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2001 J. Phys.: Condens. Matter 13 6541

(http://iopscience.iop.org/0953-8984/13/30/310)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 6541–6549 PII: S0953-8984(01)22341-8

Thermally induced photoluminescence quenching centre in hydrogenated amorphous silicon oxynitride

Hiromitsu Kato[1,5], Akira Masuzawa[1], Takashi Noma[2,3], Kwang Soo Seol[2,4] and Yoshimichi Ohki[1,2]

[1] Department of Electrical, Electronics and Computer Engineering, Waseda University, Shinjuku-ku 169-8555, Japan
[2] Advanced Research Institute for Science and Engineering, Waseda University, Shinjuku-ku 169-8555, Japan
[3] Engineering Department 1, System-LSI Division, Sanyo Electric Co. Ltd, Oizumi-Machi 370-0596, Japan
[4] RIKEN (The Institute of Physical and Chemical Research), Wako 351-0198, Japan

E-mail: 600c5050@mn.waseda.ac.jp

Received 28 February 2001, in final form 30 May 2001
Published 13 July 2001
Online at stacks.iop.org/JPhysCM/13/6541

Abstract

The effect of thermal annealing on the photoluminescence around 2.2–2.9 eV in hydrogenated amorphous silicon oxynitride films was investigated. The luminescence intensity increases monotonically with an increase in the annealing temperature for the samples with lower nitrogen contents (N/O = 0.06, 0.10 and 0.12). It shows a similar increase up to 500 °C, while it decreases abruptly above 500 °C for the samples with higher nitrogen contents (N/O = 0.14 and 0.18). The density of silicon dangling bonds depends on the annealing temperature in a manner opposite to that of the luminescence intensity in all the temperature region. Based on this correlation, it is thought that the silicon dangling bonds act as the quenching centre. Infrared absorption spectroscopy indicated that the precursor of silicon dangling bonds was the Si–H bond. Hydrogen was released at temperatures above 500 °C from Si–H bonds, resulting in a large number of silicon dangling bonds that quench the luminescence.

1. Introduction

Luminescence, which is important for optoelectronic applications, is also a good tool to characterize localized states and impurities present in the band gap or at the band tail of a material. There have been several reports on the photoluminescence (PL) properties of amorphous silicon (a-Si:H) [1–4], amorphous silicon nitride (a-SiN$_x$:H) [5–7] and amorphous

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[5] Research Fellow of the Japan Society for the Promotion of Science.

Table 1. Atomic ratio of a-SiO_xN_y : H films studied.

Sample	Atomic (%) Si	O	N	N/O	Empirical formula	Refractive index
A	35	62	3.6	0.06	$SiO_{1.8}N_{0.10}$	1.49
B	35	59	6.0	0.10	$SiO_{1.7}N_{0.17}$	1.53
C	35	57	7.0	0.12	$SiO_{1.6}N_{0.20}$	1.57
D	37	56	7.7	0.14	$SiO_{1.5}N_{0.21}$	1.62
E	38	53	9.6	0.18	$SiO_{1.4}N_{0.26}$	1.67

silicon carbide (a-SiC_x:H) [8,9]. By doing time-resolved PL analysis and by examining PL dependences on defect density and temperature, the natures of defect states have become clear.

Hydrogenated amorphous silicon oxynitride (a-SiO_xN_y:H) is one of the most important insulating materials in microelectronics [10,11]. It has a possibility of realizing an excellent electronic property similar to silicon dioxide while keeping the high permittivity of silicon nitride by choosing a proper composition of y/x [12,13]. Since its refractive index can be controlled by y/x, it can be applied to optical fibers and waveguides [14,15]. Therefore, it is important to study optical properties of this material.

