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Title	Pyrolytic transformation from polydihydrosilane to hydrogenated amorphous silicon film
Author(s)	Masuda, Takashi; Matsuki, Yasuo; Shimoda, Tatsuya
Citation	Thin Solid Films, 520(21): 6603-6607
Issue Date	2012-07-16
Туре	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/11459
Rights	NOTICE: This is the author's version of a work accepted for publication by Elsevier. Takashi Masuda, Yasuo Matsuki, Tatsuya Shimoda, Thin Solid Films, 520(21), 2012, 6603–6607, http://dx.doi.org/10.1016/j.tsf.2012.07.028
Description	



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Pyrolytic Transformation from Polydihydrosilane to Hydrogenated Amorphous Silicon Film

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10

11 Abstract

12The fabrication of thin film silicon devices based on solution processes rather than on conventional vacuum processes is of substantial interest since cost reductions may result. 13Using a solution process, we coated substrates with polydihydrosilane solution and 14studied the pyrolytic transformation of the material into hydrogenated amorphous 15silicon (a-Si:H). From thermal gravimetry and differential thermal analysis data a 16 significant reduction in weight of the material and a construction of Si-Si bonds are 17concluded for the pyrolysis temperature $T_p = 270$ to 360 °C. The appearance of 18 amorphous silicon phonon bands in Raman spectra for films prepared at $T_p \ge 330$ °C 19 20suggests the construction of a three-dimensional amorphous silicon network. Films prepared at $T_p \ge 360$ °C exhibit a hydrogen content near 10 at.% and an optical gap near 21221.6 eV similar to device-grade vacuum processed a-Si:H. However, the infrared 23microstructure factor, the spin density, and the photosensitivity require significant 24improvements.

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Keywords: CPS, cyclopentasilane, polydihydrosilane, polysilane, amorphous silicon,
solution process.

28

30 **1. Introduction**

Hydrogenated amorphous silicon (a-Si:H) films have received considerable 31interest because of their immense potential for various application in large-area 32electronic devices such as solar cells and thin-film transistors [1,2]. To date, a-Si:H 33 films are deposited using expensive vacuum-based equipment and high amounts of 34dangerous and expensive silicon-based gases. These are factors making cost reduction 3536 and large-area film deposition difficult. If a-Si:H films can be deposited using liquid 37state silicon materials and inexpensive vacuum-free equipments, this situation might change drastically. Previously, we have reported on synthesis of silicon precursor 3839 solutions consisting of polydihydrosilane $(-(SiH_2)_n)$ and an organic solvent and demonstrated the realization of solution-processed (Sol.P) poly-silicon films [3] using 40 41spin-coat and ink-jet methods. Furthermore, we have demonstrated the Sol.P a-Si:H solar cell using spin-coat method [4]. The fabrication process involved the pyrolysis of 4243polydihydrosilane followed by a spontaneous formation of a three-dimensional silicon network releasing a high amount of gases (H₂ and SiH_x). Pyrolysis experiments of 44silicon containing polymers with a purpose to fabricate efficient emitters in the UV to 45IR spectral range for light emitting diodes have been reported recently [5]. However, 46 systematic studies for the Sol.P a-Si:H films were not reported so far. The aim of the 47present research is the study of the pyrolytic transformation from a polydihydrosilane 48liquid film to an a-Si:H solid film by changing the pyrolysis temperature T_p from 270 to 49420 °C employing a fixed heating time of 15 min. To examine the pyrolytic 50transformation, thermal gravimetry (TG) and differential thermal analysis (DTA), 51Raman scattering, Fourier-transform infrared spectroscopy (FT-IR), and secondary ion 52mass spectroscopy (SIMS) measurements are applied. To characterize the electrical 53properties of Sol.P films, transmittance and reflectance spectroscopy in the UV-visible 54range (UV-VIS TR), electron spin resonance (ESR), and photoconductivity/dark 5556conductivity measurements are carried out.

