# Visible photoluminescence in hydrogenated amorphous silicon grown in microwave plasma from SiH<sub>4</sub> strongly diluted with He

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Room temperature visible photoluminescence (PL) of wide-band gap hydrogenated amorphous silicon (*a*-Si:H) thin films prepared in SiH<sub>4</sub> microwave plasma strongly diluted with He is reported. Films were characterized by means of optical and infrared absorption, hydrogen thermal desorption, and Raman scattering. The band gap of *a*-Si:H films varies within the interval 2.0–2.2 eV, corresponding PL maxima are located at 1.4–1.6 eV. The highest PL intensity was observed in samples with a position of H–Si–H symmetric stretching vibration of the  $-(SiH_2)_n$ – units near the frequency of 2100 cm<sup>-1</sup>. The strong evidence for two distinct types of PL processes is presented: one being linked with oligosilanes and the second one attributed to electron-hole recombination in tail states. © 1999 American Institute of Physics. [S0021-8979(99)02315-4]

## I. INTRODUCTION

The need for stable light-emitting silicon-based material persists despite the extensive effort devoted recently to porous silicon (PS). Although PS exhibits strong room temperature visible photoluminescence (PL) and electroluminescence, aging and operational instabilities of PS devices leave open the question about the most suitable silicon-based material for optoelectronics. Among the possible candidates, hydrogenated amorphous silicon (a-Si:H) could play an important role.<sup>1</sup> The optical band gap of conventional a-Si:H is 1.7-1.8 eV and its room temperature PL is very weak with a maximum in the near infrared (IR) region. The applicability of a-Si:H would increase if this material exhibits sufficiently bright room temperature visible PL. Several nonconventional preparation techniques of a-Si:H with PL in the visible region have already been reported. Wolford, Reimer, and Scott<sup>2</sup> observed efficient visible PL from a-Si:H prepared by homogeneous chemical vapor deposition (CVD) from  $SiH_4$ (silane) or by radio frequency (rf) plasma CVD from Si<sub>2</sub>H<sub>6</sub> (disilane) at a low substrate temperature. Furukawa and Matsumoto<sup>3</sup> prepared a-Si:H films by rf plasma CVD from disilane and the visible PL was tentatively attributed to the presence of oligosilane<sup>4</sup>  $-(SiH_2)_n$  - units (n<11). Visible PL, speculatively assigned to oligosilane units was also observed by Akiyama, Ogiwara, and Ogawa,<sup>5</sup> who used rf glow discharge silane plasma diluted with He. Oligosilane bridges were also proposed to explain the origin of visible PL of PS.<sup>6</sup> In this communication, we report on room temperature visible PL from wide gap (>2.0 eV) a-Si:H samples prepared in microwave (MW) plasma of SiH<sub>4</sub> strongly diluted with He under electron cyclotron resonance (ECR) conditions.<sup>7</sup> To our knowledge, this is the first observation of visible PL from *a*-Si:H prepared from He diluted SiH<sub>4</sub> by the MW ECR PE CVD method. Moreover, we present strong experimental evidence, based on the observation of PL intensity as a function of characteristic IR vibration frequencies, that visible PL in wide-gap *a*-Si:H is mainly due to the presence of oligosilane units, indeed.

#### **II. EXPERIMENT**

Samples of *a*-Si:H were deposited on crystalline silicon wafers for IR absorption measurements and on a glass (Corning 7059) substrate for optical measurements. The MW power of 200 W from a Hitachi 2M107A magnetron (frequency of 2.45 GHz) was applied at the chamber pressure of about 0.1 Pa. Silane-gas-flow rate of 1 sccm was used, the He-flow rate varied in the interval 25-40 sccm. The substrate temperature was kept within the interval 110-170 °C. Samples were used for measurements without any post-treatment.

