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Description	



## 30 **1. Introduction**

31 Hydrogenated amorphous silicon (a-Si:H) films have received considerable  
32 interest because of their immense potential for various application in large-area  
33 electronic devices such as solar cells and thin-film transistors [1,2]. To date, a-Si:H  
34 films are deposited using expensive vacuum-based equipment and high amounts of  
35 dangerous and expensive silicon-based gases. These are factors making cost reduction  
36 and large-area film deposition difficult. If a-Si:H films can be deposited using liquid  
37 state silicon materials and inexpensive vacuum-free equipments, this situation might  
38 change drastically. Previously, we have reported on synthesis of silicon precursor  
39 solutions consisting of polydihydrosilane ( $-(\text{SiH}_2)_n-$ ) and an organic solvent and  
40 demonstrated the realization of solution-processed (Sol.P) poly-silicon films [3] using  
41 spin-coat and ink-jet methods. Furthermore, we have demonstrated the Sol.P a-Si:H  
42 solar cell using spin-coat method [4]. The fabrication process involved the pyrolysis of  
43 polydihydrosilane followed by a spontaneous formation of a three-dimensional silicon  
44 network releasing a high amount of gases ( $\text{H}_2$  and  $\text{SiH}_x$ ). Pyrolysis experiments of  
45 silicon containing polymers with a purpose to fabricate efficient emitters in the UV to  
46 IR spectral range for light emitting diodes have been reported recently [5]. However,  
47 systematic studies for the Sol.P a-Si:H films were not reported so far. The aim of the  
48 present research is the study of the pyrolytic transformation from a polydihydrosilane  
49 liquid film to an a-Si:H solid film by changing the pyrolysis temperature  $T_p$  from 270 to  
50 420 °C employing a fixed heating time of 15 min. To examine the pyrolytic  
51 transformation, thermal gravimetry (TG) and differential thermal analysis (DTA),  
52 Raman scattering, Fourier-transform infrared spectroscopy (FT-IR), and secondary ion  
53 mass spectroscopy (SIMS) measurements are applied. To characterize the electrical  
54 properties of Sol.P films, transmittance and reflectance spectroscopy in the UV–visible  
55 range (UV–VIS TR), electron spin resonance (ESR), and photoconductivity/dark  
56 conductivity measurements are carried out.

57

## 58 **2. Experiment**

### 59 **2.1 Preparation of Sol.P films**

60 Polydihydrosilane was synthesised by a photo-induced ring-opening

61 polymerization process of cyclopentasilane ( $\text{Si}_5\text{H}_{10}$ ;CPS) [6] employing the Kipping  
62 method [7,8]. The polydihydrosilane dissolved in cyclooctane at the concentration of  
63 10–20 wt. % was spin-coated on quartz or silicon substrates under similar conditions as  
64 in previous work [9] in which we explored the stability of polydihydrosilane liquid  
65 films on various solid substrates. The pyrolysis of the polydihydrosilane was carried out  
66 at  $T_p = 270$  to  $420$  °C using a fixed heating time of 15 min. The samples were set on a  
67 hot plate in a glove box filled with nitrogen gas in order to avoid reaction with air, as  
68 CPS and polydihydrosilane easily ignite in air. The oxygen and the dew point in the  
69 glove box were less than 0.5 ppm and  $-75$  °C, respectively.

70

## 71 **2.2 Characterization**

72 The thermal analysis of polydihydrosilane was carried out using TG/DTA  
73 (EXTAR TGDTA6200 by Seiko Instruments Inc.) which was installed in the glove box.  
74 Inactive  $\text{Al}_2\text{O}_3$  was selected as a sample pan. Approximately 20–30 mg of  
75 polydihydrosilane was added dropwise on the pan. To prevent as much oxidation as  
76 possible during the measurement, the purge gas was purified via a gas purifier (by  
77 Pureron Japan Co. Ltd.) to obtain oxygen concentrations  $< 1$ ppb, and a relatively high  
78 flow rate of 200 mL/min was employed. The polydihydrosilane was heated in the  
79 temperature range between 25 and 450 °C with the heating rate of 10 °C/min.

80 The low-frequency phonon bands of the a-Si network and the local vibration of the  
81  $\text{SiH}_n$  groups in the network were probed by Raman scattering (Ramascope by  
82 Renishaw) and FT-IR (ALPHA by Bruker Optics), respectively.

