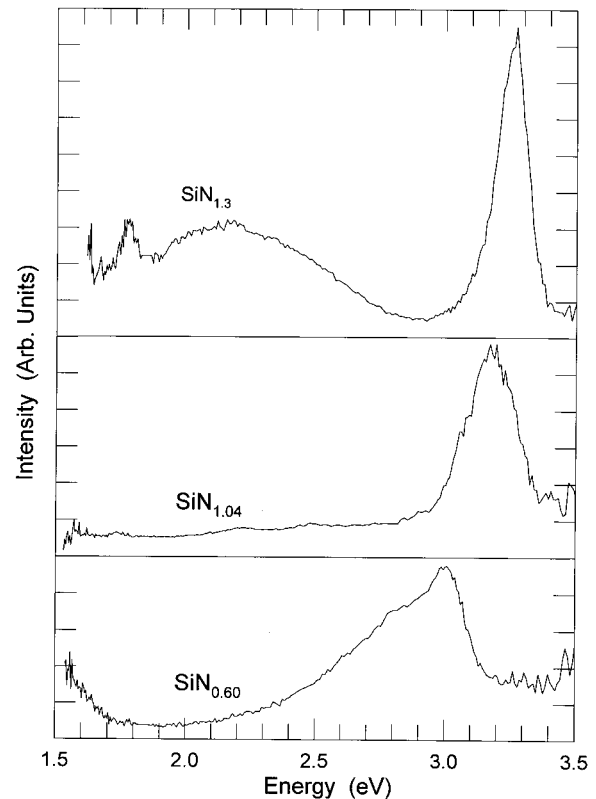


Fig. 2. Photoluminescence spectra of SiN_x with different values of x . The photoluminescence is excited by a nitrogen laser with a wavelength of 337 nm.

0.51 to 1.3 is investigated and then the luminescence mechanism, based on the spatial composition variation and large scale potential fluctuation model, for this kind of thin film will be proposed. To maximize the luminescence efficiency, the effect of silicon concentration on the density of non-radiative recombination centers is studied using electron spin resonance (ESR) measurement.

2. Experiment

The SiN_x layer was deposited on silicon, quartz or sapphire wafers with LPCVD technique using $\text{SiH}_2\text{Cl}_2/\text{NH}_3$ mixture at a temperature of 760°C . The thickness of SiN_x is about 3000 \AA which was measured by ellipsometry. Increase of the $\text{SiH}_2\text{Cl}_2/\text{NH}_3$ ratio leads to the increase of the amount of excess silicon and hence the refractive index of the SiN_x film. The refractive index (n) for SiN_x was measured by ellipsometry using a laser beam with a wavelength of 6328 \AA . The chemical composition of SiN_x (x value) was determined from X-ray photoelectron spectroscopy (XPS) measurement.

For X-ray photoelectron spectroscopy measurements, a monochromatic $\text{Al K}\alpha_{1,2}$ source was used and the intensity was measured using a HP 4252 spectrometer. Core Si 2s level and valence band spectra were measured. Photolumi-

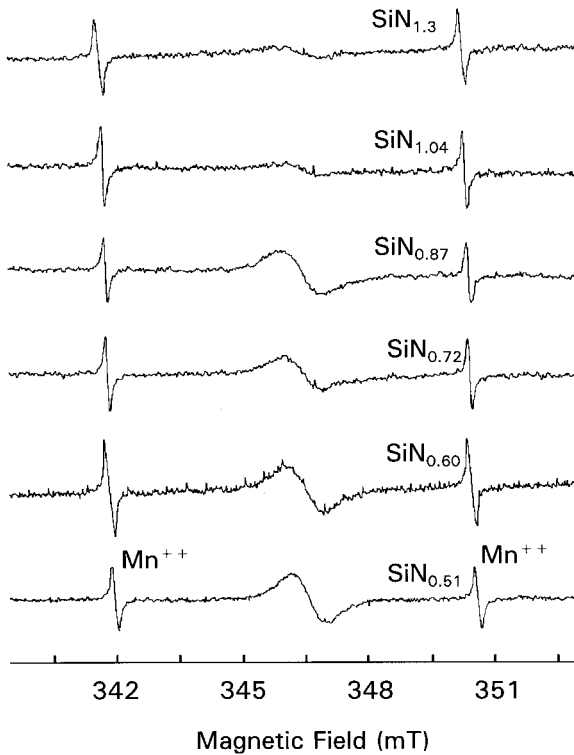


Fig. 3. ESR spectra of SiN_x of different silicon composition.

nescence spectra of SiN_x were obtained by nitrogen laser ($\lambda = 337 \text{ nm}$) excitation at 300 K. For electron spin resonance (ESR) study, a Bruker ESP-300 spectrometer with 100 kHz modulation field was used. A small amount of Mn^{2+} in MgO was used as a reference for g -value calibration and the number of spins was determined by integrating the ESR signals.