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58 **2. Experiment**

59 2.1 Preparation of Sol.P films

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

61polymerization process of cyclopentasilane (Si₅H₁₀;CPS) [6] employing the Kipping method [7,8]. The polydihydrosilane dissolved in cyclooctane at the concentration of 62 63 10–20 wt. % was spin-coated on quartz or silicon substrates under similar conditions as in previous work [9] in which we explored the stability of polydihydrosilane liquid 64 films on various solid substrates. The pyrolysis of the polydihydrosilane was carried out 65 at $T_p = 270$ to 420 °C using a fixed heating time of 15 min. The samples were set on a 66 hot plate in a glove box filled with nitrogen gas in order to avoid reaction with air, as 67 68 CPS and polydihydrosilane easily ignite in air. The oxygen and the dew point in the glove box were less than 0.5 ppm and -75 °C, respectively. 69

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71 **2.2 Characterization**

72The thermal analysis of polydihydrosilane was carried out using TG/DTA (EXTAR TGDTA6200 by Seiko Instruments Inc.) which was installed in the glove box. 73 74Inactive Al₂O₃ was selected as a sample pan. Approximately 20-30 mg of polydihydrosilane was added dropwise on the pan. To prevent as much oxidation as 7576 possible during the measurement, the purge gas was purified via a gas purifier (by 77Pureron Japan Co. Ltd.) to obtain oxygen concentrations < 1ppb, and a relatively high flow rate of 200 mL/min was employed. The polydihydrosilane was heated in the 7879temperature range between 25 and 450 °C with the heating rate of 10 °C/min.

The low-frequency phonon bands of the a-Si network and the local vibration of the SiH_n groups in the network were probed by Raman scattering (Ramascope by Renishaw) and FT-IR (ALPHA by Bruker Optics), respectively.

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

To determine the optical gap E_g and spin density N_S , we used UV-VIS TR (FilmTek-3000 by Scientific Computing International) and ESR (JES-FA100 by JEOL Ltd.), respectively. An AM-1.5G solar simulator (WXS-50S by WACOM Electric Co. Ltd.) with an intensity of 100mW/cm² was adopted for the illuminated current and

voltage measurement. The conductivity was measured on a coplanar configuration of 250 μm gap width, using aluminum contacts for samples. The dark conductivity σ_d and the photoconductivity σ_p were measured at room temperature for the films prepared at various T_p .

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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 on quartz substrate 2 \times 2 cm² in size and pyrolysed at temperatures between $T_p < 270$ 100 and $T_p = 420$ °C. The films prepared at $T_p \le 270$ °C are transparent, and a drastic change 101 from transparent to yellow color appears when T_p is increased from 270 to 300 °C. This 102103change in color can be attributed to a reduction of E_g from that of polydihydrosilane of 6.5 eV [10] to lower values. The transparency of films prepared at $T_p \leq 270$ °C 104 105corresponds to an insulator material whereas the yellow and brown color of films 106 pyrolysed at $T_p = 300-420$ °C indicates the presence of semiconductor materials. From 107 this, a transformation from a polymer to an amorphous semiconductor can be concluded to occur near $T_p = 270$ °C. 108

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

The TG data indicate a weight loss of about 58 % by heating up to 360 °C and 113consequently only 42 % of the material remained in the form of hydrogenated 114 115amorphous silicon. In agreement with thermal desorption spectroscopy (TDS) 116measurements [3] one may assume that the weight reduction is caused by desorption of H_2 and SiH_x. According to the DTG curves the major weight loss takes place at T = 100, 117200, and 300 °C. A broad exothermal peak is found in the DTA signal extending from 11880 to 450 °C with a maximum near 320 °C. These results suggest that the 119transformation from a polymer to a cross-linked amorphous silicon network (i.e. Si-Si 120bond construction) is particularly active between 300 and 360 °C and that the 121122amorphous network becomes more stable at higher temperature.

123

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

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

130 3.2.1 Raman scattering

Figs. 3(a) and 3(b) show the first-order Raman spectra of the Sol.P films prepared 131at T_p in the range of 270–330 °C and 330–420°C, respectively. The Raman data were 132133averaged over 10 measurements for each sample in a back scattering geometry using a 134He-Ne laser line (633 nm). In Fig. 3(a), typical phonon bands of a-Si:H [13,14] are visible at $T_p = 330$ °C whereas films prepared at $T_p = 270$ and 300 °C show no clear 135peaks corresponding to the amorphous silicon phonon bands. In literature, the a-Si:H 136Raman phonon bands at 476, 387, 288, and 154 cm⁻¹ have been assigned to transverse 137 138optical (TO), longitudinal optical, longitudinal acoustic, and transverse acoustic band, 139respectively. 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 full width at half maximum (FWHM) of the TO band versus T_p is plotted in Fig. 3(c). 141

The appearance of amorphous silicon phonon bands for films prepared at $T_p \ge$ 142330 °C suggests construction of the three-dimensional amorphous silicon network near 143the temperature $T_p = 330$ °C. Indeed, the Raman spectra for the Sol.P films prepared at 144 $T_p \ge 330$ °C are quite similar to typical Raman spectra for vacuum-processed (Vac.P) 145a-Si:H films [13,14]. Thus one may term the Sol.P films prepared at $T_p \ge 330$ °C Sol.P 146147a-Si:H films. Our observed FWHM of the TO band in Fig. 3(c) shows a decrease from 80.5 to 71.5 cm⁻¹ when T_p is increased from 300 to 420 °C. The decrease of the FWHM 148indicates the improvement of short-range tetrahedral ordering because of its sensitivity 149to the bond-angle fluctuations [14], so that the pyrolysis at $T_p \ge 330$ °C induces a 150modification of the amorphous network from a more distorted to a more ideal 151152tetrahedral configuration, in addition to the amorphous silicon network construction.

