OPTICAL AND ELECTRICAL PROPERTIES OF STRUCTURAL DEFECTS IN AMORPHOUS SILICON OXYNITRIDE AND SILICON NITRIDE FILMS

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Chapter 1

Introduction

1.1. OBJECTIVE

With the rapid and continuing progress of optical communication technologies, the data storage capacity and processing speed of very-large-scale integrated (VLSI) circuits are expected to be improved even more.\textsuperscript{1} In addition, much attention is paid to functional optical waveguide devices such as a wavelength selection mirror, a dispersion eliminator, and an optical amplifier.\textsuperscript{2-4} Hydrogenated amorphous silicon oxynitride ($a$-SiO$_x$N$_y$:H) and hydrogenated amorphous silicon nitride ($a$-SiN$_z$:H) have possibilities of realizing excellent insulating properties and optical transmittance because of their wide forbidden gaps. Therefore, $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H films have been receiving considerable attention not only as suitable isolators for electronic devices,\textsuperscript{1,5-10} but also as optical materials for optical fibers\textsuperscript{11-13} and waveguides.\textsuperscript{14-16}

For electronic devices, structural defects and localized states in their dielectric layers may degrade their insulating properties, leading to a lower device performance. On the other hand, for optical waveguides, structural
defects induced by ultraviolet photon irradiation\textsuperscript{2,17-19}, ion implantation\textsuperscript{20-22} and by other measures are used to implement suitable functions. From these two viewpoints, detailed information on the structures and generation mechanisms of these defects is necessary for the development of optoelectronic devices with a higher reliability.

The purpose of this thesis is to clarify optical and electrical properties of structural defects in a series of $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H films with different nitrogen contents deposited by plasma-enhanced chemical vapor deposition. The emphasis is placed on (i) identification of preexisting structural defects and thermally- or radiation-induced structural defects, (ii) characterization of localized band-tail states due to the structural disorder, and (iii) establishment of the link between these states and photoluminescence (PL), electroluminescence (EL), and electrical conduction properties.

The outline of the present thesis is as follows. In Sections 1.2 to 1.5 of this chapter, previous studies relevant to this thesis will be reviewed. In Chapter 2, characterization of localized band-tail states and clarification of relaxation processes of photogenerated carriers are carried out by comparing PL properties between $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H films. The localized band-tail
states are found to be associated with Si–N bonds, in which the carriers recombine first through an exciton-like recombination process and then through a radiative tunneling recombination process. In Chapter 3, the effects of thermal annealing on the band-tail PL intensity and the density of paramagnetic defects in $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H films are investigated. It is found that silicon dangling bonds thermally induced near Si–N bonds by hydrogen release act as a quenching center for the PL. In Chapter 4, electrical conduction at high fields is studied on a series of $a$-$\text{SiO}_x\text{N}_y$:H or $a$-$\text{SiN}_z$:H films. Carriers in the two materials are shown to be transported similarly through Poole-Frenkel sites associated with Si–N bonds. In Chapter 5, the mechanism of EL in $a$-$\text{SiO}_x\text{N}_y$:H films is investigated. The EL is attributable to recombination between the localized band-tail states, supporting the results described in Chapters 2 and 4. In Chapter 6, the refractive index change of $a$-$\text{SiO}_x\text{N}_y$:H is shown to increase by irradiation of ultraviolet photons. It is also shown that the index increase is due mainly to densification, and that the contribution of the formation of paramagnetic defects is only slight. Finally in Chapter 7, important results obtained in this thesis are summarized.
Chapter 1

1.2. PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION

Plasma-enhanced chemical vapor deposition (PECVD) is an important technique for depositing a variety of thin films at a low temperature. For example, silicon dioxide (SiO$_2$) films can be deposited at 300 to 400 °C, while conventional thermal-CVD methods generally require temperatures in the range of 600 to 800 °C to produce films of a similar quality. For PECVD, an rf power of 13.56 MHz is frequently used to generate a glow discharge plasma, in which the energy is transferred into a gas mixture. At a low pressure, the plasma is thermally non-equilibrium and the component species of the plasma, namely electrons, ions, and gas particles have their respective temperatures, $T_e$, $T_i$, and $T_g$, where $T_e \gg T_i \approx T_g \approx$ room temperature.$^{23}$ Typical energy values of particles present in a glow discharge and those of some chemical bonds are listed in Table 1-1.$^{23,24}$ Since the electron energy is much higher than most bond energies, chemical reactions in the deposition process is caused by collision of such hot-electrons. The substrate temperature remains low, since the temperatures of the gas molecules and ions, whose abundance is much higher than electrons, are very low. Consequently, films can be synthesized on a substrate at a much lower temperature by PECVD than by the conventional
CVD process. This is a major advantage of PECVD. In general, films synthesized by PECVD have desirable properties such as good adhesion, low pinhole density, good step coverage, and good uniformity.\(^{25-28}\) Nowadays, PECVD systems are widely used in electronics and photonics industries to deposit SiO\(_2\), diamond-like carbon (DLC), amorphous silicon (a-Si:H), poly-silicon (poly-Si), and many other thin films.

1.3. ELECTRONIC STRUCTURE

In crystalline Si, Si atoms are \(sp^3\) hybridized and form four bonds with adjacent Si atoms. The occupied Si–Si bonding states form the valence band and the empty Si–Si antibonding states form the conduction band, giving a gap energy of 1.1 eV. In SiO\(_2\), Si is again fourfold \(sp^3\) coordinated and O is twofold coordinated with a bond angle of \(\sim 144^\circ\).\(^{29,30}\) Oxygen O, a group VI element, has a \(s^2p^x^1p^y^1p^z^2\) configuration. The \(s^2\) electrons form a deep-laying lone-pair (non-bonding) state, while the \(p_x\) and \(p_y\) states each form Si–O bonds and the \(p_z^2\) electrons form a \(p\pi\) lone pair which lies at the top of the valence band. The gap energy of SiO\(_2\) is 9.0 eV and the Si–O bonds are \(\sim 50\%\) ionic. The electronic structure of SiO\(_2\) is typical of a lone-pair solid in which the \(p\pi\) states
form the upper valence band and the Si–Si antibonding states form the conduction band. Silicon nitride $\text{Si}_3\text{N}_4$ is also a lone-pair solid. Nitrogen $\text{N}$ is a group V element with an $s^2p^3$ configuration. It bonds by forming three $sp^2$ hybrids which form the Si–N bonds and a $p_z$ state which forms a $p\pi$ lone pair oriented normal to the Si–N bonding plane with states lying at the top of the valence band. The band gap is 5.3 eV and the Si–N bond is about 30 % ionic.$^{31-33}$

G. Lucovsky and S. Y. Lin theoretically calculated the local density of states for O impurity atoms in $\text{Si}_3\text{N}_4$ ($\text{Si}_3\text{N}_4$:O) and N impurity atoms in $\text{SiO}_2$ ($\text{SiO}_2$:N).$^{34}$ These are shown, respectively, in Figs. 1-1 and 1-2 for situations in which all valence bonding requirements are satisfied by the Si, O, and N atoms. The most important manifestations of O impurity atoms in $\text{Si}_3\text{N}_4$:O subject to this restriction, are (a) changes in the character of valence band states of the Si and N atoms that are, respectively, the nearest and next nearest neighbors to the O impurity, and (b) a band of O non-bonding $2p$ states just below the top of the valence band edge. The band of O non-bonding $2p$ states and an associated band of modified N non-bonding $2p$ states are then the only bands of new states that are potentially active in electronic transport and trapping phenomena. The
character of the valence band states for a N impurity in SiO₂:N is qualitatively similar. However, in this case, the N non-bonding 2p band lies above the highest O nonbonding 2p states of the SiO₂ host, and in this context it may be even more active than the corresponding O 2p states in Si₃N₄:O, either as trapping centers, or as a band of states for hole conduction.

1.4. DEFECTS AND THEIR ELECTRONIC STATES IN AMORPHOUS MATERIALS

The first question to address is the definition of a defect in an amorphous material. In a crystal, any departure from the perfect crystalline lattice is a defect, which could be a point defect such as a vacancy or interstitial, an extended defect such as a dislocation or stacking fault, or an impurity. A different definition is required in an amorphous material because there is no perfect lattice. The inevitable disorder of the random network is an integral part of the amorphous material and it is not helpful to think of this as a collection of many defects. By analogy with the crystal, a defect can be defined as a departure from the ideal continuous random network in which all the bonds are satisfied.³⁵
This approach immediately leads to the idea of a coordination defect in which an atom has a distinctly different bonding state from the ideal. All the electrons in the ideal network are paired in bonding or non-bonding states. However, if the local coordination of an atom is one greater or less than the ideal, then the neutral state of the atom has an unpaired electron. The addition of an electron results in paired electrons but a net charge. This type of defect therefore has the distinguishing characteristic of either a paramagnetic spin or an electronic charge, which sets it apart from the electronic states of the ideal network. The threefold coordinated silicon dangling bond is one example.

Other types of defects are possible in an amorphous network, but have less well-defined characters. For example, a hydrogenated void in $a$-Si:H is certainly a defect in the sense that it has a local structure different from the rest of the amorphous network. However, from the atomic coordination point of view, it is difficult to distinguish a void from the ideal network. If the atoms around the void have a similar distribution of bonding disorder, then the electronic states probably fall within the ensemble of bulk states and are indistinguishable from those of the bulk. Localized states of particularly large binding energy may result when the local disorder is greater than in the ideal
network. Unlike the coordination defect, this difference is quantitative rather than qualitative.

In one respect, the defects of an amorphous solid are easier to deal with than those of a crystal. Any small deviation in the local structure of the defect in a crystal results in a different state, resulting in many possible defect structures. In an amorphous material, small differences in local structure which fall within the disorder of the ideal network cannot be resolved meaningfully. Thus, fewer separate classes of defects are expected, but with their energy levels broadened out by the disorder, as illustrated schematically in Fig. 1-3.\textsuperscript{35}

Features of the two typical defects that are characteristic of and frequently observed in an amorphous material are further reviewed in the following Sections 1.4.1 and 1.4.2.

1.4.1.  Band-tail states

The three principal features of the structure of amorphous materials are the short-range order of the ideal network, the long-range disorder, and the coordination defects. The preservation of the short-range order results in a similar overall electronic structure of an amorphous material compared to the
equivalent crystal. Thus, SiO$_2$ is an insulator in both its crystalline and amorphous forms. As shown in Fig. 1-3, the abrupt band edges of a crystal are replaced by a broadened tail of states extending into the forbidden gap, which originates from the deviations of the bond length and angle arising from the long-range structural disorder. The band tails are most important despite their relatively small concentration, since electronic transport occurs at the band edge.

The optical absorption in the vicinity of the band gap, i.e., the absorption due to the band-tail states, has an exponential energy dependence\textsuperscript{35-37}

$$\alpha(h\nu) = \alpha_0 \exp\left[\frac{(h\nu - E_{\text{edge}})}{E_U}\right],$$

where $\alpha$, $h\nu$, and $E_{\text{edge}}$ are the absorption coefficient, the photon energy, and the onset photon energy, respectively. The energy $E_U$ indicates the width of the band-tail states and reflects the degree of the structural disorder. The exponential tail is called the Urbach edge after its first observation in alkali halide crystals by F. Urbach in 1953 (see Fig. 1-4\textsuperscript{37}). It is then found in $a$-Si:H, its alloys, and other amorphous materials. In $a$-SiN$_x$:H alloys\textsuperscript{38,39} it has been reported that the value of $E_U$ increases from $\sim$50 to $\sim$190 meV with an increase in nitrogen content as shown in Fig. 1-5.\textsuperscript{38} This nitrogen alloying effect is primarily ascribed to the increase in the degree of structural disorder caused by
the extension of the Si–Si bond length due to the increased number of incorporated nitrogen atoms. The average bond angle variation, which is measured from the width of the vibrational spectrum using Raman spectroscopy, can be a measure of the degree of disorder. Figure 1-6 shows an increasing $E_U$ with bonding disorder in $a$-Si:H, which is caused by changes in the deposition condition and composition.