3. Results

Fig. 1 shows the experimental Si 2p level XPS spectra (markers) for samples with different compositions. Using the constraints that the same components in different a-SiN_x samples have the same peak position and full width at half maximum (FWHM), the spectra were deconvoluted into five peaks (curves in Fig. 1) resulting from the different $\text{SiN}_\nu\text{Si}_{4-\nu}$ tetrahedrons [16]. The deconvoluted results suggested that the SiN_x structure should be a mixture of a-Si , $\text{a-Si}_3\text{N}_4$ and some subnitrides including SiN_3Si , SiN_2Si_2 , and SiNSi_3 tetrahedrons. There is evidence that Si nanoclusters exist in the investigated samples [17]. Using Raman scattering measurement, the size of the Si nanoclusters of the investigated sample is estimated to be in the range of 1.5 to 5.0 nm [17].

Fig. 2 shows the photoluminescence spectra of SiN_x in the visible and ultraviolet region. The peak intensity and energy location increase as the silicon concentration decreases. For SiN_x with low concentration of excess silicon, a narrow line

near the UV region with energy in the range of 3.0 to 3.2 eV is observed. A similar narrow line (3.12 eV) was also observed in SiN_x cathodoluminescent spectra [7,8,18]. The narrow UV line seems to be a super-luminescence phenomenon as a result of population inversion. This observation suggests that SiN_x structure may be used to design a SiN_x -based thin film laser. However, to have a high intensity and a compact light source based on this structure, double injection of electrons and holes which will take part in the radiative recombination should be used. SiN_x -based structure has several potential advantages over the porous silicon structures. It is more stable because there are no hydrogen bonds and large openings which lead to device degradation because of surface adsorption effects.

As only relative measurements of the PL were made, the exact external quantum yield of luminescence cannot be calculated. Nevertheless, we found that it is still resolvable that the PL intensity in SiN_x film is higher than that of Si-implanted SiO_2 (with implant of about 10^{16} cm^{-2}). However, since the noise in the observed PL spectra is quite large, the external quantum yield of photoluminescence cannot be very high. The low quantum yield suggests that the SiN_x film should contain significant amounts of non-radiative recombination centers.

To study the non-radiative centers in SiN_x , ESR measurements were made at room temperature. As shown in Fig. 3, ESR signals with different zero crossing values (g factors) are observed. The g factor increases from 2.0025 to 2.0044 for x decreasing from 1.3 to 0.51. These ESR signals are ascribed to the center formed by a trivalent silicon atom with an unpaired electron, i.e. $\equiv\text{Si}\cdot$. It is well known that the silicon atom in stoichiometric Si_3N_4 is bonded by three nitrogen atoms ($\text{N}_3\equiv\text{Si}\cdot$). The $\text{N}_3\equiv\text{Si}\cdot$ center has a g value of 2.0028 [19]. However, if the silicon nitride is enriched by excess silicon, i.e. $\text{SiN}_{x<4/3}$, four kinds of silicon atom with an unbridged bond, namely $\text{N}_3\equiv\text{Si}\cdot$, $\text{N}_2\text{SiSi}\cdot$, $\text{NSi}_2\text{Si}\cdot$, and $\text{Si}_3\text{Si}\cdot$, are expected. Hence, the observed ESR signal with g value in the range of 2.0025 to 2.0044 can be considered as a superposition of these four kinds of defects [20]. It is noted that as the silicon concentration increases, more defect states of $\text{N}_2\text{SiSi}\cdot$, $\text{NSi}_2\text{Si}\cdot$ and $\text{Si}_3\text{Si}\cdot$ should be found. These states have a g value between 2.0028 and 2.0055. For large amount of excess silicon ($\text{SiN}_{0.60}$ and $\text{SiN}_{0.51}$), larger amount of defect states will be contributed by $\text{Si}_3\text{Si}\cdot$ states ($g = 2.0055$). Those defects can capture both electrons and holes via a non-radiative process. As a result, the PL intensity reduces rapidly at the high-energy side as the silicon concentration increases. In addition, the change of quantum well structure due to the increase of silicon composition will affect the PL spectra. This effect will be discussed in Section 4. The estimated concentration of paramagnetic defects in SiN_x is in the range of 5×10^{18} to 10^{19} cm^{-3} and does not exceed 10^{19} cm^{-3} for all samples. The density of silicon bonds in Si_3N_4 is four times the total number of Si atoms and is about $2 \times 10^{23} \text{ cm}^{-3}$. It implies that the density of dangling bonds in SiN_x is lower than the