154 **3.2.2 FT-IR and SIMS**

Figs. 4(a) and 4(b) show the IR absorption coefficient $\alpha(\omega)$ in the wavenumber 155range of 1950–2200 cm⁻¹ and 550–750 cm⁻¹, respectively, for the Sol.P films prepared 156at $T_p = 270-420$ °C. The absorption peaks near 2000 and 2070–2090 cm⁻¹ at $T_p \ge$ 157360 °C are assigned to the stretching modes of Si-H bonds embedded in bulk material 158159and to the stretching modes of Si-H/Si-H₂ bonds at void surface, respectively [11]. The absorption band near 640 cm⁻¹ in Fig. 4(b) is attributed to the Si-H wagging mode [15] 160which is known to have a vibrational frequency near 640 cm^{-1} . Only the sample 161prepared at 270 °C deviates significantly from this value. As is seen in Fig. 4(a), the 162Si-H stretching modes of our material are all centered near 2080 cm⁻¹ except for the 163samples prepared at the rather low temperatures of 270 and 300 °C which show a Si-H 164165stretching absorption shifted to higher wavenumber.

As mentioned above, the 2070–2090 cm⁻¹ peaks at $T_p \ge 330$ °C are related to the vibration of Si-H/Si-H₂ bonded on external and internal void surfaces and the 2000 cm⁻¹ peak is attributed to Si-H vibrations in the bulk. Thus one may evaluate the sample quality by using the infrared microstructure factor *R* [2,11,12],

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

171Here, I_{2090} and I_{2000} are integrated intensities of each oscillation modes near 2070–2090 and 2000 cm⁻¹, respectively. From the spectral data in Fig. 4(a), the estimated R ranges 172173from 0.91 ($T_p = 360$ °C) to 0.80 ($T_p = 420$ °C) whereas it is known that device-grade Vac.P a-Si:H films show R < 0.2 [11,12] because of the domination of 2000 cm⁻¹ peak. 174175Large values of R for our films imply a void-rich structure. Although the origin of peak shift at $T_p \leq 330$ °C is not clear, it may be related to the oxidization or the change of 176177local 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.

To examine the degree of hydrogenation as well as the oxidation in our Sol.P films, we determine the hydrogen and oxygen concentration using FT-IR and SIMS measurements. Fig. 5 shows hydrogen and oxygen content as a function of T_p in which the closed circles and squares are, respectively, hydrogen and oxygen content obtained by SIMS measurement. The open circles show N_H/N_{Si} by FT-IR in which the density of silicon is assumed to be $N_{Si} = 5 \times 10^{22}$ cm⁻³. The density of hydrogen N_H is evaluated from $\alpha(\omega)$ in Fig. 4(b) using Eq. (2) with the proportional constant $A_{640} = 2.1 \times 10^{19}$ cm^{-2} [18],

$$N_{H} = A_{640} \int \frac{\alpha(\omega)}{\omega} d\omega \,. \quad (2)$$

Since the hydrogen content in polydihydrosilane is 67 at.%, the hydrogen 188 concentration values of 9.2–10.6 at.% (by SIMS) in films prepared at $T_p \ge 360$ °C 189190 indicate a remarkable reduction in the hydrogen content during the pyrolysis. The void-rich structure concluded from the large R value in films prepared at $T_p \ge 360$ °C is 191 presumably due to the three-dimensional shrinkage related to the weight loss. With 192regard to oxygen, the high concentration of it for the films prepared at $T_p \leq 330$ °C 193194 means that the construction of the amorphous silicon network is not dense enough so 195that it oxidises rather easily in air.