83 In addition to IR spectral analysis, SIMS (model-6300 by PHI) was applied to  
84 quantify the hydrogen and oxygen content. A 3.0 KeV  $\text{Cs}^+$  primary ion beam with an  
85 impact angle of  $60^\circ$  with respect to surface normal was used and negative secondary  
86 ions were detected. Charge build-up during profiling was compensated for by use of an  
87 electron gun with an intensity of 0.75 KeV.

88 To determine the optical gap  $E_g$  and spin density  $N_S$ , we used UV-VIS TR  
89 (FilmTek-3000 by Scientific Computing International) and ESR (JES-FA100 by JEOL  
90 Ltd.), respectively. An AM-1.5G solar simulator (WXS-50S by WACOM Electric Co.  
91 Ltd.) with an intensity of  $100\text{mW}/\text{cm}^2$  was adopted for the illuminated current and

92 voltage measurement. The conductivity was measured on a coplanar configuration of  
93 250  $\mu\text{m}$  gap width, using aluminum contacts for samples. The dark conductivity  $\sigma_d$  and  
94 the photoconductivity  $\sigma_p$  were measured at room temperature for the films prepared at  
95 various  $T_p$ .

96

### 97 **3. Results and discussion**

#### 98 **3.1 Photographic image of Sol.P films and TG/DTA results**

99 Fig. 1 shows photographic image of Sol.P films with a thickness of 50 nm, coated  
100 on quartz substrate  $2 \times 2 \text{ cm}^2$  in size and pyrolysed at temperatures between  $T_p < 270$   
101 and  $T_p = 420 \text{ }^\circ\text{C}$ . The films prepared at  $T_p \leq 270 \text{ }^\circ\text{C}$  are transparent, and a drastic change  
102 from transparent to yellow color appears when  $T_p$  is increased from 270 to 300  $^\circ\text{C}$ . This  
103 change in color can be attributed to a reduction of  $E_g$  from that of polydihydrosilane of  
104 6.5 eV [10] to lower values. The transparency of films prepared at  $T_p \leq 270 \text{ }^\circ\text{C}$   
105 corresponds to an insulator material whereas the yellow and brown color of films  
106 pyrolysed at  $T_p = 300\text{--}420 \text{ }^\circ\text{C}$  indicates the presence of semiconductor materials. From  
107 this, a transformation from a polymer to an amorphous semiconductor can be concluded  
108 to occur near  $T_p = 270 \text{ }^\circ\text{C}$ .

109 To study the pyrolysis directly, TG and DTA measurements of polydihydrosilane  
110 were carried out. Fig. 2 shows the TG signal (bold solid line) and the DTA signal (thin  
111 solid line) as a function of heating temperature  $T_h$ . Also shown is the temperature/time  
112 derivative DTG (dashed line) of the TG signal.

113 The TG data indicate a weight loss of about 58 % by heating up to 360  $^\circ\text{C}$  and  
114 consequently only 42 % of the material remained in the form of hydrogenated  
115 amorphous silicon. In agreement with thermal desorption spectroscopy (TDS)  
116 measurements [3] one may assume that the weight reduction is caused by desorption of  
117  $\text{H}_2$  and  $\text{SiH}_x$ . According to the DTG curves the major weight loss takes place at  $T = 100$ ,  
118 200, and 300  $^\circ\text{C}$ . A broad exothermal peak is found in the DTA signal extending from  
119 80 to 450  $^\circ\text{C}$  with a maximum near 320  $^\circ\text{C}$ . These results suggest that the  
120 transformation from a polymer to a cross-linked amorphous silicon network (i.e. Si-Si  
121 bond construction) is particularly active between 300 and 360  $^\circ\text{C}$  and that the  
122 amorphous network becomes more stable at higher temperature.

123

## 124 **3.2 Transformation from polydihydrosilane to a-Si:H film**

125 In 3.2.1, we study  $T_p$ -dependence of Raman spectra of amorphous phonon bands to  
126 confirm the formation of the three-dimensional amorphous silicon network. In 3.2.2 the  
127 quality of Sol.P a-Si:H films (voids and hydrogen/oxygen content) is discussed on the  
128 basis of the infrared microstructure factor [2,11,12] and of the impurity content  
129 measured by SIMS.