Another way to identify the band-tail states is PL analysis. There have been several reports on PL phenomena in $a$-Si:H, $a$-SiN$_x$:H, and hydrogenated amorphous silicon carbide ($a$-SiC$_x$:H). By doing time-resolved PL analysis and by examining PL dependencies on defect density and temperature, the natures of band-tail states have become clear. Time-resolved PL spectra in $a$-Si:H shown in Fig. 1-7, obtained by C. Tsang and R. A. Street, exhibit a shift of ~0.15 eV to a lower energy side over the investigated time scale from $10^{-8}$ to $10^{-2}$ s. The shift of ~0.15 eV is due to a distribution in the zero-phonon recombination, and is thought to originate from the band tailing. F. Giorgi and his coworkers have presented band-tail PL data for $a$-SiN$_x$:H in a wide compositional range ($0.17 \leq x \leq 1.08$), and have shown that the nitrogen incorporation yields a widening of the tail states due to
static disorder. The temperature quenching of the PL intensity is weakened by
the alloying, which is consistent with a widening of the tail states and an
increasing Coulombic pair interaction. A similar result is also reported in
\( a\)-SiC\(_x\):H (0 \( \leq \) x \( \leq \) 0.66) by L. R. Tessler and I. Solomon.\(^{51}\)

### 1.4.2. Paramagnetic defects

The paramagnetic defects have been extensively investigated by electron
spin resonance (ESR). Figure 1-8 shows the ESR spectra of two typical
dangling bonds (DBs), the \( K \) and \( N \) centers, observed in \( a\)-SiN\(_x\):H and their
coordination structures.\(^{53}\) The Si–DBs observed in \( a\)-Si:H and its alloys are
assigned to \( \equiv\text{Si} \cdot \), an unpaired electron highly localized in an \( sp \)-hybrid orbital of
the silicon atom bonded to three other atoms. As shown in Fig. 1-9,\(^{54}\) the
difference in the nearest neighboring atoms in Si–DBs is reflected to the
difference in the \( g \) value and the difference in magnetic field \( \Delta H \) at the signal
maximum and minimum. For example, the \( E' \) center (O\(_3\)=Si\( \cdot \)) has \( g \) value =
\( \sim 2.0010 \) and \( \Delta H = \sim 0.28 \) mT,\(^{54,55-58}\) the \( K \) center (N\(_3\)=Si\( \cdot \)) has \( g \) value = \( \sim 2.0030 \)
and \( \Delta H = \sim 1.25 \) mT,\(^{54,59-65}\) and the \( P_b \) center (also called the \( D \) center, Si\(_3\)=Si\( \cdot \))
has \( g \) value = \( \sim 2.0055 \) and \( \Delta H = \sim 0.75 \) mT.\(^{54,63-68}\)
With an advance of study on the generation mechanisms of these centers, several variants have been proposed. In $a$-SiO$_2$, the $E^\prime$ center is believed to be induced by a capture of hole in a neutral oxygen vacancy ($O_3\equiv Si\equiv Si\equiv O_3$) through the following reaction.

$$O_3\equiv Si\equiv Si\equiv O_3 \rightarrow O_3\equiv Si\cdot + ^+Si\equiv O_3 + e^-$$ \hspace{1cm} (1-2)

Here, $^+Si\equiv O_3$ is considered to have a planar structure. In this model, the oxygen vacancy is a hole trap and the electron generated by eq. (1-2) acts as a mobile carrier, while the remaining $^+Si\equiv O_3$ becomes a fixed charge. A similar reaction occurs at a neutral nitrogen vacancy ($N_3\equiv Si\equiv Si\equiv N_3$) in $a$-SiN$_x$:H, resulting in the $K$ center.

In the case of the interface between the Si cluster and $a$-Si$_3$N$_4$ bulk, three kinds of bonding situations shown in Fig. 1-10 are suggested by Y. Kamigaki and his coworkers: (A) $Si_3\equiv Si\equiv Si\equiv N_3$, weak covalent bond, (B) $Si_3\equiv Si\cdot$ and $N_3\equiv Si\cdot$, relaxed bond, and (C) $Si_3\equiv Si^+$ and $N_3\equiv Si^-$, split bond. The state of (B) $Si_3\equiv Si\cdot$ and $N_3\equiv Si\cdot$ can be observed by the ESR measurement. As shown in Fig. 1-10, whichever defect (A), (B), and (C) at the interface of the Si cluster captures an electron, Si dangling bonds will become $Si_3\equiv Si\cdot$ and $N_3\equiv Si^\cdot$. Similarly, whichever defect captures a hole, Si dangling bonds will become
Si\equiv\text{Si}^+ \text{ and } N_3\equiv\text{Si}. \text{ These capture mechanisms are applied to metal-nitride-oxide-semiconductor (MNOS) nonvolatile memory devices.}^{63,70,71}

The behavior of hydrogen is also related to the paramagnetic defects. It is believed that the mobility of hydrogen within the amorphous network facilitates the interconversion of defects and weak bonding configurations, without the need for large scale rearrangements of the network.\textsuperscript{35,62,72,73} By annealing above 500 °C or irradiation of ultraviolet photons, hydrogen is released from the material, and the DBs are created. In the SiO\textsubscript{2}/Si(100) interface, the $P_b$ center is generated not only by the lattice mismatch,\textsuperscript{74,75} but also by the hydrogen release through the following reaction:\textsuperscript{66,67}

\[
\text{Si}_3\equiv\text{Si} - \text{H} + (\text{annealing above } 500 \text{ °C}) \rightarrow \text{Si}_3\equiv\text{Si} - \cdot + \text{H} \quad (1-3)
\]

In a study on $a$-SiN$_x$:H by J. Robertson,\textsuperscript{62,72,73} the processes of H diffusion are explained on a diagram of the hydrogen density of states shown in Fig. 1-11. The most stable position of hydrogen in $a$-Si:H is the Si–H bond, whereas that in $a$-SiN$_x$:H alloys is the N–H bond. Therefore, N–DBs (Si$_2=\text{N}^-$) formed by annealing or irradiation are immediately terminated by hydrogen released from Si–H bonds through the following reaction:

\[
N_3\equiv\text{Si} - \text{H} + \text{Si}_2=\text{N}^- \rightarrow N_3\equiv\text{Si} - \cdot + \text{Si}_2=\text{N}^- - \text{H}. \quad (1-4)
\]
This is one of the formation processes of the $K$ center, related to the hydrogen behavior, in $a$-$SiN_x$:H alloys.

1.5. OTHER IMPORTANT REPORTS

The current density – electric field relations for the different conduction mechanisms identified in $Si_3N_4$, Ta$_2$O$_5$, SiO$_2$, SiO$_x$N$_y$, Ta$_2$O$_5$/SiO$_2$ and Ta$_2$O$_5$/Si$_3$N$_4$, and future gate dielectrics (thickness < 2 nm) are summarized in Tables 1-2 and 1-3, where $J$ denotes the current density, $E$ the electric field, $C_1$, $C_2$, and $C_3$ are constants, $q$ is the electronic charge, $k_B$ denotes the Boltzmann constant, $T$ is the absolute temperature, $m^*$ represents the effective mass of carriers in the insulator considered, $h$ is Planck’s constant, $\varepsilon_0$ denotes the permittivity of free space, and $\varepsilon_{in}$ is the high frequency dielectric constant.

Current densities $J_{EH}$, $J_{FE}$, and $J_{PF}$ described in Table 1-2 are bulk limited, i.e., the mechanism for current flow is controlled by the defects existing in the bulk of the insulator. Current density $J_{EH}$ corresponds to the electronic hopping conduction mechanism and is attributed to jump of thermally excited electrons from one isolated state to another. This process gives an ohmic $I$-$V$
characteristic, which is exponentially dependent on temperature with a thermal activation energy $\phi_a$. Current density $J_{FE}$ is called field emission\cite{78,79} and corresponds to tunneling of trapped electrons into the conduction band. The energy $\phi_t$ is shown in Fig. 1-12 and is the barrier separating traps from the conduction band. Current density $J_{PF}$ describes the Poole-Frenkel effect shown in Fig. 1-12, which results from the lowering of the Coulombic potential barrier of traps under an applied electric field\cite{76-83}. This mechanism is based on the emission of trapped electrons towards the conduction band with the barrier height $\phi_t$. A coefficient $r$ is introduced in the expression of the Poole-Frenkel effect, taking into account the influence of the trapping or acceptor centers ($1 \leq r \leq 2$).

Current densities $J_{FN}$, $J_D$, and $J_{DB}$ described in Table 1-3 represent tunneling mechanisms, and the type of the current depends on the shape of the barrier the electrons must cross (see Fig. 1-13). Here, current density $J_{FN}$ represents a Fowler-Nordheim tunneling current (triangular barrier)\cite{78,85-87}, $J_D$ a direct tunneling current (trapezoidal barrier)\cite{90-92}, and $J_{DB}$ is due to a double tunneling mechanism (double barrier: the energy barrier extends into the second dielectric)\cite{84,88,89}. In these expressions, $\phi$ represents the barrier height between
the injecting electrode and the first dielectric material, \( d \) the first insulator thickness, \( E' \) and \( m'^* \) the electric field and the effective mass in the second dielectric, \( \phi' \) the barrier height at the interface between the two dielectrics. The Fowler-Nordheim tunneling occurs when \( \phi < qdE \), the direct tunneling when \( (\phi - \phi') < qdE < \phi \), and the double tunneling mechanism when \( qdE < (\phi - \phi') \).\textsuperscript{88,89}
Chapter 1

References for Chapter 1


37 F. Urbach, Phys. Rev. 92, 1324 (1953).


TABLE 1-1. Typical energy values of particles present in a glow discharge and those of some chemical bonds. (after Refs. 23 and 24)

<table>
<thead>
<tr>
<th>Particle or Bond</th>
<th>Energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle in a Glow Discharge:</strong></td>
<td></td>
</tr>
<tr>
<td>Electron</td>
<td>1-7</td>
</tr>
<tr>
<td>Gas Molecule</td>
<td>~3 x 10^{-2}</td>
</tr>
<tr>
<td>Ion</td>
<td>~3 x 10^{-2}</td>
</tr>
<tr>
<td><strong>Chemical Bond:</strong></td>
<td></td>
</tr>
<tr>
<td>Si-Si</td>
<td>3.4</td>
</tr>
<tr>
<td>Si-O</td>
<td>8.2</td>
</tr>
<tr>
<td>Si-N</td>
<td>4.8</td>
</tr>
<tr>
<td>Si-H</td>
<td>3.1</td>
</tr>
<tr>
<td>Si-F</td>
<td>5.7</td>
</tr>
<tr>
<td>Ge-Ge</td>
<td>2.7</td>
</tr>
<tr>
<td>Ge-O</td>
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</tr>
<tr>
<td>O-O</td>
<td>5.1</td>
</tr>
<tr>
<td>N-N</td>
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<tr>
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</tr>
<tr>
<td>O-H</td>
<td>4.4</td>
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<tr>
<td>N-H</td>
<td>3.5</td>
</tr>
<tr>
<td>C-C</td>
<td>6.3</td>
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<tr>
<td>C-N</td>
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<tr>
<td>C-H</td>
<td>3.5</td>
</tr>
<tr>
<td>C-F</td>
<td>5.7</td>
</tr>
</tbody>
</table>
### Table 1-2. Theoretical expressions of the trap-assisted conduction mechanisms.

<table>
<thead>
<tr>
<th>Trap-assisted conduction mechanisms</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic hopping conduction:</td>
<td>$J_{EH} = C_1 E \exp \left( - \frac{\phi_a}{k_B T} \right)$</td>
</tr>
<tr>
<td>Field assisted emission:</td>
<td>$J_{FE} = C_2 E^2 \exp \left( - \frac{8\pi \sqrt{2m^* \phi_i^3}}{3q\hbar E} \right)$</td>
</tr>
<tr>
<td>Poole-Frenkel effect:</td>
<td>$J_{PF} = C_3 E \exp \left( - \frac{1}{k_B T} \left( \phi_i - \frac{1}{r} \sqrt{\frac{q^3 E}{\pi \epsilon_0 \epsilon_m}} \right) \right)$</td>
</tr>
</tbody>
</table>
TABLE 1-3. Theoretical expressions of the tunneling conduction mechanisms.

<table>
<thead>
<tr>
<th>Tunneling mechanisms</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fowler-Nordheim tunneling:</td>
<td>$J_{FN} = \frac{q^3 E^2}{8\pi \hbar \phi} \exp \left(- \frac{8\pi \sqrt{2m^* \phi^3}}{3hE} \right)$</td>
</tr>
<tr>
<td>Direct tunneling:</td>
<td>$J_D = \frac{q^3 E^2}{8\pi \hbar \phi} \exp \left(- \frac{8\pi \sqrt{2m^* \phi^3}}{3hE} \right) \left(1 - \left(1 - \frac{qdE}{\phi} \right)^{3/2} \right)$</td>
</tr>
<tr>
<td>Double barrier tunneling:</td>
<td>$J_{DB} = \frac{q^3 E^2}{8\pi \hbar \phi} \exp \left(- \frac{8\pi \sqrt{2m^* \phi^3}}{3hE} \right) \left(1 - \left(1 - \frac{qdE}{\phi} \right)^{3/2} \right) + \frac{\sqrt{m^*}}{E'} \left(\phi - \phi' - qdE \right)^{3/2}$</td>
</tr>
</tbody>
</table>
FIG. 1-1. (a) Average density of states for Si$_3$N$_4$ Bethe Lattice. (b) Average density of states for Si$_3$N$_4$ cluster with one oxygen atom (Si$_3$N$_4$:O). Local density of states functions for (c) oxygen alloy atom, (d) silicon host atom, and (e) nitrogen host atom. (after Ref. 34)
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Band-tail photoluminescence in hydrogenated amorphous silicon oxynitride and silicon nitride films

ABSTRACT

Photoluminescence (PL) measurements were performed on a series of hydrogenated amorphous silicon oxynitride and silicon nitride films with different nitrogen contents deposited by plasma-enhanced chemical vapor deposition. From the PL and PL excitation spectra, the Urbach energy of the sample is found to be proportional to its PL half-maximum width, regardless of whether the sample is silicon oxynitride or silicon nitride. Time-resolved PL measurements showed that PL peak energy varies with time after the excitation, showing a systematic dependence on the chemical composition in the two materials. That the PLs observed in the two materials have very similar characteristics regardless of the presence of oxygen strongly indicates that the PLs result from the same chemical structure, more specifically Si–N bonds, and that the two materials have similar band-tail states associated with the static disorder. In the two materials, it is found that the electrons and holes
photoexcited into such band-tail states recombine first through an exciton-like recombination process and then through a radiative tunneling recombination process.
2.1. INTRODUCTION

Hydrogenated amorphous silicon oxynitride (a-SiO$_x$N$_y$:H) and silicon nitride (a-SiN$_z$:H) have been receiving considerable attention not only as suitable isolators for electronic devices such as very-large-scale integrated circuits,\textsuperscript{1-4} but also as optical materials for waveguides,\textsuperscript{5,6} light emitting devices,\textsuperscript{7} and solar cells.\textsuperscript{8,9} With the rapid and continuing progress of technologies in electronics and photonics, the importance of these amorphous materials is continually increasing. Unfortunately, these films are known to contain many defects and localized states that deteriorate the device performance, especially when they are prepared by plasma-enhanced chemical vapor deposition (PECVD). From this point of view, the defects and structural disorder in the two materials have been studied by analyzing their photoluminescence (PL) properties.\textsuperscript{10-15} However, detailed properties such as the decay process and the effect of chemical composition are unknown. In this chapter, the band-tail PL in a-SiO$_x$N$_y$:H is examined by comparing its PL spectral shape, width of band-tail states, and PL lifetime distribution with those of the PL in a-SiN$_z$:H.