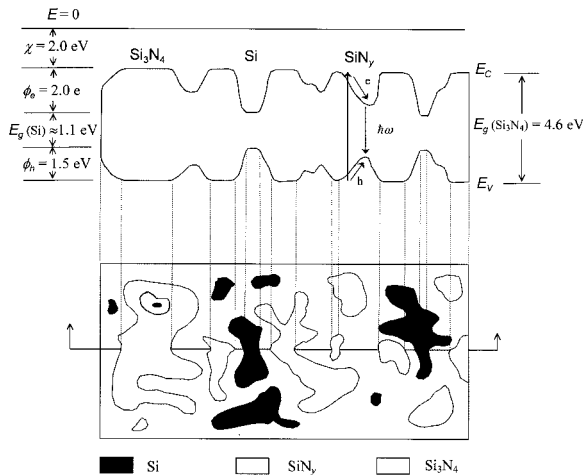


Fig. 4. Illustration of potential fluctuations in SiN_x due to spatial chemical composition fluctuations. The size of silicon nanoclusters is in the range of 1.5 to 5.0 nm.

density of silicon bonds by at least four orders in all samples. This observation indicates that the silicon atom with an un-paired electron ($\equiv\text{Si}\cdot$) is an unfavorable configuration in SiN_x when compared to Si–N and Si–Si bonded states. It was shown that $\equiv\text{Si}\cdot$ in SiN_x is a non-radiative recombination center for both holes and electrons [21]. As the concentration of these centers increases, the photoconductivity and then the photoluminescence intensity of SiN_x drops.

4. Discussion

The hypothesis of local chemical composition fluctuation has been confirmed with XPS and Raman spectroscopy measurement. Due to the non-uniform compositional distribution in SiN_x [22], the band gap will fluctuate. The lower and upper bounds of the bandgap variations are 1.1 eV (crystalline Si) and 4.6 eV (Si_3N_4), respectively. Some potential wells may be formed (see Fig. 4). However, it should be noted that Fig. 4 is for illustration only. In fact, the silicon dots/clusters may be in several different forms and certainly are not strain free and it is difficult to have an exact bandgap value for the silicon regions. Some of these potential wells may be narrow enough for carrier confinement to take place. The shift of the peak position of PL with decreasing silicon composition can also be explained with the proposed model. As the silicon composition reduces, the quantum wells will become narrower and deeper; namely, other than SiN_y , more quantum wells will be formed with the silicon nanoclusters. As a result, the PL intensity becomes higher and a sharp peak accompanied with a blue shift is observed in low silicon composition sample (see $\text{SiN}_{1.3}$ trace).

On the other hand, it was also found by polarizing the Si– SiO_2 – SiN_x –Al structures that the CV characteristic of this structure shows a hysteresis similar to the MNOS ones. The

estimated density of electron and hole traps is in the range of $(5 \pm 3) \times 10^{18} \text{ cm}^{-3}$. The polarized samples can be restored to the initial stage by annealing them at 200°C for 30 min. These results suggest that most of the traps in SiN_x have an energy level nearly equal to 1.0 eV [23]. However, since the injected electrons and holes can also be localized by other defects such as Si–Si bonds [18,24–26], the type of carrier (or both electrons and holes) being captured by the $\equiv\text{Si}\cdot$ defects in SiN_x cannot be identified in this work.

Finally, it should be noted that although carrier confinement is believed to be the major luminescence mechanism, we cannot completely rule out the possibility that the luminescence may also be contributed by some radiative defect centers. It was shown in SiO_2 that the $\equiv\text{Si}\text{--}\text{Si}\equiv$ or $=\text{Si}$: has a radiative transition with energy of 4.4 eV [4]. A similar transition may also be found in SiN_x films. Further investigation on these aspects should be attempted.