### 130 **3.2.1 Raman scattering**

131 Figs. 3(a) and 3(b) show the first-order Raman spectra of the Sol.P films prepared  
132 at  $T_p$  in the range of 270–330 °C and 330–420°C, respectively. The Raman data were  
133 averaged over 10 measurements for each sample in a back scattering geometry using a  
134 He-Ne laser line (633 nm). In Fig. 3(a), typical phonon bands of a-Si:H [13,14] are  
135 visible at  $T_p = 330$  °C whereas films prepared at  $T_p = 270$  and 300 °C show no clear  
136 peaks corresponding to the amorphous silicon phonon bands. In literature, the a-Si:H  
137 Raman phonon bands at 476, 387, 288, and 154  $\text{cm}^{-1}$  have been assigned to transverse  
138 optical (TO), longitudinal optical, longitudinal acoustic, and transverse acoustic band,  
139 respectively. Fig. 3(b) shows the Raman spectra of the Sol.P films prepared at  $T_p = 330$ ,  
140 360, 390, and 420 °C, where the intensity was normalized to the same TO height. The  
141 full width at half maximum (FWHM) of the TO band versus  $T_p$  is plotted in Fig. 3(c).

142 The appearance of amorphous silicon phonon bands for films prepared at  $T_p \geq$   
143 330 °C suggests construction of the three-dimensional amorphous silicon network near  
144 the temperature  $T_p = 330$  °C. Indeed, the Raman spectra for the Sol.P films prepared at  
145  $T_p \geq 330$  °C are quite similar to typical Raman spectra for vacuum-processed (Vac.P)  
146 a-Si:H films [13,14]. Thus one may term the Sol.P films prepared at  $T_p \geq 330$  °C Sol.P  
147 a-Si:H films. Our observed FWHM of the TO band in Fig. 3(c) shows a decrease from  
148 80.5 to 71.5  $\text{cm}^{-1}$  when  $T_p$  is increased from 300 to 420 °C. The decrease of the FWHM  
149 indicates the improvement of short-range tetrahedral ordering because of its sensitivity  
150 to the bond-angle fluctuations [14], so that the pyrolysis at  $T_p \geq 330$  °C induces a  
151 modification of the amorphous network from a more distorted to a more ideal  
152 tetrahedral configuration, in addition to the amorphous silicon network construction.

153

### 154 3.2.2 FT-IR and SIMS

155 Figs. 4(a) and 4(b) show the IR absorption coefficient  $\alpha(\omega)$  in the wavenumber  
156 range of 1950–2200  $\text{cm}^{-1}$  and 550–750  $\text{cm}^{-1}$ , respectively, for the Sol.P films prepared  
157 at  $T_p = 270\text{--}420$  °C. The absorption peaks near 2000 and 2070–2090  $\text{cm}^{-1}$  at  $T_p \geq$   
158 360 °C are assigned to the stretching modes of Si-H bonds embedded in bulk material  
159 and to the stretching modes of Si-H/Si-H<sub>2</sub> bonds at void surface, respectively [11]. The  
160 absorption band near 640  $\text{cm}^{-1}$  in Fig. 4(b) is attributed to the Si-H wagging mode [15]  
161 which is known to have a vibrational frequency near 640  $\text{cm}^{-1}$ . Only the sample  
162 prepared at 270 °C deviates significantly from this value. As is seen in Fig. 4(a), the  
163 Si-H stretching modes of our material are all centered near 2080  $\text{cm}^{-1}$  except for the  
164 samples prepared at the rather low temperatures of 270 and 300 °C which show a Si-H  
165 stretching absorption shifted to higher wavenumber.

166 As mentioned above, the 2070–2090  $\text{cm}^{-1}$  peaks at  $T_p \geq 330$  °C are related to the  
167 vibration of Si-H/Si-H<sub>2</sub> bonded on external and internal void surfaces and the 2000  $\text{cm}^{-1}$   
168 peak is attributed to Si-H vibrations in the bulk. Thus one may evaluate the sample  
169 quality by using the infrared microstructure factor  $R$  [2,11,12],