2.2. EXPERIMENT
The \( a\text{-SiO}_x\text{N}_y\text{:H} \) films were deposited using a dual-frequency PECVD system. A mixture of \( \text{SiH}_4 \), \( \text{N}_2\text{O} \), and \( \text{N}_2 \) gases was excited in a parallel-plate reactor where a rf power of 13.56 MHz was supplied with a maximum power of 0.54 kW. At the same time, a lower-frequency power of 400 kHz was also supplied with a maximum power of 0.38 kW to reduce the structural stress of the deposited film. Three types of films with different atomic ratios were prepared by changing the flow ratio of \( \text{SiH}_4 \) to the sum of the other two gases, while the total pressure was kept constant around \( 2.4\times10^2 \) Pa. The films were deposited onto a \( p \)-type (100) silicon monocrystal substrate set on a stage whose temperature was kept constant at 400 °C. Three types of \( a\text{-SiN}_z\text{:H} \) films were similarly deposited using a mixture of \( \text{SiH}_4 \), \( \text{N}_2 \), and \( \text{NH}_3 \) gases. The elemental compositions of Si, O, and N were estimated through x-ray photoelectron spectroscopy (XPS, JEOL JPS-90MX). The refractive index was measured by ellipsometry (ULVAC ESM-1) at a wavelength of 632.8 nm with a He–Ne laser.

In order to obtain PL spectra, two photon sources were used. One is synchrotron radiation (SR) under multibunch operation at the BL1B line of UVSOR Facility (Institute for Molecular Science, Okazaki, Japan) and the other is a KrF excimer laser (wavelength: 248 nm = 5.0 eV, pulse width: \( \sim\)25 ns, pulse
energy: ~100 mJ/cm$^2$, Lambda Physik Compex 205). The spectra were measured using a monochromator equipped with an intensified charge-coupled device (ICCD) array. As for PL excitation (PLE) spectra, the SR photons under multibunch were used. The photon energy to be detected was fixed at the PL peak energy using an interference filter (transmittance: ~40%, full width at half maximum: ~15 nm) and the intensity of detected photons was monitored by a photomultiplier (Hamamatsu R955) as a function of the excitation SR photon energy.

Nanosecond-order PL decay characteristics were measured using the SR photons under single-bunch operation (time interval of SR pulses: 177.6 ns, apparent pulse width: 550 ps). The number of photons with energies around the PL peak through the interference filter was counted by a microchannel-plate photomultiplier (Hamamatsu R3809U-52) with a time-correlated single-photon counting technique. Time-resolved PL spectra were measured using the excimer laser and a monochromator equipped with an intensified charge-coupled device (ICCD) array. The ICCD array was gated by a pulse generator connected to a delay circuit, and the delay time between the laser pulse and the gate-on pulse was monitored with an oscilloscope. The gate-on duration or the
PL observation period was adjusted from 50 ns to 4 µs so that clear PL spectra could be obtained.

2.3. RESULTS

The elemental compositions of all the $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H films have been determined by XPS as shown in Table 2-1. For $a$-$\text{SiO}_x\text{N}_y$:H films (samples D to F), the nitrogen and the silicon contents increase with an increase in the gas flow ratio of $\text{SiH}_4$ to the sum of the other two gases [$\text{SiH}_4/(\text{N}_2\text{O} + \text{N}_2)$]. The silicon content increases for $a$-$\text{SiN}_z$:H films (samples G to I) with a similar increase in the gas flow ratio of $\text{SiH}_4$ to the other two gases. If the apparent chemical composition of $a$-$\text{SiO}_x\text{N}_y$:H is expressed by the relation, $1/2x(\text{SiO}_2)+1/4y(\text{Si}_3\text{N}_4)$, the value $(1/2)x+(3/4)y$ becomes unity. The value becomes less than unity if silicon is present in surplus as compared to the above equation. Namely, the value can be regarded as an abundance ratio of atoms other than silicon to silicon atoms. For the sake of simplicity, the value is called the abundance ratio. The ratio deviates from unity in the order from sample D to F, indicating that silicon is the least abundant in sample D and the most abundant in sample F. For $a$-$\text{SiN}_z$:H, the value $(3/4)z$ is the abundance
ratio, which indicates that samples G and I are the least and the most abundant in silicon, respectively.

Figure 2-1 shows typical PL spectra in $a$-$SiO_{x}N_{y}$:H and $a$-$SiN_{z}$:H films observed at 10 K and their PLE spectra monitored at respective PL peak energies. A Gaussian-shaped broad PL band is observed in all the samples. The following three systematic trends can be observed as the abundance ratio increases regardless of whether the sample is $a$-$SiO_{x}N_{y}$:H or $a$-$SiN_{z}$:H.

(i) The PL spectrum shifts toward a higher energy.

(ii) It becomes broader.

(iii) The PLE threshold energy shifts toward a higher energy.

These trends are in agreement with the finding by other authors for $a$-$SiN_{x}$:H$^{16-18}$ and amorphous silicon carbide ($a$-$SiC_{x}$:H)$^{19,20}$ It is considered that the PLs shown in Fig. 2-1 are essentially identical and are due to radiative recombination within the localized states at the band-tail.$^{10-15}$

The objective of the present research is to elucidate various aspects of this band-tail PL. Appearance of similar PL has been often reported for various amorphous materials such as $a$-$SiN_{x}$:H, $a$-$SiC_{x}$:H, and amorphous silicon ($a$-$Si$:H).$^{16-23}$
If the PL is related to band-tail states, the Urbach edge energy $E_{\text{edge}}$ and the Urbach energy $E_U$ can be estimated from the onset portion of the PLE spectrum. Generally, $E_{\text{edge}}$ and $E_U$ are defined by the following equation:

$$\alpha(h\nu) = \alpha_0 \exp \left[ \frac{(h\nu - E_{\text{edge}})}{E_U} \right],$$

(2-1)

where $\alpha$ and $h\nu$ are the absorption coefficient and the photon energy, respectively. In PL excitation studies on $a$-$\text{SiN}_x$:$\text{H}$ alloys by W. A. Jackson et al.\textsuperscript{17} and on $a$-$\text{Si}$:$\text{H}$ and its alloys by T. M. Searle and W. A. Jackson,\textsuperscript{21} the PLE spectrum was used instead of $\alpha(h\nu)$ on the assumption that the low-energy side of an excitation spectrum is proportional to $\alpha$. Therefore, the PLE spectrum is also used instead of $\alpha(h\nu)$ in the present band-tail analysis. Figure 2-2 shows thus calculated $E_{\text{edge}}$ and $E_U$. As the silicon abundance becomes less, $E_{\text{edge}}$ and $E_U$ increase monotonically in both cases of $a$-$\text{SiO}_x\text{N}_y$:$\text{H}$ and $a$-$\text{SiN}_z$:$\text{H}$.

Figure 2-3 shows the normalized PL intensity as a function of the measurement temperature in the range of 10–300 K observed in samples E and H. The temperature dependence of the PL peak energy and that of the full width at half maximum (FWHM) of the PL band are shown in Fig. 2-4. The PL intensity decreases by an order of magnitude with an increase in the temperature, while the PL peak energy and the PL FWHM are almost
independent. We have confirmed that almost the same dependence is observed in all the other samples.

To analyze the recombination processes of the photogenerated carriers, time-resolved PL measurements have been performed at room temperature. Figure 2-5 shows typical time-resolved PL spectra measured in samples E and G. Curve (i) is the spectrum obtained by measuring over the whole time region of 0.1 s without any delay. Curves (ii) to (vi) correspond to the spectra measured during given periods after the laser excitation. Furthermore, curve (i*) is the spectrum obtained by subtracting the curve (ii) from the curve (i). The PL peak energies were determined by fitting the PL spectra to Gaussian curves. A shift of the PL peak as a function of the delay time was observed, i.e., first to red, then to blue, and back to red again. Note that similar peak shifts were observed in all the samples.

Figure 2-6 shows the details of the shift as a function of time after excitation. The ordinate is the difference in the peak energy between each spectrum and the spectrum measured from 25 ns to 75 ns, e.g., curve (ii) in Fig. 2-5. The horizontal bar at each data point corresponds to the gate-on duration or the time interval used for the spectrum measurement. In all the samples, the
PL peak energy shifts to a lower energy in the time regions from $\sim 10^{-8}$ to $\sim 2 \times 10^{-7}$ s and from $\sim 7 \times 10^{-6}$ to $\sim 10^{-4}$ s, while it shifts to a higher energy in the middle region from $\sim 2 \times 10^{-7}$ to $\sim 7 \times 10^{-6}$ s. The latter blueshift is more clearly seen in sample E than in F and in sample G than in H.

The height of the time-resolved PL spectrum was divided by the gate-on duration, and is shown as a function of the delay time in Fig. 2-7(a). The PL decays are nonexponential, ranging from $\sim 10^{-8}$ to $10^{-4}$ s, which indicates that the PL has a broad lifetime distribution. Hence, it is convenient to analyze the PL decay by assuming a distribution function $G(\tau)$ of lifetime $\tau$. The function $G(\tau)$ is expressed by the equation,

$$G(\tau) = \text{const. } I \left( d \ln I / d \ln \tau \right),$$

(2-2)

where $I$ is the PL intensity and $\tau$ is the lifetime. Figure 2-7(b) shows the product $\tau G(\tau)$ drawn by choosing $G(\tau)$ so as to yield the best fits to the decays according to the procedure suggested by C. Tsang and R. A. Street.23 The lifetime distribution $\tau G(\tau)$ has a component that stretches over a wide range from $10^{-6}$ to $10^{-4}$ s besides a steeply dropping component around $10^{-7}$ s.

In Fig. 2-7(b), a steep drop in $\tau G(\tau)$ is seen at $\sim 10^{-7}$ s, the same time range wherein the initial redshift in the time-resolved spectra is observed. In order to
study this further, the PL decay at this early stage was investigated using SR. Figure 2-8 shows typical nanosecond-order decay curves of PL in samples E and H excited by SR photons with an energy of 5.0 eV at 10 K. The decay curves monitored at respective PL emission peaks are nonexponential and can be expressed by a stretched exponential function,

\[ I'(t) \propto (\beta / \tau')(\tau' / t)^{1-\beta} \exp \left[ -(t / \tau')^\beta \right], \tag{2-3} \]

where \( I' \) is the PL intensity, \( t \) the time, \( \tau' \) the effective lifetime, and \( \beta \) a parameter that has a value between 0 and 1. The curves in Fig. 2-8 are the results of the least-squares fit of the decay profiles to eq. (2-3). The data satisfy eq. (2-3) well, which is consistent with many reports indicating that the PL decay is described by the above equation for many amorphous materials.\(^{10,14,18,24-28}\) The lifetime \( \tau' \) is calculated to be 8.3 ns for sample E and 14.5 ns for sample H, while \( \beta \) is 0.4 for the two samples.

The time at which \( \tau G(\tau) \) shows the peak in Fig. 2-7(b) changes as a function of the abundance ration as shown by the circles in Fig. 2-9. Note that the PL intensity observed in sample I was too weak for this analysis. The changes in the effective lifetime \( \tau' \) calculated for all the samples are also shown in Fig. 2-9 by the triangles. Both the two quantities become longer with an
increase in the abundance ratio for both $a$-Si$_{x}$O$_{y}$N$_{z}$:H and $a$-SiN$_{z}$:H.

2.4. DISCUSSION

Appearance of band-tail PL has been reported in many amorphous materials.$^{16-23}$ Following explanations are accepted to understand typical features of the band-tail PLs in $a$-SiN$_{z}$:H$^{16-18}$ and $a$-SiC$_{x}$:H.$^{19,20}$ As the nitrogen or carbon content increases, the band-gap energy increases, which leads to a blueshift of $E_{\text{edge}}$. This shifts the PL peak to a higher energy. In addition, nitrogen or carbon alloying induces the structural disorder, resulting in an increase in the width of the localized states denoted by $E_{U}$. This broadens the FWHM of the PL band. These phenomena have been called 'antiparallel band-edge fluctuations', which is long-range disorder associated with spatial fluctuation of the elemental composition.$^{17,18,20,21}$

As shown in Figs. 2-1 and 2-2, the PL peak energy and values of $E_{\text{edge}}$ and $E_{U}$ increase monotonically as the abundance ratio or the nitrogen content increases in the present $a$-SiN$_{z}$:H films. This confirms that the PL in the present $a$-SiN$_{z}$:H films is due to the band-tail recombination. Similar shifts were also observed in $a$-Si$_{x}$O$_{y}$N$_{z}$:H films. Figure 2-10 shows the relation
between \( E_{\text{edge}} \) and the PL peak energy, where a striking similarity between the two materials is illustrated. This similarity strongly indicates that the PLs observed in the present two kinds of samples are due to the same mechanism (= band-tail recombination) at the same chromophore. Using silicon oxynitride films prepared by rapid thermal nitridation of silicon dioxide in a hydrogen-free NO ambience, we have already clarified that the chromophore is the Si–N bond and has no relation to hydrogen.\(^{11}\) In this case, it could be considered that \( a\text{-SiN}_x\text{H} \) with a lot more Si–N bonds than in \( a\text{-SiO}_x\text{N}_y\text{H} \) should give a stronger PL. However, this is not always the case in our results. The PL intensity is a function of the number of luminescence centers, the radiative recombination probability, and the non-radiative recombination probability. Since different materials would have different probabilities, the PL intensity is not always in proportion to the number of Si–N bonds.