Optical and IR absorption, hydrogen thermal desorption, Raman scattering, and PL were measured for 13 samples. To investigate PL properties as a function of temperature, samples were fixed in a variable temperature cryostat. PL spectra were excited by the 488 nm Ar<sup>+</sup> laser line (P= 30 mW cm<sup>-2</sup>) and measured in the temperature range 75– 295 K. PL was analyzed in a 20 cm monochromator (Jobin Yvon HT20) and detected with a S1-type photomultiplier tube. The signal was processed with a photon counter. PL spectra were corrected for the spectral response of the experimental setup. IR absorption spectra were measured at

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FIG. 1. Tauc plots of a-Si:H films VP6, WP2, XP3, UP3, and XP1. The straight line indicates the fit for sample XP1.

room temperature by means of the Fourier-transform infrared apparatus Nicolet IMPACT 400 in the normal transmission mode.

Optical absorption coefficient values at room temperature were determined from transmission measurements and the values of the reflectance coefficients of the air-film  $(R_1)$ , film-substrate  $(R_2)$ , and substrate-air  $(R_3)$  interfaces according to the procedure described in Ref. 8. Using the values  $R_1=0.33$ ,  $R_2=0.17$ , and  $R_3=0.04$  we obtained absorption spectra and from the Tauc plots (plots of  $(\alpha h \nu)^{1/2}$  vs  $h \nu$ ) the values of the band gap were determined. Raman spectra were excited with the 514.5 nm line of an Ar<sup>+</sup> laser at a power of ~100 mW (spectral width ~3.3 cm<sup>-1</sup>). Thermal desorption spectroscopy (TDS), a method based on the mass spectrometry of thermally evolved gases from the studied samples, was used to evaluate the total hydrogen content in our *a*-Si:H films and also to provide information about hydrogen bonding configuration inside the samples.

#### **III. RESULTS**

The optical absorption measurements of *a*-Si:H give the primary information about changes of valence and conduction bands of amorphous Si due to the incorporation of hydrogen into the amorphous network. In Fig. 1 there are Tauc plots for samples VP6, WP2, XP3, UP3, and XP1. The band gaps are in the interval 2.0–2.2 eV, the gap opening with respect to the standard device grade *a*-Si:H amounts 0.2–0.4 eV.<sup>9</sup>

IR spectra represent an important source of information about hydrogen bonding in *a*-Si:H. Figure 2 shows IR absorption spectra for the same series of *a*-Si:H films. Spectra are ordered in the direction of the increasing wave number of the vibration in the vicinity of 2090 cm<sup>-1</sup> (from 2084 cm<sup>-1</sup> for the VP6 sample to 2111 cm<sup>-1</sup> for the XP1 sample). The peak located in the vicinity of 2090 cm<sup>-1</sup> is assigned to the SiH<sub>2</sub> and  $-(SiH_2)_n$  stretching modes.<sup>3,10</sup> The blueshift of this peak with the increasing number of the  $-SiH_2$ - units is usually explained by the increase of the effective electronegativity due to the  $-(SiH_2)_n$  formation. The symmetric stretching vibration of the samples with the strongest PL



FIG. 2. IR absorption spectra of *a*-Si:H films VP6, WP2, XP3, UP3, and XP1.

appears at 2100 cm<sup>-1</sup> which almost coincides with the stretching vibration of the  $-(SiH_2)_2-$  unit.<sup>3</sup> It should be stressed that the standard (narrow-band gap) *a*-Si:H exhibits only a vibration of the mode peaked at 2000 cm<sup>-1</sup>, associated with Si–H vibrations. Appearance of visible PL is thus accompanied by the shift of the stretching vibration peak from 2000 to 2084–2110 cm<sup>-1</sup>. This indicates an important role of oligosilanes in the PL mechanism.<sup>5</sup>

Another source of information on hydrogen bonding in our *a*-Si:H films was TDS. An example of a thermal desorption curve (sample VP2) is in Fig. 3. There are two desorption peaks—one with a maximum at about 300 °C, the other with a maximum in the vicinity of 530 °C. For comparison there is also depicted a desorption curve of standard device grade *a*-Si:H with only a high temperature peak (maximum at about 470 °C). This observation represents the second proof for different hydrogen bonding in standard and our He-diluted *a*-Si:H films. The low temperature peak has been



FIG. 3. Thermal desorption curve for a-Si:H film VP2.