$$170 R = I_{2090}/(I_{2000}+I_{2090}). \quad (1)$$

171 Here,  $I_{2090}$  and  $I_{2000}$  are integrated intensities of each oscillation modes near 2070–2090  
172 and 2000  $\text{cm}^{-1}$ , respectively. From the spectral data in Fig. 4(a), the estimated  $R$  ranges  
173 from 0.91 ( $T_p = 360$  °C) to 0.80 ( $T_p = 420$  °C) whereas it is known that device-grade  
174 Vac.P a-Si:H films show  $R < 0.2$  [11,12] because of the domination of 2000  $\text{cm}^{-1}$  peak.  
175 Large values of  $R$  for our films imply a void-rich structure. Although the origin of peak  
176 shift at  $T_p \leq 330$  °C is not clear, it may be related to the oxidization or the change of  
177 local environment of the Si-H dipole [16,17]. This suggests that the films prepared at  $T_p$   
178  $\leq 330$  °C have quite poor quality.

179 To examine the degree of hydrogenation as well as the oxidation in our Sol.P films,  
180 we determine the hydrogen and oxygen concentration using FT-IR and SIMS  
181 measurements. Fig. 5 shows hydrogen and oxygen content as a function of  $T_p$  in which  
182 the closed circles and squares are, respectively, hydrogen and oxygen content obtained  
183 by SIMS measurement. The open circles show  $N_H/N_{Si}$  by FT-IR in which the density of  
184 silicon is assumed to be  $N_{Si} = 5 \times 10^{22} \text{ cm}^{-3}$ . The density of hydrogen  $N_H$  is evaluated

185 from  $\alpha(\omega)$  in Fig. 4(b) using Eq. (2) with the proportional constant  $A_{640} = 2.1 \times 10^{19}$   
186  $\text{cm}^{-2}$  [18],

$$187 \quad N_H = A_{640} \int \frac{\alpha(\omega)}{\omega} d\omega. \quad (2)$$

188 Since the hydrogen content in polydihydrosilane is 67 at.%, the hydrogen  
189 concentration values of 9.2–10.6 at.% (by SIMS) in films prepared at  $T_p \geq 360$  °C  
190 indicate a remarkable reduction in the hydrogen content during the pyrolysis. The  
191 void-rich structure concluded from the large  $R$  value in films prepared at  $T_p \geq 360$  °C is  
192 presumably due to the three-dimensional shrinkage related to the weight loss. With  
193 regard to oxygen, the high concentration of it for the films prepared at  $T_p \leq 330$  °C  
194 means that the construction of the amorphous silicon network is not dense enough so  
195 that it oxidises rather easily in air.

196

### 197 **3.3 Relationship between TG/DTA and Raman/IR data**

198 In this section we discuss the relationship between the TG/DTA results and the  
199 changes of the Raman and FT-IR spectra with rising preparation temperature and  
200 speculate about the formation of the amorphous silicon network. Our previous TDS  
201 results [3] indicated that Si-Si bonds in polydihydrosilane start to break near 280 °C  
202 followed by breaking of Si-H bonds at near 300 °C. Since the breaking of Si-H bonds in  
203 the polydihydrosilane is necessary for formation of the three-dimensional amorphous  
204 silicon network, this network apparently is forming at temperature exceeding 300 °C.

205 The decrease in the TG curve from 25 to 280 °C and the positive DTA curve in Fig.  
206 2 indicate that the breaking and reconstruction of Si-Si bonds proceeds locally even at  
207 temperatures less than 280 °C. The drastic change of TG (visible in a peak in DTG)  
208 between 270 and 360 °C suggests a release of high amounts of  $\text{H}_2$  and  $\text{SiH}_x$  due to the  
209 thermal decomposition of molecules via the breaking of Si-H and Si-Si bonds. The  
210 broad exothermal peak in DTA near 320 °C likely corresponds to the construction of the  
211 three-dimensional silicon network due to formation of Si-Si bonds and release of  
212 hydrogen. The construction of the three-dimensional amorphous silicon network and the  
213 strong reduction of the hydrogen content are confirmed by the Raman data (Fig. 3) and  
214 by the FT-IR and SIMS results as shown in Fig. 5.