The bandwidth of PL induced by the band-tail recombination should depend positively on the width of the localized states,\(^{16-21}\) although the mechanism that determines the PL bandwidth is still to be discussed in amorphous materials. While the Stokes-shift model attributes the PL bandwidth to a strong electron-phonon coupling,\(^{22,29,30}\) the static disorder or
zero-phonon model assigns it to the distribution of carriers in either band tail resulting from structural disorder.\textsuperscript{17,18,20,21} Since the two mechanisms can coexist, the FWHM of the PL band, $\Delta E_{\text{PL}}$, is given by\textsuperscript{18,20-22}

$$
(\Delta E_{\text{PL}})^2 = (\xi E_U)^2 + (\Delta E_{\text{e-ph}})^2,
$$

(2-4)

where $\xi$ is a coefficient, $E_U$ the Urbach energy, and $\Delta E_{\text{e-ph}}$ the increment in FWHM associated with the Stokes shift. Figure 2-11 shows the relation between $E_U$ and $\Delta E_{\text{PL}}$, indicating that $\Delta E_{\text{PL}}$ is proportional to $E_U$ in each material. That each straight line passes the origin of the coordinate axes indicates that the effect of $E_U$, or that of structural disorder is more predominant than that of the electron-phonon coupling. Moreover, it has been known that $E_U$ is composed of thermal disorder due to thermally induced network vibration and static disorder due to pure structural randomness.\textsuperscript{22} If $E_U$ is mainly due to the thermal disorder, the PL FWHM should depend on the temperature. However, it is almost constant in the range of 10–300 K as shown in Fig. 2-4, indicating that the effect of the static disorder is dominant in both materials.

Next, we discuss how the photogenerated carriers recombine via such localized band-tail states. As shown in Figs. 2-5 and 2-6, the PL peak shifts depending on the delay time, first to red, then to blue, and back to red again.
Moreover, the broad distribution of PL lifetime, ranging from \( \sim 10^{-8} \) to \( 10^{-4} \) s, is seen. This is another piece of evidence supporting the view that the PL is due to the band-tail recombination in the present two materials.\(^{14,19,31-33}\) It is assumed that three different effects, namely, thermalization, Coulombic interaction, and distribution of localized states, influence the recombination process. The photogenerated carriers lose their energy by thermalization at the band-tail states, which induces the first redshift.\(^{14,32,33}\) Assuming a tunneling process in the recombination, the PL lifetime becomes longer because the recombination probability decreases if the distance between the electron-hole pair is longer, while the Coulombic energy loss decreases. Hence, the PL shifts to a higher energy as the delay time increases.\(^{14,19,32,33}\) The blueshift is more evident in sample E than in F and in sample G than in H. Namely, it is clearer in samples with lower permittivities (see the refractive indices listed in Table 2-1). This indicates that the blueshift results from the Coulombic interaction. The final redshift is attributable to the extent of localization of carriers. Electrons and holes in the deeper states are more localized, which leads to a longer lifetime of the electron-hole pair in the frame of the radiative tunneling model.\(^{14,19,32,33}\)
As shown in Fig. 2-7(b), the PL has two decay components. The fast decay component is known to be commonly observed in $a$-$SiC_x$:H$^{19}$ and $a$-$SiN_z$:H$^{18,28}$ but is absent in $a$-$Si$:H. This means that exciton-like recombination of electron-hole pairs is the radiative mechanism for the fast component, since strong Coulombic force due to the presence of carbon or nitrogen atoms accelerates the radiative recombination rate.$^{14,31}$ The electron-hole pairs that survived the exciton-like recombination are then thermalized into localized states. It is considered that recombination through radiative tunneling of these electron-hole pairs is responsible for the slow decay component, as in the case of similar PL decays reported in $a$-$Si$:H,$^{22,32}$ amorphous silicon oxide ($a$-$SiO_x$:H),$^{33}$ $a$-$SiC_x$:H$^{19,31}$ and $a$-$SiN_z$:H.$^{14}$

Finally, focusing on the width of the localized band-tail states, the structural inhomogeneity is compared between $a$-$SiO_xN_y$:H and $a$-$SiN_z$:H. The slopes of the straight lines shown in Fig. 2-11 are ~6.1 and ~3.4 for $a$-$SiO_xN_y$:H and $a$-$SiN_z$:H, respectively. It might be considered that these values should be similar in the two materials, since the PL origins are identical. The reason for this is that $a$-$SiO_xN_y$:H has a narrower band tail than $a$-$SiN_z$:H as is clearly indicated in Fig. 2-2 by its smaller values of $E_U$. On the other hand, if we
compare PL lifetimes between the two materials with the same abundance ratio, the lifetime is shorter in $a$-SiO$_x$N$_y$:H than in $a$-SiN$_z$:H as shown in Fig. 2-9. In the case of the band-tail recombination, a broader band tail brings a longer lifetime, since the photogenerated carriers can be thermalized into deeper localized states. All these results indicate that the degree of the structural disorder is smaller in $a$-SiO$_x$N$_y$:H than in $a$-SiN$_z$:H. It is natural to consider that Si–O bonds are more flexible than Si–N bonds, since oxygen takes twofold coordination, whereas nitrogen takes threefold coordination. Therefore, the Si–O bonds can relieve the internal stress, which makes the structural disorder in $a$-SiO$_x$N$_y$:H smaller.

2.5. CONCLUSION

Characterization of the PLs observed in $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H films is carried out by investigating the PL band shape and the recombination process of photogenerated carriers. The PLs in the two materials have many similarities, and are considered to be due to the recombination between localized band-tail states associated with Si–N bonds. Further analyses on the PL decay process indicate that the recombination consists of two processes, namely, an
exciton-like recombination process and a radiative tunneling recombination process.

The PL peak energy becomes higher and the width of the PL spectrum becomes wider if the abundance ratio of (nitrogen + oxygen) or that of nitrogen increases. This is caused by the increase in the band-gap energy and the increase in the width of band-tail states induced by the presence of nitrogen and oxygen. The width of band-tail states or the degree of structural inhomogeneity is smaller in $a$-SiO$_x$N$_y$:H than in $a$-SiN$_z$:H. It is considered that the presence of oxygen atoms relieves the internal stress.
Chapter 2

References for Chapter 2


33 R. A. Street, Solid State Commun. 34, 157 (1980).
TABLE 2-1. Ratios of gas flow rates, elemental compositions, abundance ratios of atoms other than silicon to silicon atoms, and refractive indices of $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas flow ratio</th>
<th>Atomic %</th>
<th>Abundance ratio</th>
<th>Refractive index</th>
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</thead>
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<tr>
<td></td>
<td>$\text{SiH}_4/(\text{N}_2\text{O}+\text{N}_2)$</td>
<td>$\text{Si}$</td>
<td>$\text{O}$</td>
<td>$\text{N}$</td>
</tr>
<tr>
<td>D</td>
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<td>56</td>
<td>7.7</td>
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<td>53</td>
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</tr>
<tr>
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<td>51</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>$\text{SiH}_4/(\text{NH}_3+\text{N}_2)$</td>
<td>$\text{Si}$</td>
<td>-</td>
<td>$\text{N}$</td>
</tr>
<tr>
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<td>55</td>
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<td>-</td>
<td>49</td>
</tr>
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<td>52</td>
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</table>
FIG. 2-1. PL (open circles) and PLE (solid lines) spectra in $a$-SiO$_x$N$_y$:H (a) and $a$-SiN$_z$:H (b) films observed at 10 K. Broken vertical lines indicate the detection limits.
FIG. 2-2. The Urbach edge energy $E_{\text{edge}}$ (circles) and the Urbach energy $E_U$ (triangles) as a function of the abundance ratio. Closed and open symbols are for $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H, respectively.
FIG. 2-3. Temperature dependence of the normalized PL intensity in the range of 10–300 K. Closed and open circles are for samples E and H, respectively.
FIG. 2-4. Temperature dependence of the PL peak energy (triangles) and that of the PL FWHM $\Delta E_{\text{PL}}$ (circles) in the range of 10–300 K. Closed and open symbols are for samples E and H, respectively.
FIG. 2-5. Typical time-resolved PL spectra excited by 5.0-eV photons, observed in samples E (a) and G (b). Numerals following (i) to (vi) indicate given observation periods.
FIG. 2-6. Shift of the PL peak energy as a function of the time after excitation. Numerals next to the sample names are their abundance ratios.
FIG. 2-7. PL decays (a) and PL lifetime distribution (b) measured in $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H films, excited by 5.0-eV photons at room temperature. The lifetime distribution stretches over a time range from $10^{-8}$ to $10^{-4}$ s. Numerals next to the sample names are their abundance ratios.
FIG. 2-8. Nanosecond-order decay at 10 K monitored at each PL peak in samples E (a) and H (b). Excitation was done by photons with an energy of 5.0 eV.
FIG. 2-9. The time at which $\tau G(\tau)$ shows the peak (circles) and the effective lifetime $\tau'$ (triangles) as a function of the abundance ratio. Closed and open symbols are for $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H, respectively.
FIG. 2-10. Correlation between the Urbach edge energy $E_{\text{edge}}$ and the PL peak energy. Closed and open circles are for $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H, respectively.
FIG. 2-11. Relation between the Urbach energy $E_U$ and the FWHM of the PL spectrum $\Delta E_{PL}$. Closed and open circles are for $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H, respectively.
Chapter 3

Thermally induced photoluminescence quenching centers in hydrogenated amorphous silicon oxynitride and silicon nitride

ABSTRACT

The effects of thermal annealing on the band-tail photoluminescence phenomena in hydrogenated amorphous silicon oxynitride and silicon nitride films were investigated. The luminescence intensity increases monotonically with an increase in the annealing temperature from room temperature to 800 °C for the silicon oxynitride films 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 silicon oxynitride films with higher nitrogen contents (N/O = 0.14 and 0.18) and for the silicon nitride film. 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. The obtained results can be explained well by a theoretical analysis, in which the dangling bonds are assumed to act as the quenching center. 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.
3.1. 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 silicon carbide ($a$-SiC\(_x\)::H).\(^8\),\(^9\) By doing time-resolved PL analysis and by examining PL dependencies on defect density and temperature, the natures of defect states have become clear. However, the PL in hydrogenated amorphous silicon oxynitride ($a$-SiO\(_x\)N\(_y\)::H) has not been examined well as compared to PLs observed in other hydrogenated amorphous films. In this chapter, the effect of thermal treatment on the property of the band-tail PL is examined, focusing on its relation to thermally induced paramagnetic defect centers for $a$-SiO\(_x\)N\(_y\)::H films with different y/x ratios and for $a$-SiN\(_z\)::H film. The generation mechanism of defect centers and the PL quenching process are discussed.

3.2. EXPERIMENT

The $a$-SiO\(_x\)N\(_y\)::H films were deposited on a p-type (100) silicon monocrystal
substrate by plasma-enhanced chemical vapor deposition (PECVD) using a mixture of SiH₄, N₂O, and N₂ gases. The substrate temperature was 400 °C and the plasma frequency was 13.56 MHz. By changing the flow rate of SiH₄, five types of films with different nitrogen contents, samples A to E, were prepared as shown in Table 3-1. Similarly, the a-SiNₓ:H film (sample H) was deposited by PECVD using a mixture of SiH₄, NH₃, and N₂ gases. The atomic ratios of Si, O, and N were estimated through x-ray photoelectron spectroscopy (JEOL JPS-90MX). The film thickness and the refractive index were measured by ellipsometry (ULVAC ESM-1).

For annealing, the samples were kept at a temperature ranging from 200 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 13 K 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 excited by a KrF excimer laser (wavelength: 248 nm = 5.0 eV; pulse width: ~25 ns; pulse energy: ~100 mJ/cm², 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 13 K. The PL excitation (PLE) spectrum was obtained at 13 K 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).

3.3. RESULTS AND DISCUSSION

3.3.1. Effect of paramagnetic defects on the band-tail PL

Figure 3-1 shows typical PL and PLE spectra observed in unannealed samples A to E and H. As described in Chapter 2, the PLs in samples D, E, and H are of the same nature and they should be regarded as the same PL due to a radiative recombination between band-tail states associated with Si–N bonds. In the present $a$-Si$_x$O$_{1-x}$N$_y$:H, the PL and PLE peak energies shift to a lower energy from 2.9 to 2.2 eV and from 5.1 to 4.6 eV, respectively, with an increase in the nitrogen content, if we neglect the small side peak appeared in the PLE spectra of samples A and B. The forbidden gap energy of $a$-Si$_x$O$_{1-x}$N$_y$:H becomes smaller with an increase in the nitrogen content. This is consistent with the PLE peak shift. Therefore, it is considered that the present PL at 2.2–2.9 eV observed in the two materials is due to the band-tail PL.
Figure 3-2 shows the relation between the annealing temperature and the normalized PL intensity obtained for samples A to E and H. 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, E, and H. It is well known that both radiative and non-radiative processes are involved in PL. Therefore, the PL intensity $I_{PL}$ is given by

$$I_{PL} \propto \frac{P_R}{P_R + P_{NR}}$$

(3-1)

where $P_R$ and $P_{NR}$ are the radiative and nonradiative recombination probabilities, respectively. It is considered that the annealing below 500 °C decreases $P_{NR}$, resulting in the increase of PL intensity. The annealing above 500 °C is considered to decrease and increase $P_{NR}$ for samples A to C and for samples D, E, and H, respectively.