TABLE I. Deposition parameters of *a*-Si:H films VP6, WP2, XP3, UP3, XP1, and characterization by means of optical (Tauc gaps) and IR spectroscopy (position of the H–Si–H symmetric stretch vibration of  $-(SiH_2)_n$ -units and H content), thermal desorption spectrometry (H content), and normalized spectrally integrated PL intensities  $I_{PL}$ .

	VP6	WP2	Sample XP3	UP3	XP1
Deposition parameters					
SiH <sub>4</sub> flow rate [sccm]	1	1	1	1	1
He flow rate [sccm]	40	35	25	35	35
Deposition temperature [°C]	170	145	140	110	125
Microwave power [W]	200	200	200	200	200
Sample thickness $[\mu m]$	1.55	1.58	2.20	1.88	0.99
Sample characterization					
Tauc gap $E_{\text{Tauc}}$ [eV]	2.07	2.14	2.03	2.13	2.09
$\nu_{\mathrm{H-Si-H}}  [\mathrm{cm}^{-1}]$	2084	2099	2100	2103	2111
H content [at. %]	20	19	13	51	26
$I_{\rm PL}$ [r.u.]	0.06	0.51	1.00	0.18	0.25

attributed to debonding of  $-SiH_2-$  in internal surfaces, cracks, or between columns in *a*-Si:H, the high temperature peak comes from the bulk of the films.<sup>11,12</sup> Characterization parameters of our selected sample set are summarized in Table I.

The most important parameter of our *a*-Si:H films from the point of view of potential applications is its PL. Figure 4 displays room temperature PL spectra of samples VP6, WP2, XP3, UP3, and XP1. PL spectra are corrected for the spectral response of our experimental setup and normalized to the absorbed excitation power (determined by means of the sample thickness and the value of the absorption coefficient at the excitation wavelength). Room temperature PL from most luminescing samples is visible with the naked eye. The PL maxima were centered in the interval 800–900 nm (1.4– 1.6 eV), similarly to PS, but the integral PL intensity of wide gap *a*-Si:H is about two orders of magnitude lower under otherwise identical experimental conditions.<sup>13</sup>



What is the origin of the PL from our MW ECR PE CVD samples of *a*-Si:H prepared from SiH<sub>4</sub> under conditions of strong He dilution? From the earlier mentioned coincidence of the symmetric stretching vibration wave number of the samples exhibiting the maximum of PL intensity and that of the  $-(SiH_2)_2$ - unit, we can suppose that this visible PL is related to the deexcitation of the oligosilane units and/or their local environment. Let us examine this correlation more closely. For this purpose we have depicted the dependence of the spectrally integrated PL on the wavenumber of the symmetric stretching mode near 2090 cm<sup>-1</sup> for all our samples. As we can see in Fig. 5, there is a surprisingly strong correlation between the integral PL intensity and the



FIG. 4. PL spectra of *a*-Si:H films VP6, WP2, XP3, UP3, and XP1 at room temperature; excitation wavelength 488 nm, excitation power 30 mW cm<sup>-2</sup>.



FIG. 5. Correlation between the integral PL intensity and the symmetric H–Si–H stretching vibration of  $-(SiH_2)_n$  groups for all the samples. Samples presented in Table I are indicated by label.



FIG. 6. Raman spectrum of sample UP3 excited by Ar<sup>+</sup> laser line 514.5 nm.

wavenumber corresponding to the single  $-(SiH_2)_2$ - unit and a vague correlation with other oligosilane units (forming rather "noisy" background in Fig. 5). Another argument in favor of this interpretation are the results from hydrogen thermal desorption measurements. It follows from Fig. 3 that in our *a*-Si:H films there is a large content of oligosilane hydrogen bonding with respect to the device grade *a*-Si:H. On the basis of these observations we can thus conclude that oligosilane units are responsible for observed variations in the integral PL intensity from our samples.