215



## 216 **3.4. Influence of pyrolysis on the electrical properties of Sol.P a-Si:H films**

### 217 **3.4.1 Optical gap**

218 Fig. 6 shows results of absorption measurements in the UV–visible range of Sol.P  
219 films prepared at  $T_p = 300$  to  $420$  °C. The data are depicted in a Tauc plot [19] as

$$220 (\alpha E)^{1/2} = B^{1/2}(E - E_g), \quad (3)$$

221 where  $\alpha$  is the optical absorption coefficient,  $E$  is the photon energy in eV,  $B$  is a  
222 constant, and  $E_g$  is the optical gap (called “Tauc gap”). The fitting procedure yields  $E_g =$   
223  $2.40$ ,  $1.92$ ,  $1.64$ ,  $1.64$ , and  $1.64$  eV for the film prepared at  $T_p = 300$ ,  $330$ ,  $360$ ,  $390$ , and  
224  $420$  °C, respectively, as shown in Fig. 6(b). The parameter  $B$  is found to be  $5.7 \times 10^5$   
225 and  $7.7 \times 10^5$  eV<sup>-1</sup>cm<sup>-1</sup> for  $T_p = 300$  and  $330$  °C, and  $6.7 \times 10^5$  eV<sup>-1</sup>cm<sup>-1</sup> for  $T_p \geq$   
226  $360$  °C. It is known that  $E_g$  in Vac.P a-Si:H films varies with the hydrogen content [2].  
227 Accordingly, the  $T_p$ -dependence of  $E_g$  in Fig. 6(b) can be understood by the  
228 dehydrogenation during pyrolysis as shown in Fig. 5. For  $T_p$  exceeding  $360$  °C the  
229 absorption is no longer dependent on the hydrogen content, and gives  $E_g = 1.64$  eV. This  
230 is consistent with  $E_g = 1.5$ – $1.6$  eV observed in Vac.P unhydrogenated amorphous silicon  
231 films [2,20].

232

### 233 **3.4.2. Conductivity and spin density**

234 Typical values of  $\sigma_d$ ,  $\sigma_p$  and  $N_S$  at room temperature are plotted in Fig. 7 as a  
235 function of  $T_p$ . With rising  $T_p$  from  $300$  to  $330$  °C,  $\sigma_d$  increases slightly, followed by a  
236 drastic decrease at  $T_p = 360$  °C, and attains  $5.1 \times 10^{-11}$  S/cm at  $T_p = 420$  °C, while  $\sigma_p$  is  
237 of the order of  $10^{-7}$  S/cm, except for the minimum at  $T_p = 360$  °C. The value of  $N_S$   
238 starting from  $2.5 \times 10^{16}$  cm<sup>-3</sup> exhibits a maximum in a film prepared at  $T_p = 360$ °C, and  
239 attains  $2.8 \times 10^{17}$  cm<sup>-3</sup> for the high- $T_p$  films. Since the paramagnetic spin density  
240 corresponds to the concentration of dangling bonds which act as a trapping site, the  
241 reduction of  $N_S$  may lead to the increase of  $\sigma_p$  [21]. The increase of  $N_S$  in the range from  
242  $T_p = 300$  to  $360$  °C is attributed mainly to the increase of dangling bonds due to the  
243 breaking of the Si-H and Si-Si bonds. In contrast, the decrease of  $N_S$  in the range from  
244  $T_p = 360$  to  $420$  °C suggests that the high  $T_p$  serves as an annealing effect to reduce the  
245 number of dangling bonds (See also the FWHM data in Fig. 3(c)). A photosensitivity  
246 (i.e. ratio of  $\sigma_p$  to  $\sigma_d$ ) of Sol.P films prepared at  $T_p \geq 360$  °C exhibits the order of  $10^3$ ,

247 whereas that of device-grade Vac.P a-Si:H films show  $10^5$ – $10^6$  [2,22]. This low  
248 photosensitivity indicates a rather poor quality of our films presumably related to the  
249 high value of  $N_S > 10^{17} \text{ cm}^{-3}$  for  $T_p \geq 360$  °C. Note that device-grade Vac.P a-Si:H films  
250 are known to have  $N_S < 10^{16} \text{ cm}^{-3}$  [2].

251

#### 252 **4. Conclusion**

253 In this study, we have emphasized that the pyrolytic transformation from  
254 polydihydrosilane to amorphous silicon near 300–360 °C plays an essential role for the  
255 formation of a Sol.P a-Si:H films. The drastic changes of Raman spectra between  $T_p =$   
256 300 and 330 °C give evidence for the construction of a three-dimensional amorphous  
257 silicon network in this temperature range, as supported also by the TG/DTA results. The  
258 electrical properties of the Sol.P a-Si:H films are much affected by the pyrolytic  
259 transformation from a polymer to a-Si:H. Compared to device-grade Vac.P a-Si:H films  
260 [2], the spin density is larger by one order of magnitude, and the photosensitivity is  
261 smaller by one to two orders of magnitude. The infrared absorption of the Si-H  
262 stretching modes indicates a void-rich material. Further work appears necessary to  
263 improve the Sol.P a-Si:H material with the aim of fabrication of a-Si:H solar cells from  
264 liquid phase precursors.