Figure 3-3 shows the ESR spectra observed in the unannealed samples A to E and H. The $g$ value at the zero-cross and the difference in magnetic field $\Delta H$ at the signal maximum and minimum are shown in Table 3-2. From these $g$ values, the induced paramagnetic defects are attributable to silicon dangling
bonds (Si–DBs: \( \cdot \text{Si} = \text{\equiv} \), where \( \equiv \) and \( \cdot \) denote three separate bonds and an unpaired electron, respectively). The difference in the nearest neighboring atoms is reflected to the difference in the \( g \) value and \( \Delta H \). For example, the \( E' \) center (\( \cdot \text{Si=O}_3 \)) has \( g \) value = 2.0010 and \( \Delta H = 0.28 \) mT, the \( K \) center (\( \cdot \text{Si=N}_3 \)) has \( g \) value = 2.0030 and \( \Delta H = 1.25 \) mT, and the \( D \) center (\( \cdot \text{Si=Si}_3 \)) has \( g \) value = 2.0055 and \( \Delta H = 0.75 \) mT.\(^{11-13}\) As shown in Table 3-2, all the \( g \) values are less than 2.0055. This implies that there are relatively few \( D \) centers in the present samples, which is reasonable judging from the atomic compositions shown in Table 3-1.

Figure 3-4 shows the relation between the annealing temperature and the paramagnetic spin density obtained for samples A to E and H. 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, E, and H annealed at temperatures above 500 °C, while they disappeared for samples A and B. By comparing the annealing temperature dependence of PL intensity (shown in Fig. 3-2) and that of spin density (shown in Fig. 3-4), a good agreement can be seen. If the paramagnetic defects increase \( P_{\text{NR}} \), this agreement is easily explained. Namely, the Si–DBs is considered to act as a
quenching center in the recombination process of the band-tail PL.

As shown in Table 3-2, the \( g \) value of Si–DBs obtained for samples C to E and H 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, \( P_{NR} \) should consist of the contribution of the original structure \( P_{NR(0)} \) and that of thermally induced one \( P_{NR(T)} \). For samples A and B, since the PL intensity increases monotonically with an increase in the annealing temperature, it is considered that \( P_{NR(0)} \) continuously decreases. If the original structure of Si–DB is the same in all the samples, \( P_{NR(0)} \) should similarly decrease for samples C to E and H. Since the PL intensity decreases on annealing at temperatures above 500 °C for samples D, E, and H, it is considered that \( P_{NR(T)} \) increases on annealing, resulting in an increase in \( P_{NR} \).

An analysis based on a simple theoretical model\(^4\) is carried. Assuming that \( P_{NR} \) is determined by carrier tunneling to the dangling bonds, the transition probability to a defect state by quantum mechanical tunneling, i.e., \( P_{NR} \) is

\[
P_{NR} = \nu_0 \exp \left( -2 \frac{R}{R_0} \right),
\]

(3-2)

where \( \nu_0 \) is the attempt frequency, commonly taken to be between \( 10^{11} \) and \( 10^{12} \).
$R$ is the distance to a defect, and $R_0$ is the tunneling radius or the localization length. The average distance to a defect is

$$R = \left( \frac{4}{3\pi N_D} \right)^{-1/3},$$ (3-3)

where $N_D$ is the Si–DBs density. The average nonradiative recombination probability $P_{AV}$ to defect states is then approximately

$$P_{AV} \approx \nu_0 \exp \left[ -\frac{2}{R_0} \left( \frac{4\pi N_D}{3} \right)^{-1/3} \right].$$ (3-4)

Using eq. (3-4) in eq. (3-1) and radiative recombination lifetime $\tau_R$ ($\tau_R = 1/<P_R>$, where $<P_R>$ is the average of $P_R$), $I_{PL}$ can be expressed as follows:

$$I_{PL}(N_D) \propto \frac{1}{1 + \tau_R P_{AV}} = \frac{1}{1 + \tau_R \nu_0 \exp \left[ -\frac{2}{R_0} \left( \frac{4\pi N_D}{3} \right)^{-1/3} \right]}.$$ (3-5)

Equation (3-5) can be fitted to the experimental points in Fig. 3-5 using $R_0$ and the product $\tau_R \nu_0$ as fitting parameters. From the fitting, the tunneling radius $R_0$ is estimated to be $\sim 1.4$ nm and the term $\tau_R \nu_0$ to be $\sim 110$ in sample D. Similarly the estimated values of $R_0 \approx 1.2$ nm and $\tau_R \nu_0 \approx 100$ are obtained in sample E, and $R_0 \approx 1.6$ nm and $\tau_R \nu_0 \approx 110$ in sample H. The corresponding theoretical curves are shown by the solid curves in Fig. 3-5. The values of $R_0$ for the present samples are smaller than the value of $R_0$, $\sim 3.2$ nm, obtained by L. S.
Sidhu and his coworkers for $a$-Si:H,\textsuperscript{4} indicating that the electrons and holes in the present samples are more localized in the band-tail states than those in $a$-Si:H. Moreover, assuming $\nu_0 \approx 10^{11}$ Hz, $\tau_R \approx 10^{-9}$ s is obtained, which is consistent with the PL lifetime described in Chapter 2.

The experimental data is also fitted to the model proposed by C. Tsang and R. A. Street, which gives:\textsuperscript{15}

$$I_{\text{PL}}(N_D) \propto I_0 \exp\left(-\frac{4}{3} \pi R_C^3 N_D\right), \quad (3-6)$$

where $I_0$ is the PL intensity in the low $N_D$ limit and $R_C$ is the capture radius defined as where the radiative and nonradiative tunneling probabilities are equal. As shown by the broken curves in Fig. 3-5, the fitting does not provide good fits to the experimental data at defect levels over $\sim 10^{19}$ cm$^{-3}$, where the theoretical curves based on eq. (3-6) drop off much more rapidly than the experimental data.

The good agreements of experimental data with eq. (3-5) support the simple model. Therefore, as already mentioned in Chapter 2, it is considered that the main recombination channel is thermalization of electrons into band-tail states followed by either radiative recombination or tunneling to defect centers and nonradiative recombination. From this, it is shown that the Si–DBs act as
the quenching center of the band-tail PL in $a$-$SiO_xN_y: H$ and $a$-$SiN_z: H$ films.

3.3.2. Thermally induced process of Si–DBs

Figure 3-6 shows IR spectra observed in the unannealed samples A to E and H. The absorption due to N–H bonds at 3340 cm$^{-1}$ is similar in all the samples. The absorption due to Si–H bonds at 2150–2250 cm$^{-1}$ observed in samples D and E is composed of two absorption components centered at 2150 and 2240 cm$^{-1}$. It has been reported that the absorption peak due to Si–H bonds appears around 2250, 2150, and 2000 cm$^{-1}$ in $a$-$SiO_2$, $a$-$Si_3N_4$, and $a$-$Si:H$, respectively,\textsuperscript{16,17} depending on the nearest neighboring atoms. As shown in Fig. 3-6, only samples D, E, and H have the absorption peak at 2150 cm$^{-1}$. This absorption at 2150 cm$^{-1}$ characteristic to samples D, E, and H 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, E, and H 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 neighboring atoms to ⋅Si should increase. This is demonstrated in Table 3-2. 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, E, and H in Fig. 3-5. Figure 3-7 shows the Si–H density calculated from the IR absorption intensity and the normalized PL intensity for samples E and H, each as a function of the density of paramagnetic centers. 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 3-8(a) 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 3-8(b) shows the changes in the normalized PL intensity and Si–DBs density for sample E induced by thermal treatment and the following 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 centers for the band-tail PL in $a$-$\text{SiO}_x\text{N}_y$:$\text{H}$ and $a$-$\text{SiN}_z$:$\text{H}$.
3.4. CONCLUSION

The effects of thermal annealing on the band-tail PL in $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H films were 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 and a theoretical analysis, it is considered that the silicon dangling bonds act as the quenching center 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.
References for Chapter 3


TABLE 3-1. Elemental compositions and refractive indices of $a$-$\text{SiO}_x\text{N}_y$:$\text{H}$ and $a$-$\text{SiN}_z$:$\text{H}$ films studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si (atomic %)</th>
<th>O (atomic %)</th>
<th>N (atomic %)</th>
<th>N/O</th>
<th>Empirical formula</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>35</td>
<td>62</td>
<td>3.6</td>
<td>5.8×10^{-2}</td>
<td>$\text{SiO}<em>{1.8}\text{N}</em>{0.10}$</td>
<td>1.49</td>
</tr>
<tr>
<td>B</td>
<td>35</td>
<td>59</td>
<td>6.0</td>
<td>1.0×10^{-1}</td>
<td>$\text{SiO}<em>{1.7}\text{N}</em>{0.17}$</td>
<td>1.53</td>
</tr>
<tr>
<td>C</td>
<td>35</td>
<td>57</td>
<td>7.0</td>
<td>1.2×10^{-1}</td>
<td>$\text{SiO}<em>{1.6}\text{N}</em>{0.20}$</td>
<td>1.57</td>
</tr>
<tr>
<td>D</td>
<td>37</td>
<td>56</td>
<td>7.7</td>
<td>1.4×10^{-1}</td>
<td>$\text{SiO}<em>{1.5}\text{N}</em>{0.21}$</td>
<td>1.63</td>
</tr>
<tr>
<td>E</td>
<td>38</td>
<td>53</td>
<td>9.6</td>
<td>1.8×10^{-1}</td>
<td>$\text{SiO}<em>{1.4}\text{N}</em>{0.26}$</td>
<td>1.68</td>
</tr>
<tr>
<td>H</td>
<td>50</td>
<td>-</td>
<td>49</td>
<td>-</td>
<td>$\text{SiN}_{0.98}$</td>
<td>1.99</td>
</tr>
</tbody>
</table>
TABLE 3-2. Change of the \( g \) value and that of \( \Delta H \) calculated from ESR spectra by the thermal annealing temperature.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA to 400 °C</td>
<td>( g )</td>
<td>2.0008</td>
<td>2.0012</td>
<td>2.0022</td>
<td>2.0035</td>
<td>2.0038</td>
<td>2.0032</td>
</tr>
<tr>
<td></td>
<td>( \Delta H ) (mT)</td>
<td>0.27</td>
<td>0.32</td>
<td>0.75</td>
<td>0.81</td>
<td>0.82</td>
<td>0.79</td>
</tr>
<tr>
<td>500 °C to 900 °C</td>
<td>( g )</td>
<td>-</td>
<td>-</td>
<td>2.0034</td>
<td>2.0041</td>
<td>2.0043</td>
<td>2.0034</td>
</tr>
<tr>
<td></td>
<td>( \Delta H ) (mT)</td>
<td>-</td>
<td>-</td>
<td>0.58</td>
<td>0.64</td>
<td>0.76</td>
<td>0.80</td>
</tr>
</tbody>
</table>
FIG. 3-1. PL and PLE spectra observed in unannealed samples A to E and H.
FIG. 3-2. Relation between the annealing temperature and the normalized PL intensity obtained for samples A to E and H. NA: not annealed.
FIG. 3-3. ESR spectra observed in unannealed samples A to E and H.
FIG. 3-4. Relation between the annealing temperature and the paramagnetic spin density obtained for samples A to E and H. The broken line indicates the detection limit. NA: not annealed.
FIG. 3-5. Normalized PL intensities as a function of Si–DBs density obtained for samples D (circles), E (rectangles), and H (triangles). Solid and broken curves are drawn based on eqs. (3-5) and (3-6), respectively.
FIG. 3-6. 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 and H.
FIG. 3-7. Si–H density (open symbols) calculated from the IR absorption intensity and the normalized PL intensity (solid symbols) for samples E (a) and H (b), each as a function of the density of paramagnetic centers.
FIG. 3-8. (a) ESR spectra obtained for sample E annealed at 900 °C; (i) before the hydrogen treatment, (ii) after the hydrogen treatment. (b) Changes in the normalized PL intensity and Si–DBs density for sample E induced by thermal treatment and the following hydrogen treatment. NA: not annealed.
Similarities in the electrical conduction processes in hydrogenated amorphous silicon oxynitride and silicon nitride

ABSTRACT

Electrical conduction at high fields was examined on a series of hydrogenated amorphous silicon oxynitride and silicon nitride films with different nitrogen contents deposited by plasma-enhanced chemical vapor deposition. It was shown that the conduction is attributable to the Poole-Frenkel emission in the two materials. The energy depth of the Poole-Frenkel sites and its dependence on the sample’s chemical composition are quite similar between the two samples. It is considered that the Poole-Frenkel sites in the two materials are identical.
4.1. INTRODUCTION

Hydrogenated amorphous silicon oxynitride ($a$-SiO$_{x}$N$_{y}$:H) and silicon nitride ($a$-SiN$_{z}$:H) films deposited using plasma-enhanced chemical vapor deposition (PECVD) have a wide range of applications ranging from insulating dielectrics in thin-film transistors$^{1-3}$ to more conductive films for light emitting devices.$^{4-6}$ Depending on how they are deposited and operated, however, thin-film devices made with $a$-SiO$_{x}$N$_{y}$:H and $a$-SiN$_{z}$:H contain various quantities of localized states due to structural disorders and defects, many of which are charged and cause an increase in their conductivities. In this viewpoint, much effort has been devoted to clarify the conduction mechanism in these materials.$^{7-10}$

Through analyses of the photoluminescence characteristics described in Chapters 2 and 3, it was clarified that these materials possess localized band-tail states associated with Si–N bonds. In this chapter, the effects of these states on the electrical conduction processes in these materials at high fields are investigated.