Several papers have been reported on optical properties such as PL, optical absorption and infrared absorption for a-SiO_xN_y:H films [16–18]. In our previous paper [18], we showed that there are two PLs in a-SiO_xN_y:H. One is the PL around 4.3 eV that appears in films with a low nitrogen content. This is originated from the silicon homobond (Si–Si) or the oxygen vacancy in SiO_2. The other PL at 2.2–2.9 eV is observed in films with a high nitrogen content and is due to radiative recombination between localized states below the conduction band and above the valence band. However, this latter PL in a-SiO_xN_y:H has not been examined well as compared to PLs observed in other hydrogenated amorphous films such as a-Si:H, a-SiN_x:H and a-SiC_x:H. In the present paper, the effect of thermal treatment on the property of PL at 2.2–2.9 eV is examined, focusing on its relation to thermally induced paramagnetic defect centres for a-SiO_xN_y:H films with different y/x ratios. The generation mechanism of defect centres and the PL quenching process are discussed.

2. Experimental procedures

The a-SiO_xN_y:H films were deposited on a p-type (100) silicon monocrystal substrate by plasma enhanced chemical vapour deposition using a mixture of SiH_4, N_2O and N_2 gases. The substrate temperature was 400 °C and the plasma frequency was 13.56 MHz. By changing the flow rate of SiH_4, five types of film with different nitrogen contents were prepared as shown in table 1. The atomic ratios of Si, O and N were estimated through x-ray photoelectron spectroscopy (JEOL JPS-90MX). With an increase in the flow rate of SiH_4, the nitrogen and silicon contents were increased. Furthermore, with an increase in the nitrogen content, the atomic composition deviates from the stoichiometric ratio, $SiO_{2z}N_{4/3(1-z)}$, where z is a parameter with a value between 0 and 1. The film thickness measured by ellipsometry (ULVAC ESM-1) was about 100 nm, and the refractive index, also measured by ellipsometry, was changed from 1.49 to 1.67 with an increase in the nitrogen content.

For annealing, the samples were kept at a temperature ranging from 200 °C to 900 °C in vacuum (5.0×10^{-2} Pa) with a rapid thermal annealing apparatus for 10 min. Photoluminescence was measured at room temperature and at −260 °C with a monochromator (Jobin-Yvon HR320) and an intensified charge coupled device array (Princeton Instruments

ICCD-576G/RBT). In the case of the room temperature measurement, the PL was exited by a KrF excimer laser (wavelength: 248 nm = 5.0 eV; pulse width: ~25 ns; pulse energy: ~300 mJ cm^{-2}, Lambda Physik Compex 205), while it was excited by synchrotron radiation (SR) at BL1B line of UVSOR facility (Institute for Molecular Science, Okazaki, Japan) at −260 °C. The PL excitation (PLE) was obtained at −260 °C using SR. The structural change induced by the thermal annealing was examined by Fourier transform infrared absorption (IR, JEOL JIR-Winspec 50) and electron spin resonance (ESR, JEOL JES-PX 1060).

3. Results and discussion

Figure 1 shows typical PL and PLE spectra observed in unannealed samples A to E. Dotted curves are estimated tails of the PLE peaks present at higher energies. The PL and PLE peak energies shift to a lower energy from 2.88 eV to 2.23 eV and from 5.14 eV to 4.57 eV, respectively, with an increase in the nitrogen content, if we neglect the small side peak that appeared in the PLE spectra of samples A and B. The full width at half maximum of PL is about 0.8 eV, which is independent of the atomic ratio.

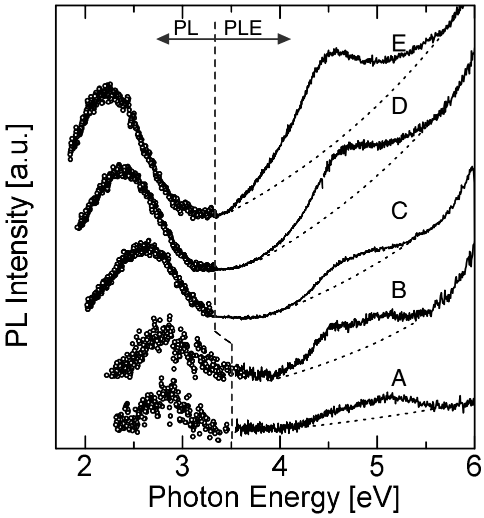

Figure 1. PL and PLE spectra observed in unannealed samples A to E. Dotted curves are estimated tails of the PLE peaks present at higher energies.