5. Conclusions

In this work, the photoluminescence (PL) properties of SiN_x ($0.51 < x < 1.3$) films have been studied and a visible luminescence near the UV region is observed. We found that the PL intensity and peak location are governed by the excess silicon composition. These observations have been explained with the potential fluctuation in the band structure and the non-radiative recombination centers. Due to the distribution of silicon nanoclusters or the change of chemical composition in SiN_x , band gap variation occurs which in turn results in the forming of potential wells. These potential wells give rise to the carrier confinement and then photoluminescence results. However, the PL intensity is not very high because of the presence of non-radiative recombination centers ($\text{N}_3\text{Si}\cdot$, $\text{N}_2\text{SiSi}\cdot$, $\text{NSi}_2\text{Si}\cdot$, or $\text{Si}_3\text{Si}\cdot$) which are studied using electron spin resonance (ESR) measurement. The ESR results suggest that the excess silicon concentration should be low in order to have a strong PL. As the silicon concentration increases, the density of non-radiation centers will also increase and the quantum yield reduces.

References

- [1] A.G. Gullis, L.T. Canham, G.M. Williams, P.W. Smith, O.D. Dossier, *J. Appl. Phys.* 75 (1994) 493.
- [2] T. Shimizu-Iwayama, K. Fujita, S. Nakao, et al., *J. Appl. Phys.* 75 (1994) 7779.
- [3] S. Hayashi, T. Nagareda, Y. Kanzawa, K. Yamamoto, *Jpn. J. Appl. Phys.* 32 (1993) 3840.
- [4] H. Nishikawa, E. Watanabe, D. Ito, M. Takiyama, A. Liki, Y. Ohki, *J. Appl. Phys.* 78 (1995) 842.
- [5] Y. Kanemitsu, T. Futagi, T. Matsumoto, H. Mimura, *Phys. Rev. B* 49 (1994) 14723.
- [6] L. Tsybeskov, S.P. Duttagupta, K.D. Hirschman, P.M. Fauchet, *Appl. Phys. Lett.* 68 (1996) 2058.
- [7] V.A. Gritsenko, P.A. Pundur, *Solid State Phys. (Sov)* 28 (1986) 3239.

- [8] V.A. Gritsenko, *Silicon Nitride in Electronics*, Elsevier, New York, 1988.
- [9] S.M. Prokes, W.E. Carlos, *J. Appl. Phys.* 78 (1995) 2671.
- [10] V.A. Gritsenko, Y.P. Kostikov, N.A. Romanov, *Lett.* 34 (1981) 3.
- [11] L. Tsybeskov, K.L. Moore, D.G. Hall, P.M. Fauchet, *Phys. Rev. B* 54 (1996) R8362.
- [12] D.J. DiMaria, J.R. Kirtley, E.J. Pakulis, D.W. Dong, T.S. Kuan, F.L. Pesavento, T.N. Theis, J.A. Cutro, S.D. Brorson, *J. Appl. Phys.* 56 (1984) 401.
- [13] V.A. Gritsenko, *Structure and Electronic Properties of Amorphous Insulators in Silicon MIS Structures*, Science, Novosibirsk, 1993, p. 280.
- [14] V.A. Gritsenko, E.E. Meerson, *Microelectron. (Sov)* 17 (1988) 249.
- [15] V.A. Gritsenko, E.E. Meerson, *Phys. Stat Sol. A* 62 (1980) K131.
- [16] L. Kubler, R. Huang, E. Hill, et al., *J. Vac. Sci. Technol. A* 4 (1986) 2323.
- [17] A. Volidin, M.D. Efremov, V.A. Gritsenko, *Solid State Phenom.* 57-58 (1997) 501.
- [18] P.A. Pundur, J.G. Shavalgin, V.A. Gritsenko, *Phys. Stat. Sol. A* 94 (1986) K107.
- [19] W.L. Warren, P.M. Lenahan, *Phys. Rev. B* 4 (1993) 1773.
- [20] H. Ishii, S. Oozora, M. Kumeda, T. Shimizu, *Phys. Stat. Sol. b* 114 (1982) K111.
- [21] W.L. Warren, J. Kanicki, F.C. Rong, E.H. Poindexter, *J. Electrochem Soc.* 139 (1992) 880.
- [22] V.A. Gritsenko, I.P. Petrenko, S.N. Svitashva, H. Wong, *Appl. Phys. Lett.* 72 (1998) 462.
- [23] E. H. Nicollian and J. R. Brews, *MOS (Metal Oxide Semiconductor) Physics and Technology*, Wiley, New York, 1982.
- [24] V.A. Gritsenko, A.D. Milov, *JETP Lett. (Rus)* 64 (1996) 531.
- [25] V.A. Gritsenko, E.E. Meerson, I.V. Travkov, *Microelectron. (Sov)* 6 (1987) 42.
- [26] V.A. Gritsenko, Y. N. Morokov, Y.N. Novikov, *Appl. Surf. Sci.* 113-114 (1997) 417.