4.2. EXPERIMENT
The $a$-Si$_{x}$N$_{y}$:H films were deposited using a dual-frequency PECVD system. A mixture of SiH$_4$, N$_2$O, and N$_2$ gases was excited in a parallel-plate reactor where a rf power of 13.56 MHz was supplied with a maximum power of 0.54 kW. At the same time, a lower-frequency power of 400 kHz was also supplied with a maximum power of 0.38 kW to reduce the structural stress of the deposited film. Three types of films with different atomic ratios were prepared by changing the flow ratio of SiH$_4$ to the sum of the other two gases. The films were deposited onto a $p$-type (100) silicon monocrystal substrate set on a stage whose temperature was kept constant at 400 °C. Three types of $a$-SiN$_z$:H films were similarly deposited using a mixture of SiH$_4$, N$_2$, and NH$_3$ gases. The elemental compositions of Si, O, and N estimated through x-ray photoelectron spectroscopy (XPS, JEOL JPS-90MX) and the refractive index measured by ellipsometry (ULVAC ESM-1) with a He–Ne laser at a wavelength of 632.8 nm are shown in Table 4-1.

The electrical properties were examined by measuring the conduction current using a high resistance meter (Advantest R8340) and the capacitance using a high frequency C-V meter (Sanwa Mega Bytek MI-494) for the sample having a metal-insulator-semiconductor (MIS) structure consisting of the lower
silicon substrate, the film and an evaporated gold upper electrode with an effective area of $7.9 \times 10^{-3}$ cm$^2$. The conduction current was measured by applying a negative dc voltage to the gold electrode while changing its value from 0 to 150 V in a stepwise manner with a step of 0.15 V. Its temperature dependence was also measured from 273 to 398 K in a stepwise manner with a step of 25 K. The relative permittivity was calculated from the capacitance of the accumulation layer measured at room temperature.

4.3. RESULTS AND DISCUSSION

Figure 4-1 shows the conduction current density $J$ measured at room temperature as a function of the electric field intensity $E$ obtained for all the samples. The following three systematic trends can be observed as the abundance ratio increases regardless of whether the sample is $a$-$\text{SiO}_x\text{N}_y$::H or $a$-$\text{SiN}_z$::H.

(i) The high-field end of each curve indicating the point of dielectric breakdown shifts to a higher electric field.

(ii) Each curve can be divided into two regions. The onset of the high-field region shifts to a higher electric field.
(iii) The slope of each curve at the high-field region decreases.

Sample C or G with the highest abundance ratio exhibits the highest breakdown field, the smallest slope, and the lowest leakage current if compared at the same electric field, while sample E or I with the lowest abundance ratio exhibits the lowest breakdown field, the steepest slope, and the highest leakage current.

Focusing on the high-field region, the conduction process is discussed. The Poole-Frenkel (PF) emission [eq. (4-1)] and the Fowler-Nordheim (FN) tunneling [eq. (4-2)] are frequently observed in silicon nitride at high fields.\(^7,^8\)

\[
J_{\text{PF}} = C_{\text{PF}} E \exp\left[ -\frac{1}{kT} \left( \phi_{\text{PF}} - \sqrt{\frac{q^3 E}{\pi \epsilon_0 \epsilon_{\text{in}}}} \right) \right], \quad (4-1)
\]

\[
J_{\text{FN}} = \frac{q^3 E^2}{8\pi h \phi_{\text{FN}}} \exp\left[ -\frac{8\pi \sqrt{2m^* \phi_{\text{FN}}}}{3qhE} \right]. \quad (4-2)
\]

Here \(C_{\text{PF}}\) is a constant with the dimension of conductivity, \(q\) is the electronic charge, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(\phi_{\text{PF}}\) is the energy depth of the PF sites, \(\epsilon_0\) is the permittivity of free space, \(\epsilon_{\text{in}}\) is the permittivity of the insulating layer, \(h\) is the Planck constant, \(\phi_{\text{FN}}\) is the barrier height between the Fermi level of the metal and the conduction band of the insulating layer, and \(m^*\) is the effective mass of the electron. The PF current density \(J_{\text{PF}}\) is bulk limited, i.e., the current is controlled by the defect states
present below the conduction band and above the valence band. The FN current density $J_{\text{FN}}$ occurs as a result of carrier tunneling through a triangular potential barrier.

Figure 4-2(a) shows a PF plot drawn based on the $J-E$ relation observed in sample I, while Fig. 4-2(b) shows its FN plot. Similar PF and FN plots were drawn for all the $J-E$ curves shown in Fig. 4-1, and the field regions where the PF or the FN relation governs the conduction current were estimated by drawing straight lines with the least-squares method as shown in Fig. 4-2. Figure 4-3 compares such estimated regions. It is clear that the high-field conduction is more governed by the PF process regardless of whether the sample is $a$-SiO$_x$N$_y$:H or $a$-SiN$_z$:H.

The relative permittivity of each film was calculated using eq. (4-1) from the slope of the PF curve, e.g., the slope of the broken line shown in Fig. 4-2(a) in case of sample I. Figure 4-4 shows the relative permittivity as a function of the abundance ratio. The relative permittivity values calculated from the capacitance values of the accumulation layers are also shown in Fig. 4-4. The permittivity values calculated by both two ways decrease with an increase in the abundance ratio, consistently with the refractive index shown in Table 4-1.
Although the permittivity value calculated from the slope and the one calculated from the capacitance do not agree with each other, their dependencies on the abundance ratio are similar.

Figure 4-5 shows the Arrhenius plot of the conductivity $\sigma$. Here, $\sigma$ is obtained according to the following procedures. As shown in Fig. 4-1, the $J-E$ curve strongly depends on the sample’s abundance ratio. It is reasonable to adopt the conductivity value around the midpoint of the $J-E$ curve in the high-field region. From this viewpoint, $\sigma$ is calculated at the electric field where the current density measured at 298 K is equal to $1\times10^{-6}$ A/cm$^2$ for each sample, based on the results shown in Fig. 4-1. The logarithmic conductivity shown in Fig. 4-5 is inversely proportional to the measurement temperature. As expressed by eqs. (4-1) and (4-2), the PF current theoretically depends on the temperature, whereas the FN current does not. Therefore, the above-mentioned two facts indicate that the high-field conduction is due to the PF emission.

Figure 4-6 shows the energy depth $\phi_{PF}$ as a function of the abundance ratio estimated from the Arrhenius plot shown in Fig. 4-5. The depth $\phi_{PF}$ increases monotonically from 0.85 eV to 1.21 eV with an increase in the abundance ratio. Furthermore, the large value of $\phi_{PF}$ should be responsible for the low conduction
current and high breakdown field in the samples with high abundance ratios, the characteristics clearly shown in Fig. 4-1.

The energy depth $\phi_{PF}$ is an important parameter in the PF process. It is interesting to see how $\phi_{PF}$ governs the PF processes in the different but similar two materials, $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H. Figure 4-7 shows the region where the conduction current in each sample obeys the PF relation. Namely, the circles represent the maximum field intensities in the regions, while the triangles represent the minimum field intensities. A striking similarity between the two materials is illustrated, which indicates that the PF sites in the present two kinds of samples are due to the same origin regardless of the presence of oxygen. This is consistent with the conclusion obtained from photoluminescence analyses in Chapter 2 that $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H possess similar localized band-tail states associated with Si–N bonds. Moreover, the width of these localized states was also clarified in Chapter 2 to become broader with an increase in the abundance ratio, indicating that the carriers are localized in deeper states. This is consistent with the present result shown in Fig. 4-6. Therefore, it is concluded that the electrical conduction in $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H at high fields is governed by the PF process through the localized
states associated with Si–N bonds located either below the conduction band or above the valence band.

**4.4. CONCLUSION**

The author has examined the electrical conduction mechanism in $a$-SiO$_{x}$N$_{y}$:H and $a$-SiN$_{z}$:H, and has found that the current at high fields is governed by the Poole-Frenkel emission in both materials. From the similarity on many aspects of conduction process, it is considered that the carriers in the two materials are transported similarly through the Poole-Frenkel sites associated with Si–N bonds.
References for Chapter 4


TABLE 4-1. Ratios of gas flow rates, elemental compositions, abundance ratios of atoms other than silicon to silicon atoms, and refractive indices of $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H films tested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas flow ratio</th>
<th>Atomic %</th>
<th>Abundance Ratio</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{SiH}_4/(\text{N}_2\text{O}+\text{N}_2)$</td>
<td>Si</td>
<td>O</td>
<td>N</td>
</tr>
<tr>
<td>C</td>
<td>$2.4\times10^{-2}$</td>
<td>35</td>
<td>57</td>
<td>7.0</td>
</tr>
<tr>
<td>D</td>
<td>$3.0\times10^{-2}$</td>
<td>37</td>
<td>56</td>
<td>7.7</td>
</tr>
<tr>
<td>E</td>
<td>$3.7\times10^{-2}$</td>
<td>38</td>
<td>53</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>$\text{SiH}_4/(\text{NH}_3+\text{N}_2)$</td>
<td>Si</td>
<td>-</td>
<td>N</td>
</tr>
<tr>
<td>G</td>
<td>$5.1\times10^{-2}$</td>
<td>44</td>
<td>-</td>
<td>55</td>
</tr>
<tr>
<td>H</td>
<td>$8.6\times10^{-2}$</td>
<td>50</td>
<td>-</td>
<td>49</td>
</tr>
<tr>
<td>I</td>
<td>$1.2\times10^{-1}$</td>
<td>52</td>
<td>-</td>
<td>47</td>
</tr>
</tbody>
</table>
FIG. 4-1. Relation between the electric field intensity $E$ and conduction current density $J$ measured in all the samples at room temperature.
FIG. 4-2. A Poole-Frenkel (PF) plot (a) and a Fowler-Nordheim (FN) plot (b) obtained for sample I. The broken straight line indicates either the PF or the FN relation, drawn by the least-squares fit to the data at high fields.
FIG. 4-3. Regions of electric field intensities in which the $J$-$E$ characteristics agree with the PF relation (broken lines) or with the FN relation (solid lines), obtained for all the samples.
FIG. 4-4. Permittivities calculated from the PF plots (circles) and those calculated from the capacitance values of the accumulation layers (triangles). Solid and open symbols are the data obtained for $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H, respectively.
FIG. 4-5. Arrhenius plots of conductivities obtained for all the samples. Broken lines are drawn by the least-squares exponential fit to the data.
FIG. 4-6. Change in the energy depth of PF sites $\phi_{PF}$ as a function of the abundance ratio. Solid and open circles are the data obtained for $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H, respectively.
FIG. 4-7. Changes in the maximum (circles) and the minimum (triangles) electric field intensities of the regions, in which the $J$-$E$ characteristics agree with the PF relations. Solid and open symbols are the data obtained for $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H, respectively.
Visible electroluminescence in hydrogenated amorphous silicon oxynitride

ABSTRACT

The mechanism of electroluminescence in hydrogenated amorphous silicon oxynitride was investigated. The luminescence can be observed only in the samples annealed at high temperatures. It depends on the direction of the applied electric field, and its peak photon energy decreases from 2.3 to 1.8 eV as the nitrogen content increases. From the measurements of conduction current and Fourier transform infrared absorption spectroscopy, it was found that the electrical conduction in the electric field region where the luminescence was observed is governed by the Poole-Frenkel process at the defect centers induced by the high temperature annealing. The electroluminescence is considered to be caused by electronic transition between the band-tail states associated with Si–N bonds.
5.1. INTRODUCTION

Hydrogenated amorphous silicon oxynitride (a-SiO$_x$N$_y$:H) has a possibility of realizing an excellent electronic property similar to silicon dioxide while keeping a high permittivity value of silicon nitride by choosing a proper composition of $y/x$. Since its refractive index can be controlled by changing the $y/x$ ratio, it also has a possible application to optical fibers and waveguides. Moreover, luminescence of this material has been reported by several authors, which may open the door for its application to all-Si-based optoelectronics technology. This chapter reports a visible electroluminescence (EL) of a-SiO$_x$N$_y$:H. The EL energy changes from red to yellow depending on the nitrogen content, which is attractive for optoelectronics. The EL mechanism is also discussed based on the results of conduction current measurement and Fourier transform infrared (FTIR) absorption spectroscopy.

5.2. EXPERIMENT

The a-SiO$_x$N$_y$:H films were deposited on a $p$-type (100) silicon monocrystal substrate by plasma-enhanced chemical vapor deposition (PECVD) using a mixture of SiH$_4$, N$_2$O, and N$_2$ gases. The substrate temperature was 400 °C and
the plasma frequency was 13.56 MHz. By changing the flow rate of SiH₄, three types of films with different nitrogen contents were prepared as shown in Table 5-1. The elementary compositions of Si, O, and N were estimated through x-ray photoelectron spectroscopy (JEOL JPS-90MX). The thickness and refractive index measured by ellipsometry (ULVAC ESM-1) are also shown in Table 5-1.