Figure 2 shows the relations among the PL peak energy, PLE peak energy and the minimum energy that obeys the Urbach rule estimated from the edge of the PLE spectra. The Urbach edge energy was obtained from the high energy tails of PLE spectra to estimate the optical absorption edge. The dependence of the PLE peak energy and that of the minimum Urbach-obeying energy on the PL peak energy agree fairly well with each other. This suggests that the PL is induced by the inter-band excitation from the valence band to the conduction band.

As reported in our previous paper [18], the present PL in a-SiO$_x$N$_y$:H and that observed in a-SiN$_x$:H have many similar points in their PL and PLE spectra and the PL lifetime. It is considered that the PL in a-SiN$_x$:H is governed by a radiative recombination process between localized states [6, 7, 18]. The forbidden gap energy of a-SiO$_x$N$_y$:H becomes smaller with an increase in the nitrogen content [17]. This is consistent with the PLE peak shift shown in figure 2. Therefore, it is considered that the present PL at 2.2–2.9 eV is due to a radiative

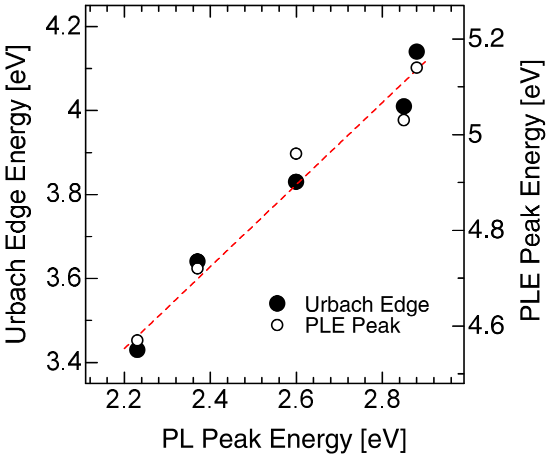

Figure 2. Relations among the PL peak energy, PLE peak energy and the minimum Urbach-obeying energy.

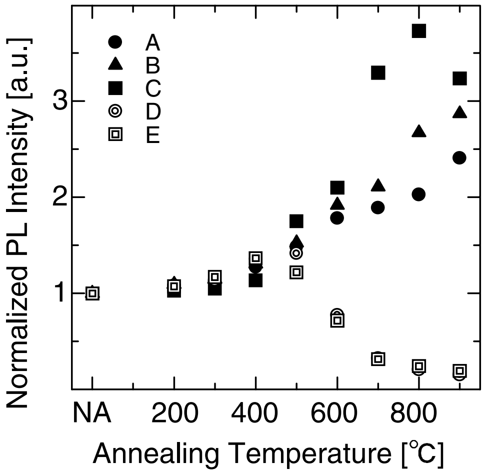

Figure 3. Relation between the annealing temperature and the normalized PL intensity obtained for samples A to E. NA: not annealed.

recombination between localized states below the conduction band and above the valence band.

Figure 3 shows the relation between the annealing temperature and the normalized PL intensity obtained for samples A to E. The PL intensity increases slightly on annealing at temperatures below 500 °C for all the samples, and it continues to increase at annealing temperatures above 500 °C for samples A to C. In contrast, it decreases abruptly on annealing at temperatures above 500 °C for samples D and E. The intensity of PL, I_{PL}, is generally expressed by

$$I_{PL} \propto \frac{k_R}{k_R + k_{NR}}$$

where k_R and k_{NR} are the radiative and nonradiative recombination rates, respectively. It

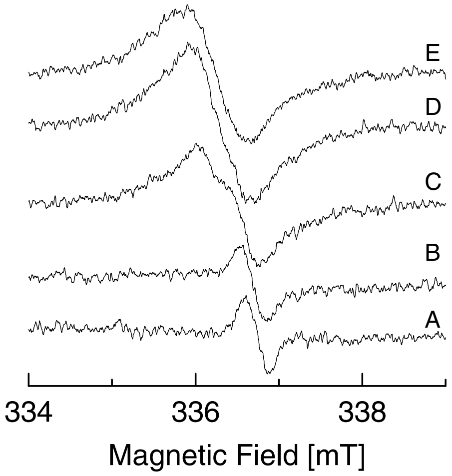

Figure 4. ESR spectra observed in unannealed samples A to E.