On the other hand, silicon nanocrystallites could be also responsible for both the gap widening and the visible PL—they have already been observed in *a*-Si:H from MW ECR PE CVD of SiH<sub>4</sub> diluted with Ar by Choi *et al.*<sup>14</sup> In order to address the possible role of Si nanocrystallites in our *a*-Si:H films, Raman spectra were measured. Figure 6 depicts a typical Raman spectrum of our films (sample UP3). We can see only a broad band centered at about 480 cm<sup>-1</sup> and no resolved peak at 520 cm<sup>-1</sup> characteristic for crystalline Si. We can therefore exclude the silicon nanocrystallites as luminescence centers in our samples.

An alternative mechanism for radiative deexcitation in a-Si:H is an electron-hole tunneling from tail states.<sup>15</sup> In order to clarify the role of this recombination mechanism in our a-Si:H samples, we measured the temperature dependence of PL within the temperature range of 75–295 K. Assuming the density of states close to the band edges is expressed in terms of exponential band tails, the thermal quenching of the PL intensity I(T) is governed by the formula<sup>15,16</sup>

$$\ln[I_0/I(T) - 1] = T/T_0, \tag{1}$$

where  $T_0$  is a characteristic temperature (see details in Refs. 1, 15, and 16). Figure 7 shows a plot of the integral PL intensity as well as a plot of  $(I_0/I(T)-1)$  versus *T* for sample WP2. For temperatures T>120 K, the temperature dependence follows closely the theoretical behavior given by Eq. (1). From the fitting procedure, the value of  $T_0$  was determined. The value  $T_0=62\pm 2$  K for the WP2 sample is close to the value of 64 K obtained previously for a wide band gap *a*-Si:H sample prepared from a He diluted SiH<sub>4</sub> rf glow discharge plasma.<sup>9</sup> Therefore, we can anticipate that



FIG. 7. Temperature dependence of the spectrally integrated PL intensity for sample WP2.

also recombination through the tail states is partially responsible for the observed PL, even though discrepancies exist concerning the PL spectral shift with temperature<sup>9</sup> and also concerning PL lifetime measurements.<sup>17</sup>

An open question remains the relative contribution of these two radiative channels in the PL mechanism. At room temperature, we have observed a different ordering of the PL intensities in our sample set to that at T=75 K, and we suppose therefore that the thermal quenching can be sample dependent. This question requires more data and further study is in progress.

### V. SUMMARY

*a*-Si:H samples deposited from a silane plasma strongly diluted with He by means of the MW ECR PE CVD method exhibit room temperature visible PL. Maximum PL brightness correlates with the IR stretching vibration mode in the close vicinity of  $2100 \text{ cm}^{-1}$  corresponding to the  $-(\text{SiH}_2)_2$ -unit. On the basis of the IR measurements, hydrogen thermal desorption, and PL temperature dependence in the interval 120-300 K, we assume that both the deexcitation linked with the presence of oligosilane  $-(\text{SiH}_2)_n$ - units and the electron-hole recombination in localized tail states in the *a*-Si:H band gap are involved in the PL mechanism.

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<sup>&</sup>lt;sup>4</sup>We use in this article the term oligosilane for  $-(\text{SiH}_2)_n$  when  $n \le 15$  although in physical journals the term polysilane prevails (also in case when n=2). Our notation takes into account IUPAC recommendations [A. D. Jenkins, P. Kratochvíl, R. F. T. Stepto, U. W. Suter, Pure Appl. Chem. **68**, 2287 (1996)] according to which properties of oligomers (contrary to polymers) vary with the removal of one or few of the units. The blueshift of H–Si–H stretching mode wavenumber with number of – SiH<sub>2</sub>– units ( $n \le 15$ ) is an example when a physical property depends on

the number of "monomers" and therefore in these cases the term oligomer is more appropriate.

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