For annealing, the samples were kept at a temperature ranging from 500 to 900 °C in vacuum ($3.0 \times 10^{-2}$ Pa) with a rapid thermal annealing apparatus for 10 min. The chemical change induced was examined by FTIR absorption spectroscopy (JEOL JIR-WINSPEC50). The electrical properties were examined by measuring the conduction current using a high resistance meter (Advantest R8340) and the capacitance-voltage characteristics at 1 MHz using a HF C-V meter (Sanwa Mega Bytek MI-494) for the sample having evaporated gold electrodes with an effective area of $7.9 \times 10^{-3}$ cm². In the EL measurements, a semitransparent gold electrode with an effective area of $4.0 \times 10^{-1}$ cm² and a transmittance of about 30% was vacuum evaporated as the upper electrode. Photoluminescence (PL) was measured under excitation by a KrF excimer laser (wavelength: 248 nm = 5.0 eV; pulse width: ~25 ns; pulse energy: ~100 mJ/cm²,
Lambda Physik COMPEX205). These luminescence spectra were measured at room temperature using a monochromator (Jobin-Yvon HR320) equipped with an intensified charge coupled device array (Princeton Instruments ICCD-576G/RBT).

5.3. RESULTS AND DISCUSSION

Open circles in Fig. 5-1 show the EL spectra observed in the samples annealed at 900 °C. The peak energy decreases with an increase in the nitrogen content from 2.3 eV in sample C to 1.8 eV in sample E. It was found that EL appeared only in the annealed samples, and the lowest annealing temperature necessary to observe EL is different among the samples, and is 800 °C in sample C, 700 °C in sample D, and 600 °C in sample E.

Solid curves in Fig. 5-1 show PL spectra in the samples annealed at 900 °C. The shift of the PL peak energy is similar to that of the EL peak energy. Figure 5-2 compares the peak shift among EL and PL in the annealed samples and the PL in the unannealed samples, which clearly shows a similarity among the three peak shifts, even though the peak positions are different. It is considered that the peak shift is due to the decrease in the band gap energy with an increase in
the nitrogen content. The fact that both the EL and the 2.2–2.9 eV PL are observed in the same samples with a similar tendency of peak shift suggests that the same radiation process is involved in the two luminescence mechanisms.

The EL is observed only under the forward bias condition when the polarity of the $p$-type silicon is positive. Figure 5-3 shows the relationship between the applied electric field and EL intensity of sample E annealed at 900 °C. The conduction current density measured under the same condition is also shown. The EL intensity and the current density become larger in quite similar manners with an increase in the applied electric field. This indicates that the conduction carriers play an important role in EL. As described in Chapter 4, the conduction mechanism for the unannealed $a$-$\text{SiO}_x\text{N}_y$:H is governed by the Poole-Frenkel (PF) process. A similar process was obtained from the present annealed samples C to E. The electric field, where the EL becomes observable, is about 6, 4, and 3 MV/cm in samples C to E, respectively. From these results it is considered that the conduction is governed by the PF process when the EL appears.

For the EL observed in silicon oxide,\textsuperscript{12,13} silicon nitride,\textsuperscript{14} and silicon oxynitride\textsuperscript{10,11} with a metal-insulator-semiconductor structure, two models have
been proposed. One is the hot carrier model, where electrons and holes are assumed to be accelerated significantly so that they can run close to the conduction and valence bands.\textsuperscript{12} In the other model, i.e., in the injection model, while electrons and holes are assumed to be injected from electrodes, no further significant acceleration is postulated.\textsuperscript{10,11,13,14} If the carriers in the present samples are generated by the PF effect and are transported by a hopping process, it is difficult to assume that they are accelerated so much. The carriers are thought to be barely transported via the PF sites, holding the minimum necessary energy. However, in the case of PL, electrons excited by UV photons to a level much higher than the bottom of the conduction band can contribute to the PL. Therefore the energy of photons emitted in EL should coincide with the lowest energy of photons emitted in PL. This is clearly demonstrated if we compare the EL spectra and the PL spectra shown in Fig. 5-1.

When the \textit{p}-type silicon is positively biased, holes are easily injected into the $a$-$\text{SiO}_x\text{N}_y$; H layer, while electrons can be injected from the gold electrode. The injected electrons and holes are transported through the localized PF sites to luminescence centers where they recombine with each other, releasing the excess energy. This is considered to be the mechanism of EL.
Next, the effect of thermal annealing is discussed. The IR spectroscopy measurements revealed that the present samples have absorption peaks around 1000, 2200, and 3340 cm\(^{-1}\), which are attributable to the superposition of Si–O and Si–N stretching, Si–H stretching, and N–H stretching, respectively.\(^{15}\) Figure 5-4 shows the change in the IR absorption intensities due to the N–H and Si–H bonds observed in samples C to E. These intensities decrease with an increase in the annealing temperature. In the case of silicon nitride, it has been reported that the Si–H and N–H bonds are broken at high temperatures and that H\(_2\) molecules come out of the material.\(^{16}\) It is considered that hydrogen is also released from the present silicon oxynitride sample by the annealing. If the hydrogen terminating imperfections such as dangling bonds come out, many defect states will appear within the forbidden gap.

Figure 5-5 shows the relation between the annealing temperature and the current density for samples C to E measured at the 6 MV/cm. The current density increases with an increase in the annealing temperature. The activation energy estimated from the measurement temperature dependence of current density as a function of the annealing temperature decreases with an increase in the annealing temperature. If the annealing beyond 500 °C induces hopping
sites, the activation energy becomes smaller and the conduction current becomes larger. This helps electrons and holes reach the luminescence centers and recombine there with each other.

Finally, a few words about the luminescence centers would be added. There have been papers\textsuperscript{7,10} reporting that the EL and the PL in silicon oxynitride are due to Si–Si or Si–H bonds. However, as shown in Fig. 5-4, Si–H bonds disappear when the EL appears. The PL around 2.7 eV originated from the silicon homobonds (Si–Si) in SiO\textsubscript{2} has a decay constant as slow as 10 ms, while the PL around 2.2–2.9 eV in silicon oxynitride has a decay constant as fast as 3.7 ns as described in Chapter 2. Unfortunately, no such clear judgment can be done for EL, since it is virtually impossible to measure its decay constant. However, the EL peak energy is related to the nitrogen content as shown in Fig. 5-2 and the EL was observed only in the samples for which the 2.2–2.9 eV PL is the only PL at least in the energy region around there. Therefore it is highly probable that the EL luminescence center is associated with Si–N bonds.

5.4. CONCLUSION

The $a$-Si\textsubscript{O\textsubscript{x}N\textsubscript{y}}:H films ($1.4 < x < 1.6$, $0.20 < y < 0.26$) deposited by PECVD
exhibit EL around 1.8–2.3 eV after they were thermally annealed. The EL is attributable to the recombination between the localized states associated with Si–N bonds located below the conduction band and above the valence band. The annealing induces many carrier transport centers that help electrons and holes reach the localized states.
References for Chapter 5


TABLE 5-1. Elemental compositions, refractive indices, and thicknesses of $a$-SiO$_x$N$_y$:H films tested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(atomic %)</th>
<th>N/O</th>
<th>Empirical formula</th>
<th>Refractive index</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>O</td>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>35</td>
<td>57</td>
<td>7.0</td>
<td>$1.2 \times 10^{-1}$</td>
<td>SiO$<em>{1.6}$N$</em>{0.20}$</td>
</tr>
<tr>
<td>D</td>
<td>37</td>
<td>56</td>
<td>7.7</td>
<td>$1.4 \times 10^{-1}$</td>
<td>SiO$<em>{1.5}$N$</em>{0.21}$</td>
</tr>
<tr>
<td>E</td>
<td>38</td>
<td>53</td>
<td>9.6</td>
<td>$1.8 \times 10^{-1}$</td>
<td>SiO$<em>{1.4}$N$</em>{0.26}$</td>
</tr>
</tbody>
</table>
FIG. 5-1. EL spectra (denoted by open circles) and PL spectra (solid curves) in samples C to E annealed at 900 °C.
FIG. 5-2. Relation between the nitrogen content (N/O or \( y/x \) in \( a\text{-SiO}_x\text{N}_y\text{H} \)) and the peak position of luminescence. Closed circles are for the PL in the unannealed samples, open circles are for the PL in the samples annealed at 900 °C, and squares are for the EL in the annealed samples.
FIG. 5-3. The EL intensity (circles) and the conduction current density (broken curve) in sample E annealed at 900 °C as a function of electric field intensity.
FIG. 5-4. Change in IR absorption intensities due to the Si–H bonds at 2200 cm\(^{-1}\) (denoted by open symbols) and the N–H bonds at 3340 cm\(^{-1}\) (solid symbols) induced by the thermal annealing. Circles, triangles, and squares indicate the data obtained for samples C to E, respectively. NA: not annealed.
FIG. 5-5. Relationship between the annealing temperature and the current density measured at 6 MV/cm. Circles, triangles, and squares indicate the data obtained for samples C to E, respectively. NA: not annealed.
ABSTRACT

Refractive index change is shown to be induced by the irradiation of ultraviolet photons in hydrogenated amorphous silicon oxynitride films prepared by plasma-enhanced chemical vapor deposition. The mechanism of the index change and its dependence on the nitrogen content were investigated by electron spin resonance and scanning electron microscopy. It is concluded that the index change is due mainly to densification, and that the contribution of the formation of paramagnetic defects is only slight. To demonstrate the versatility of this refractive index change, a planar diffraction grating was fabricated.
6.1. INTRODUCTION

The importance of hydrogenated amorphous silicon oxynitride ($a$-SiO$_x$N$_y$:H) films fabricated by plasma-enhanced chemical vapor deposition (PECVD) is increasing for low-cost highly integrated optical devices, since the refractive index of $a$-SiO$_x$N$_y$:H is changeable over a wide range from 1.45, the value of silicon dioxide, to 2.00, that of silicon nitride, and since this allows considerable freedom in designing the structure of integrated optical devices. Because the material is a compound of silicon, it is easily incorporated in the present fiber optic and large scale integrated circuit technologies. Moreover, as a PECVD-synthesized film, it has many advantages such as a low deposition temperature, large deposition area, ease of composition control, and excellent step coverage.

Several papers have been reported on the effects of elemental composition or thermal annealing on the refractive index of $a$-SiO$_x$N$_y$:H. However, no papers have been reported on the refractive index change induced by ultraviolet (UV) photon irradiation, which potentially promises direct drawing of a waveguide and direct fabrication of a waveguide with a buried periodic refractive index that can be used as an optical grating. This chapter describes
experimental measurements of the refractive index change induced in $a$-$SiO_xN_y:H$ films by UV photon irradiation and discusses its mechanism. Moreover, a diffraction grating was fabricated using a phase lattice method to demonstrate the versatility of $a$-$SiO_xN_y:H$ as a material for optical devices.

### 6.2. EXPERIMENT

The $a$-$SiO_xN_y:H$ films were deposited using a dual-frequency PECVD system. A mixture of SiH$_4$, N$_2$O, and N$_2$ gases was excited in a parallel-plate reactor where a RF power of 13.56 MHz was applied with a maximum power of 0.54 kW. At the same time, to reduce the structural stress, a low-frequency power of 400 kHz was also applied with a maximum power of 0.38 kW. Five types of films with different nitrogen contents were prepared by changing the flow ratio of SiH$_4$ to the sum of the other two gases, while the total pressure was kept constant around $2.4 \times 10^2$ Pa. The films were deposited onto a $p$-type silicon monocrystal wafer (100) set on a stage whose temperature was kept at 400 °C.

The elemental compositions of Si, O, and N were estimated through x-ray photoelectron spectroscopy (XPS JEOL-90MX). The refractive index and the
thickness were measured by ellipsometry (Ulvac ESM-1) at a wavelength of 632.8 nm. Note that the accuracy of measurements is $\pm 0.005$ for refractive index and $\pm 0.3$ nm for thickness. A KrF excimer laser (wavelength: 248 nm = 5.0 eV; pulse width: ~25 ns, Lambda Physik Compex 205) was used as the UV irradiation source. The electron spin resonance (ESR) spectra were obtained by JEOL JES-FA 300 at the $X$-band frequency. The density of paramagnetic centers was evaluated by double numerical integration of first-derivative spectra and comparison with the signal from diphenylpicrylhydrazyl ($g = 2.0036$) of a known weight. The accuracy of the standard is believed to be $\pm 20\%$. All the measurements were done at room temperature.

### 6.3. RESULTS

Table 6-1 shows the $a$-SiO$_x$N$_y$:H films studied, together with their ratios of gas flow rates, elemental compositions, and thicknesses. Figures 6-1(a), (b), and (c) show the changes in the refractive index ($\Delta n$) and that of the thickness in samples C to E, respectively, induced by the irradiation of photons, with an energy density of 100 mJ/cm$^2$ per pulse and a pulse frequency of 10 Hz, from the KrF excimer laser. For samples A and B in which the nitrogen content is less
than 6.0 atomic %, it was not possible to measure $\Delta n$ by ellipsometry at least up to the irradiation of $2.5 \times 10^5$ pulses. The induced refractive index $\Delta n$ obtained for sample C is $\sim +1.5 \times 10^{-2}$ with the irradiation of $2.5 \times 10^5$ pulses [shown in Fig. 6-1(a)], and the one for D is $\sim +4.3 \times 10^{-2}$ with the irradiation of $1.5 \times 10^4$ pulses [Fig. 6-1(b)], while the one for E is $\sim +6.2 \times 10^{-2}$ with the irradiation of $1.8 \times 10^3$ pulses [Fig. 6-1(c)]. At the same time, the thickness decreases by 2.5, 5.3, and 5.6 nm in samples C to E, respectively.