Table 2. The g value and ΔH calculated from ESR spectra.

Annealing temperature		Sample				
		A	B	C	D	E
NA to 400 °C	g	2.0008	2.0012	2.0022	2.0035	2.0038
	ΔH (mT)	0.27	0.32	0.75	0.81	0.82
500 °C to 900 °C	g	—	—	2.0034	2.0041	2.0043
	ΔH (mT)	—	—	0.58	0.64	0.76

NA: not annealed.

is considered that the annealing below 500 °C decreases k_{NR}, resulting in the increase of PL intensity. The annealing above 500 °C is considered to decrease and increase k_{NR} for samples A to C and for samples D and E, respectively.

Figure 4 shows the ESR spectra observed in the unannealed samples A to E. The g value at the zero-cross and ΔH (the difference in magnetic field at the signal maximum and minimum) are shown in table 2. From these g values, the induced paramagnetic defects are attributable to silicon dangling bonds (Si–DBs: $\cdot\mathrm{Si} \equiv$, where $\equiv$ and $\cdot$ denote three separate bonds and an unpaired electron, respectively). The difference in the nearest neighbouring atoms is reflected to the difference in the g value and ΔH. For example, the E′ centre ($\cdot\mathrm{Si} \equiv \mathrm{O}_3$) has g value $= 2.0010$ and $\Delta H = 0.28$ mT, the K centre ($\cdot\mathrm{Si} \equiv \mathrm{N}_3$) has g value $= 2.0030$ and $\Delta H = 1.25$ mT and the D centre ($\cdot\mathrm{Si} \equiv \mathrm{Si}_3$) has g value $= 2.0055$ and $\Delta H = 0.75$ mT [19–21]. As shown in table 2, all the g values are less than 2.0055. This implies that there are relatively few D centres in the present samples, which is reasonable judging from the atomic compositions shown in table 1.

Figure 5 shows the relation between the annealing temperature and the paramagnetic spin density obtained for samples A to E. By the annealing at temperatures below 500 °C, the spin density decreases for all the samples. The paramagnetic defects were induced to a large extent for samples D and E annealed at temperatures above 500 °C, while they disappeared for samples A and B. By comparing the annealing temperature dependence of PL intensity (shown

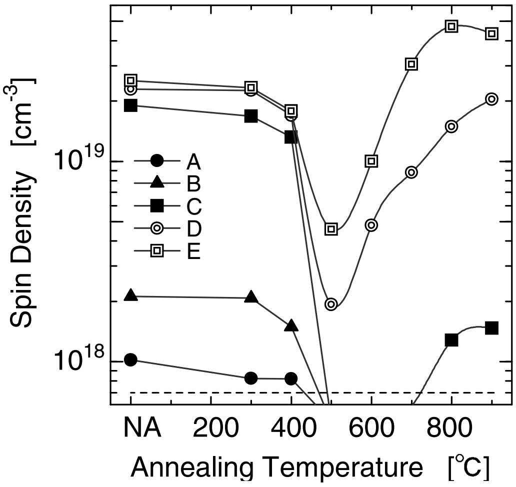

Figure 5. Relation between the annealing temperature and the paramagnetic spin density obtained for samples A to E. The broken line indicates the detection limit. NA: not annealed.

in figure 3) and that of spin density (shown in figure 5), a good agreement can be seen. If the paramagnetic defects increase k_{NR}, this agreement is easily explained. Namely, the Si–DB is considered to act as a quenching centre in the recombination process of the 2.2–2.9 eV PL.