265

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270

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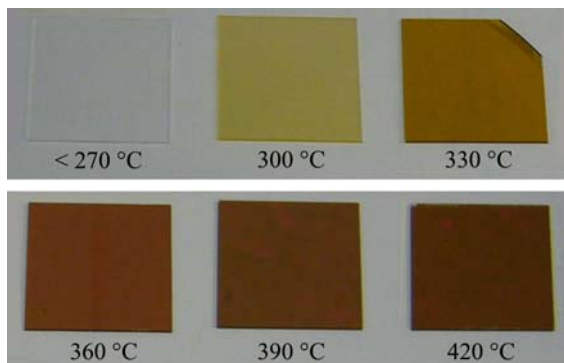
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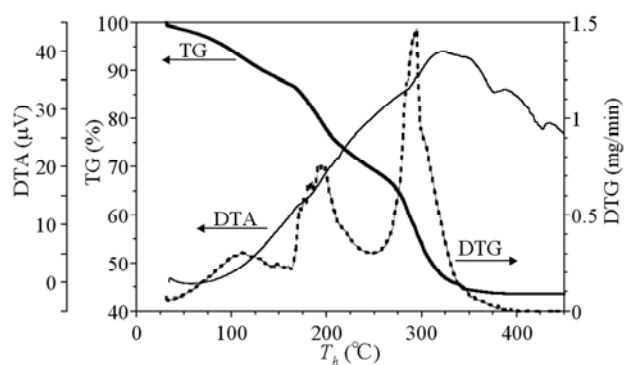
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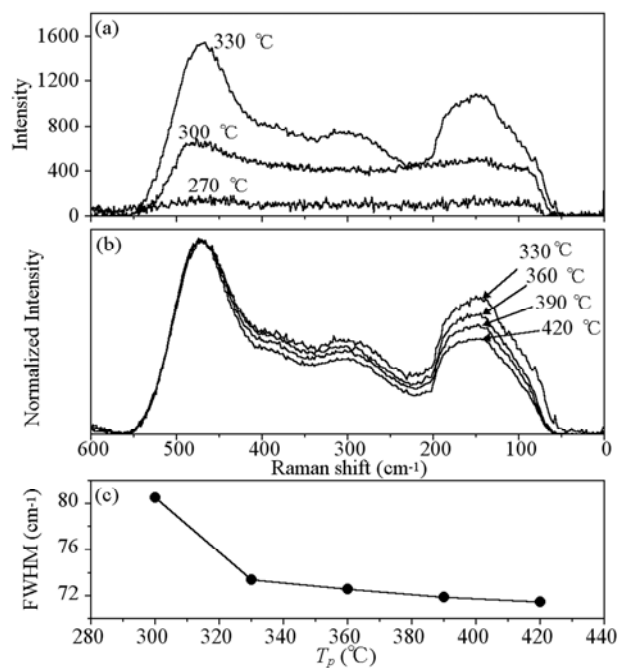
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309 Fig. 1 Photographic image of Sol.P films coated on quartz substrate. The films were  
 310 pyrolysed at  $T_p = 270\text{--}420$  °C. Substrate size is  $2 \times 2$  cm<sup>2</sup>.



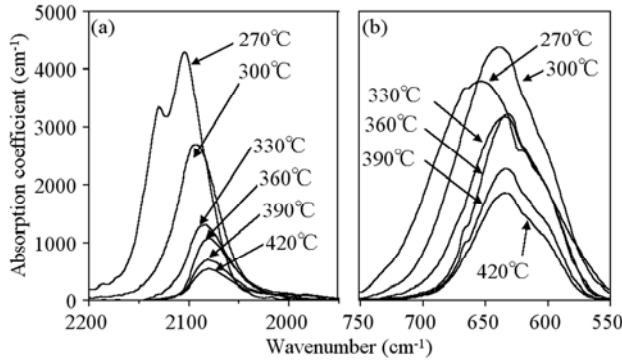
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312 Fig. 2 TG (bold solid line), DTA (thin solid line), and DTG (dashed line) curves of  
 313 polydihydrosilane as a function of heating temperature.