Figure 6-2 shows the average index change induced by one pulse of the KrF excimer laser, $\Delta n$/pulse, as a function of the nitrogen content. As the nitrogen content increases, the value of $\Delta n$/pulse increases abruptly from $6.0 \times 10^{-8}$ observed in sample C to $3.4 \times 10^{-5}$ in sample E. This result clearly indicates that the UV sensitivity of $a$-$\text{SiO}_x\text{N}_y$:H becomes higher with a larger nitrogen content.

The ESR measurements were carried out for the samples irradiated by photons under the same conditions. Figures 6-3 and 6-4 show the ESR spectra and the densities of paramagnetic centers induced by the photon irradiation, respectively. Note that the spectra shown in Fig. 6-3 are those obtained after the photon irradiation of the aforementioned numbers of pulses, i.e., $2.5 \times 10^5$, $1.5 \times 10^4$, and $1.8 \times 10^3$ pulses for samples C to E, respectively, and that the
densities shown in Fig. 6-4 are the averaged densities of paramagnetic defects induced by one pulse. The induced paramagnetic centers are attributable to silicon dangling bonds (Si–DBs).

Fabrication of a diffraction grating was performed on sample D using a phase mask made of a high quality fused silica plate transparent to the KrF excimer laser. The phase mask has a one-dimensional periodic surface-relief structure with a square-shaped cross section. The photons to fabricate the grating are from the KrF excimer laser and their energy density, pulse frequency, and the irradiation time were 310 mJ/cm² per pulse, 10 Hz, and 1 h, respectively. Figure 6-5 shows the surface of the grating observed by a scanning electron microscopy (SEM). A clear square-toothed pattern with periodicity of around 1 µm can be observed. Furthermore, a Fraunhofer diffraction pattern was successfully observed when a He–Ne laser beam was injected to the surface of this diffraction grating with an incidence angle of 75°. The periodicity of the square-toothed pattern on the grating can be estimated from the Fraunhofer diffraction pattern using the equation:

$$\sin \phi = -\sin \theta + \frac{m\lambda}{d}, \quad (6-1)$$

where \(\lambda\) is the wavelength, \(d\) the periodicity of the square pattern, \(\theta\) the
incidence angle, $\phi$ the diffraction angle, and $m$ the order of diffraction. The estimated periodicity is around 1 $\mu$m, which agrees with the SEM image. This simply demonstrates that the present $a$-SiO$_x$N$_y$:H can be processed by UV photon irradiation.

### 6.4. DISCUSSION

The induced refractive index change shown in Fig. 6-1 is large enough to fabricate waveguides or gratings.$^{1,5,8,16}$ Moreover, as shown in Fig. 6-2, the photosensitivity of $a$-SiO$_x$N$_y$:H can be easily controlled by the nitrogen content. To search for the best fabrication condition, the generation mechanism of the index change should be clarified. It is well known that there are two origins of the index increase, i.e., the densification of the material$^{14,17-20}$ and the paramagnetic defects.$^{21-24}$ As shown in Fig. 6-1, the thickness decreases in a manner opposite to the refractive index, indicating that the films are densified by the photon irradiation. The effect of densification on the index change was estimated using the Lorentz-Lorenz equation,$^{25,26}$ by assuming that the compaction occurred only in the direction of the thickness, since the estimation of the compaction in the surface direction was impossible. The contribution of
the densification to the induced index change turns out to be 98, 87, and 70 \% for samples C to E, respectively, as shown in Fig. 6-6. The densification obviously plays a major role in the increase of the refractive index.

Next, the effect of paramagnetic defects is discussed. The refractive index change due to the absorption increase can be in principle estimated using the Kramers-Kronig relation.\(^{21}\) However, it is virtually impossible to obtain the sample’s absorption spectrum in the UV region due to strong absorption by the silicon substrate. Therefore, we tried to use the following Smakula formula:\(^{27}\)

\[
Nf = 0.87 n \alpha \omega / \left( n^2 + 2 \right)^2, \tag{6-2}
\]

where \(n\) is the refractive index, \(\alpha\) the absorption coefficient in cm\(^{-1}\) at the peak of the absorption band, \(\omega\) the full width at half maximum (FWHM) in eV, \(N\) the defect density in cm\(^{-3}\), and \(f\) is the oscillator strength. As mentioned above, it is impossible to estimate the FWHM of the absorption due to the paramagnetic defects. The observed paramagnetic defects shown in Fig. 6-3 are solely Si–DBs. As a typical Si–DB, the \(E'\) center that has an absorption band at 5.8 eV is well-known. If these Si–DBs are assumed to be \(E'\) centers, the absorption coefficient induced in each sample by the paramagnetic defects can be calculated, since the oscillator strength and FWHM of the absorption at 5.8
eV are known.\textsuperscript{28} The value of refractive index change induced by the paramagnetic defects can then be calculated using the Kramers-Kronig relation. The contribution of the paramagnetic defects to the index change was thus estimated to be 4.3 % for sample C, 7.4 % for sample D, and 7.7 % for sample E, as shown in Fig. 6-6. The induced defects do not play a significant role in the increase of the refractive index. The fact that the sum of the two contributions is not equal to 100 % is likely to be simply due to the inaccuracies of the ellipsometry and ESR measurements.

6.5. CONCLUSION

The photo-induced refractive index change in hydrogenated amorphous silicon oxynitride films with different nitrogen contents prepared by plasma-enhanced chemical vapor deposition was investigated. The index change induced by one pulse of the KrF excimer laser increases abruptly as the nitrogen content increases from 7.0 to 9.6 atomic %, whereas the observable index change is not induced in the films with nitrogen contents less than 6.0 atomic %. It is confirmed that the photorefractivity is due mainly to the densification, and that the role of the induced defects is small. It is also
demonstrated that the photorefractivity can be utilized for the fabrication of optical gratings.
References for Chapter 6


9 E. M. Dianov, K. M. Golant, R. R. Khrapko, A. S. Kurkov, and A. L. Tomashuk,


27 A. Smakula, Z. Phys. 59, 603 (1930).

TABLE 6-1. Ratios of gas flow rates, elemental compositions, and thicknesses of $\alpha$-SiO$_x$N$_y$:H films studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas flow rate $\text{SiH}_4/(\text{N}_2\text{O}+\text{N}_2)$</th>
<th>Composition (atomic %)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1.0 \times 10^{-2}$</td>
<td>35  62  3.6</td>
<td>117.3</td>
</tr>
<tr>
<td>B</td>
<td>$1.7 \times 10^{-2}$</td>
<td>35  59  6.0</td>
<td>117.3</td>
</tr>
<tr>
<td>C</td>
<td>$2.4 \times 10^{-2}$</td>
<td>35  57  7.0</td>
<td>117.4</td>
</tr>
<tr>
<td>D</td>
<td>$3.0 \times 10^{-2}$</td>
<td>37  56  7.7</td>
<td>111.9</td>
</tr>
<tr>
<td>E</td>
<td>$3.7 \times 10^{-2}$</td>
<td>38  53  9.6</td>
<td>112.3</td>
</tr>
</tbody>
</table>
FIG. 6-1. Changes in the refractive index and the thickness in samples C (a), D (b), and E (c), induced by irradiation of photons from the KrF excimer laser. The solid and open circles indicate the refractive index and the thickness, respectively.
FIG. 6-2.  Relation between the average refractive index change induced by one pulse of the KrF excimer laser and the nitrogen content.
FIG. 6-3. The ESR spectra obtained for samples C (a), D (b), and E (c), induced by the photon irradiation of the KrF excimer laser.
FIG. 6-4. Average density of paramagnetic defects induced by one pulse of the KrF excimer laser.
FIG. 6-5. A SEM image of the surface of a diffraction grating fabricated by the photon irradiation through a phase mask. A square-toothed pattern with periodicity of around 1 µm is seen. Each pattern consists of two bands with a nearly similar width of 0.5 µm. They are slightly different in color, and the darker one is a dented region densified by the irradiation.
FIG. 6-6. Comparison of the contribution to the photo-induced refractive index increase between the densification (open bars) and the absorption due to paramagnetic centers (solid bars). Letters below the abscissa are the sample names.
Summary

To conclude this thesis, important results obtained in this research are summarized here.

Chapter 2

Photoluminescence (PL) measurements were performed on a series of hydrogenated amorphous silicon oxynitride \((a\text{-SiO}_x\text{N}_y\text{:H})\) and silicon nitride \((a\text{-SiN}_z\text{:H})\) films with different nitrogen contents deposited by plasma-enhanced chemical vapor deposition. Characterization of the PLs was carried out by investigating the PL band shape and the recombination process of photogenerated carriers. The PLs in the two materials have many similarities, and both are considered to be due to the recombination between localized band-tail states associated with Si–N bonds. From further analyses on the PL decay process, the recombination was found to consist of two processes, namely, an exciton-like recombination process and a radiative tunneling recombination process.
The PL peak energy becomes higher and the width of the PL spectrum becomes wider if the abundance ratio of (nitrogen + oxygen) or that of nitrogen increases. This is caused by the increase in the band-gap energy and the increase in the width of band-tail states induced by the presence of nitrogen and oxygen. The width of band-tail states or the degree of structural inhomogeneity is smaller in $a$-$\text{SiO}_x\text{N}_y$:H than in $a$-$\text{SiN}_z$:H. It is considered that the presence of oxygen atoms relieves the internal stress.

Chapter 3

The effects of thermal annealing on the band-tail PL and the density of silicon dangling bonds (Si–DBs) in $a$-$\text{SiO}_x\text{N}_y$:H and $a$-$\text{SiN}_z$:H films were investigated. 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 $a$-$\text{SiO}_x\text{N}_y$:H films with lower nitrogen contents (N/O = 0.06, 0.10, and 0.12). In contrast, it decreases abruptly on annealing at temperatures above 500 °C for $a$-$\text{SiO}_x\text{N}_y$:H with higher nitrogen contents (N/O = 0.14 and 0.18) and $a$-$\text{SiN}_z$:H films. The density of Si–DBs depends on the annealing temperature in a manner opposite to that of the PL intensity in the
entire annealing temperature region from room temperature (= not annealed) to 900 °C. The obtained results can be explained well by a theoretical analysis, in which the dangling bonds are assumed to act as the quenching center. As already mentioned in Chapter 2, it is considered that the main recombination channel is thermalization of electrons into band-tail states followed by either radiative recombination or tunneling to defect centers and nonradiative recombination. It is considered from infrared absorption spectroscopy that the precursor of Si–DBs is the Si–H bond present near Si–N bonds. Hydrogen is released at temperatures above 500 °C from Si–H bonds, resulting in a large number of Si–DBs that quench the band-tail PL in $a\text{-SiO}_{x}N_{y}:H$ and $a\text{-SiN}_{z}:H$ films.

Chapter 4

Electrical conduction at high fields was examined on a series of $a\text{-SiO}_{x}N_{y}:H$ and $a\text{-SiN}_{z}:H$ films with different nitrogen contents. The conduction is considered to be attributable to the Poole-Frenkel (PF) emission in the two materials. The energy depth of the PF sites and its dependence on the sample’s chemical composition are quite similar between the two materials,
which indicates that the PF sites in the present two kinds of samples are due to the same origin regardless of the presence of oxygen. Moreover, the energy depth of the PF sites increases monotonically from 0.85 to 1.21 eV with an increase in the abundance ratio. These results are consistent with the conclusion obtained from PL analyses in Chapter 2 that $a$-SiO$_x$N$_y$:H and $a$-SiN$_z$:H possess similar localized band-tail states associated with Si–N bonds and the width of these localized states becomes broader with an increase in the abundance ratio.

Chapter 5

The mechanism of electroluminescence (EL) in $a$-SiO$_x$N$_y$:H films was investigated. The luminescence can be observed only in the samples annealed at high temperatures. It depends on the direction of the applied electric field, and its peak photon energy decreases from 2.3 to 1.8 eV as the nitrogen content increases. The fact that both the EL and the band-tail PL are observed in the same samples with a similar tendency of peak shift suggests that the same radiation process is involved in the two luminescence mechanisms. However, the carriers responsible for the EL were clarified in Chapter 4 to be barely
transported via the PF sites, holding the minimum necessary energy, whereas the electrons responsible for the PL were excited by UV photons to a level much higher than the bottom of the conduction band. For this reason, the energy of photons emitted in EL coincides with the lowest energy of photons emitted in PL. The injected electrons and holes are transported through the localized PF sites to luminescence centers where they recombine with each other, releasing the excess energy. This is considered to be the mechanism of EL. These obtained results support the conclusions drawn in Chapters 2 and 4.

Chapter 6

The photo-induced refractive index change in $a$-$\text{SiO}_x\text{N}_y$:H films with different nitrogen contents was investigated. The index change induced by one pulse of the KrF excimer laser increases abruptly as the nitrogen content increases from 7.0 to 9.6 atomic %, whereas the observable index change is not induced in the films with nitrogen contents less than 6.0 atomic %. The thickness decreases in a manner opposite to the refractive index, indicating that the films are densified by the photon irradiation. From the estimation of the contribution of densification to the index change using the Lorentz-Lorenz
equation and that of the absorption increase induced by Si–DBs using the Kramers-Kronig relation and the Smakula formula, the photorefractivity was found to be due mainly to the densification. Fabrication of optical gratings using the photorefractivity was also demonstrated.
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