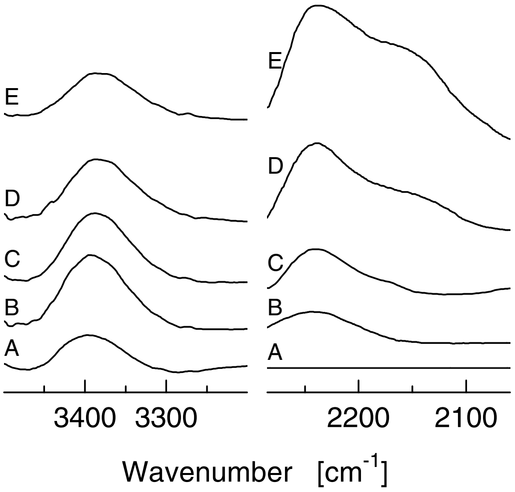

Figure 6. IR spectra due to Si–H bonds at 2150–2250 cm^{-1} and N–H bonds around 3340 cm^{-1} observed in unannealed samples A to E.

As shown in table 2, the g value of Si–DBs obtained for samples C to E changes to a different value on annealing at temperatures above 500 °C. Since the g value reflects the structure, it should be considered that the annealing above 500 °C induces a new structure of Si–DB. Thus, k_{NR} should consist of the contribution of the original structure $k_{\mathrm{NR}(0)}$ and that of the thermally induced one $k_{\mathrm{NR}(T)}$. For samples A and B, since the PL intensity increases monotonically with an increase in the annealing temperature, it is considered that $k_{\mathrm{NR}(0)}$ continuously decreases. If the original structure of Si–DB is the same in all the samples, $k_{\mathrm{NR}(0)}$

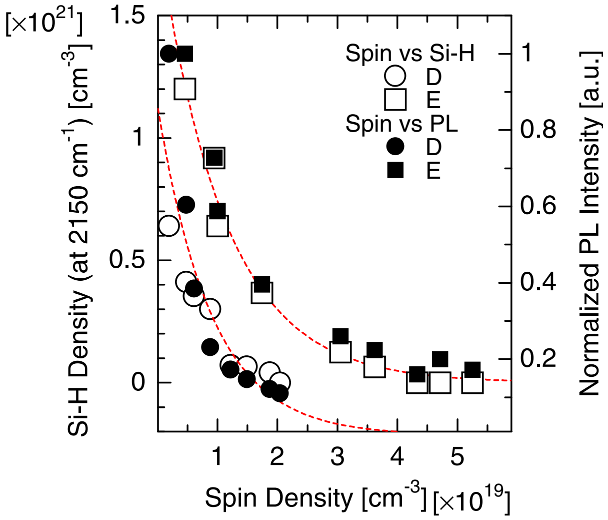

Figure 7. Si–H density (open symbols) calculated from the IR absorption intensity and the normalized PL intensity (solid symbols) for samples D and E, each as a function of the density of paramagnetic centres.

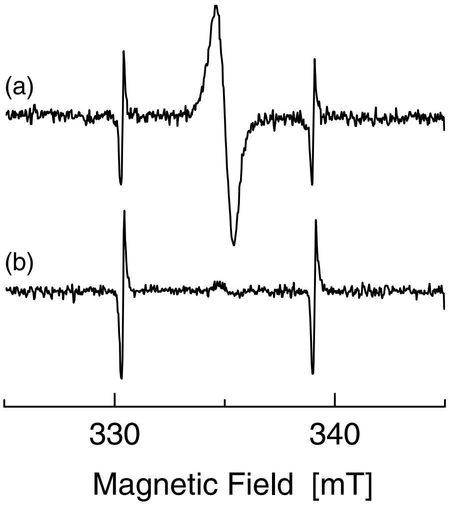

Figure 8. ESR spectra obtained for sample E annealed at 900 °C. (a) Before the hydrogen treatment. (b) After the hydrogen treatment.

should similarly decrease for samples C to E. Since the PL intensity decreases on annealing at temperatures above 500 °C for samples D and E, it is considered that $k_{NR(T)}$ increases on annealing, resulting in an increase in k_{NR}.