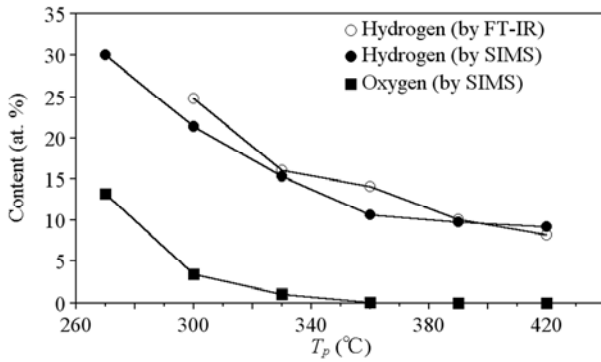


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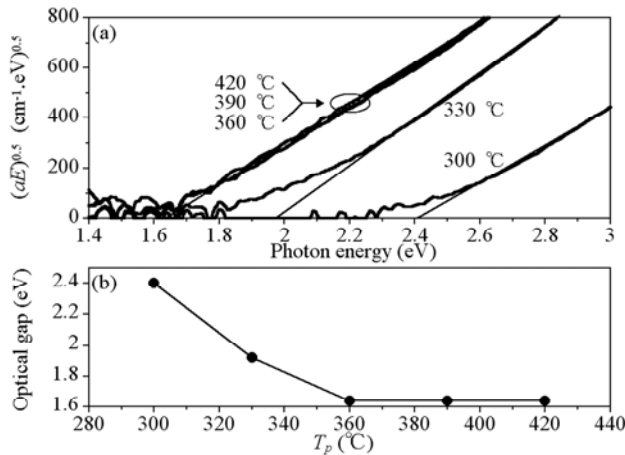
315 Fig. 3 (a) Raman spectra from the Sol.P films prepared at  $T_p = 270, 300,$  and  $330$  °C. (b)  
 316 Raman spectra from the films prepared at  $T_p = 330, 360, 390,$  and  $420$  °C. The intensity  
 317 was normalized to the same TO height. (c) FWHM of the TO Raman band versus  $T_p$ .



318  
 319 Fig. 4 FT-IR absorbance spectra at (a)  $1950\text{--}2200\text{ cm}^{-1}$  and (b)  $550\text{--}750\text{ cm}^{-1}$  for Sol.P  
 320 films prepared at  $T_p = 270\text{--}420$  °C on single crystalline silicon substrates.

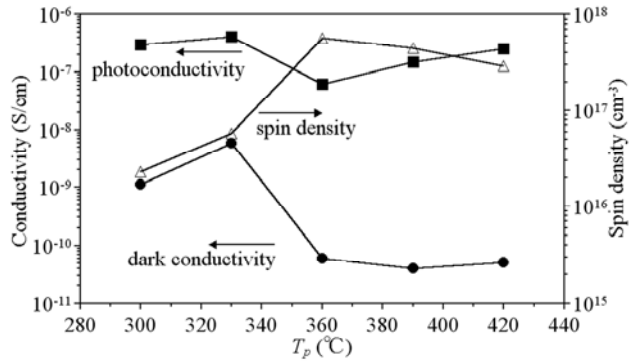


321  
 322 Fig. 5 Hydrogen and oxygen content versus  $T_p$ . The closed circles and squares give the  
 323 hydrogen and oxygen concentrations, respectively, from SIMS measurements. The open  
 324 circles give the hydrogen content estimated from the IR absorption data analyzing the  
 325 wagging mode near  $640\text{ cm}^{-1}$ .



326

327 Fig. 6 (a) Tauc plot of the Sol.P films on a quartz substrate. The films were prepared at  
 328  $T_p = 300\text{--}420\text{ }^\circ\text{C}$ . (b) Plot of  $E_g$  versus  $T_p$ .



329  
 330 Fig. 7 Conductivity and spin density in Sol.P films prepared at  $T_p = 300\text{--}420\text{ }^\circ\text{C}$ . The  
 331 value of  $\sigma_d$  and  $\sigma_p$  at room temperature and of  $N_S$  are depicted by closed circles, closed  
 332 squares, and open triangles, respectively.