Next, the thermally induced process of Si–DBs is discussed. Figure 6 shows IR spectra observed in the unannealed samples A to E. The absorption due to N–H bonds at 3340 cm^{-1} is similar in all the samples. That due to Si–H bonds at 2150–2250 cm^{-1} observed in samples D and E is composed of two absorption bands centred at 2150 cm^{-1} and 2240 cm^{-1}. It has been reported that the absorption peak due to Si–H bonds depends on the nearest neighbouring

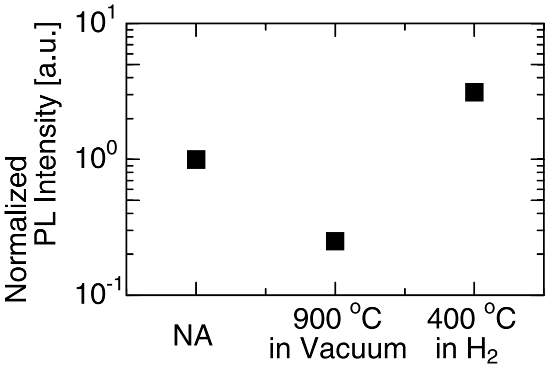

Figure 9. Change in the normalized PL intensity for sample E induced by thermal treatment and the following hydrogen treatment. NA: not annealed.

atoms, and that it is around 2250 cm^{-1}, 2150 cm^{-1} and 2000 cm^{-1} in SiO_2, Si_3N_4 and in a-Si:H, respectively [22, 23]. As shown in figure 6, only samples D and E have the absorption peak at 2150 cm^{-1}. This absorption at 2150 cm^{-1} characteristic of samples D and E decreases on annealing and almost diminishes at temperatures above 800 °C. This fact indicates that the precursor of thermally induced Si–DBs observed only in samples D and E is the Si–H bond present near Si–N bonds. If Si–DBs are induced near Si–N bonds, the probability of nitrogen and silicon being present as the nearest neighbouring atoms to Si should increase. This is demonstrated in table 2. As mentioned above, the present PL is due to Si–N bonds. If Si–DBs are induced near Si–N bonds by the hydrogen release from Si–H bonds, the PL will be quenched. This is exactly what we have observed for samples D and E in figures 3 and 5. Figure 7 shows the Si–H density calculated from the IR absorption intensity and the normalized PL intensity for samples D and E, each as a function of the density of paramagnetic centres. This strongly indicates that the Si–DBs thermally induced near Si–N bonds by the hydrogen release quench the PL.

In order to confirm that the hydrogen release really induces paramagnetic defects, the reverse reaction was examined. Sample E annealed at 900 °C was kept in hydrogen at 400 °C and at 10^6 Pa for 24 h. Figure 8 shows the ESR spectra obtained for sample E annealed at 900 °C before and after the hydrogen treatment. The thermally induced Si–DBs clearly disappeared on hydrogen treatment. Figure 9 shows the change in the normalized PL intensity for sample E induced by the hydrogen treatment. The PL intensity changes in a manner exactly opposite to that of the density of Si–DBs. It is concluded that Si–DBs near Si–N bonds induced by hydrogen release from Si–H bonds act as quenching centres for the 2.2–2.9 eV PL in a-SiO_xN_y:H.

4. Conclusion

The effect of thermal annealing on the photoluminescence around 2.2–2.9 eV in hydrogenated amorphous silicon oxynitride films was investigated. The density of silicon dangling bonds depends on the annealing temperature in a manner opposite to that of the luminescence intensity in the entire annealing temperature region from room temperature (= not annealed) to 900 °C. Based on this correlation, it is considered that the silicon dangling bonds act as the quenching centre for the luminescence. Infrared absorption spectroscopy indicated that the precursor of silicon dangling bonds was the Si–H bond present near Si–N bonds. Hydrogen was released at temperatures above 500 °C from Si–H bonds, resulting in a large number of silicon dangling bonds that quench the luminescence.

Acknowledgments

This work was partly supported by the 2000 Joint Studies Program of the UVSOR Facility, Institute for Molecular Science, Okazai, Japan, by a Grant-in-Aid for JSPS Fellows and by a Grant-in-Aid (No 12450132) for Scientific Research and a High-Tech Research Grant from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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