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187

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

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

The decrease in the TG curve from 25 to 280 °C and the positive DTA curve in Fig. 205206 2 indicate that the breaking and reconstruction of Si-Si bonds proceeds locally even at temperatures less than 280 °C. The drastic change of TG (visible in a peak in DTG) 207between 270 and 360 °C suggests a release of high amounts of H₂ and SiH_x due to the 208 thermal decomposition of molecules via the breaking of Si-H and Si-Si bonds. The 209 210broad exothermal peak in DTA near 320 °C likely corresponds to the construction of the three-dimensional silicon network due to formation of Si-Si bonds and release of 211hydrogen. The construction of the three-dimensional amorphous silicon network and the 212213strong reduction of the hydrogen content are confirmed by the Raman data (Fig. 3) and by the FT-IR and SIMS results as shown in Fig. 5. 214

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

217 **3.4.1 Optical gap**

Fig. 6 shows results of absorption measurements in the UV–visible range of Sol.P films prepared at $T_p = 300$ to 420 °C. The data are depicted in a Tauc plot [19] as $(\alpha E)^{1/2} = B^{1/2}(E - E_p),$ (3)

where α is the optical absorption coefficient, E is the photon energy in eV, B is a 221constant, and E_g is the optical gap (called "Tauc gap"). The fitting procedure yields $E_g =$ 2222.40, 1.92, 1.64, 1.64, and 1.64 eV for the film prepared at $T_p = 300, 330, 360, 390$, and 223420 °C, respectively, as shown in Fig. 6(b). The parameter B is found to be 5.7×10^5 224and 7.7 × 10⁵ eV⁻¹cm⁻¹ for $T_p = 300$ and 330 °C, and 6.7 × 10⁵ eV⁻¹cm⁻¹ for $T_p \ge$ 225360 °C. It is known that E_g in Vac.P a-Si:H films varies with the hydrogen content [2]. 226227Accordingly, the T_p -dependence of E_g in Fig. 6(b) can be understood by the dehydrogenation during pyrolysis as shown in Fig. 5. For T_p exceeding 360 °C the 228 absorption is no longer dependent on the hydrogen content, and gives $E_g = 1.64$ eV. This 229is consistent with $E_g = 1.5-1.6$ eV observed in Vac.P unhyrogenated amorphous silicon 230231films [2,20].

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233 **3.4.2. Conductivity and spin density**

234Typical values of σ_d , σ_p and N_s at room temperature are plotted in Fig. 7 as a function of T_p . With rising T_p from 300 to 330 °C, σ_d increases slightly, followed by a 235drastic decrease at $T_p = 360$ °C, and attains 5.1×10^{-11} S/cm at $T_p = 420$ °C, while σ_p is 236of the order of 10^{-7} S/cm, except for the minimum at $T_p = 360$ °C. The value of N_S 237 starting from 2.5×10^{16} cm⁻³ exhibits a maximum in a film prepared at $T_p = 360$ °C, and 238attains 2.8 \times 10¹⁷ cm⁻³ for the high- T_p films. Since the paramagnetic spin density 239240 corresponds to the concentration of dangling bonds which act as a trapping site, the reduction of N_S may lead to the increase of σ_p [21]. The increase of N_S in the range from 241 $T_p = 300$ to 360 °C is attributed mainly to the increase of dangling bonds due to the 242breaking of the Si-H and Si-Si bonds. In contrast, the decrease of N_S in the range from 243 $T_p = 360$ to 420 °C suggests that the high T_p serves as an annealing effect to reduce the 244number of dangling bonds (See also the FWHM data in Fig. 3(c)). A photosensitivity 245(i.e. ratio of σ_p to σ_d) of Sol.P films prepared at $T_p \ge 360$ °C exhibits the order of 10^3 , 246

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

251

252 **4. Conclusion**

In this study, we have emphasized that the pyrolytic transformation from 253254polydihydrosilane to amorphous silicon near 300-360 °C plays an essential role for the formation of a Sol.P a-Si:H films. The drastic changes of Raman spectra between T_p = 255300 and 330 °C give evidence for the construction of a three-dimensional amorphous 256257silicon network in this temperature range, as supported also by the TG/DTA results. The 258electrical properties of the Sol.P a-Si:H films are much affected by the pyrolytic transformation from a polymer to a-Si:H. Compared to device-grade Vac.P a-Si:H films 259260[2], the spin density is larger by one order of magnitude, and the photosensitivity is smaller by one to two orders of magnitude. The infrared absorption of the Si-H 261262stretching modes indicates a void-rich material. Further work appears necessary to 263improve the Sol.P a-Si:H material with the aim of fabrication of a-Si:H solar cells from 264liquid phase precursors.

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266 Acknowledgements

We thank Prof. S. Katayama for his discussion and valuable comments in the present work. This study was funded by the Exploratory Research for Advanced Technology (ERATO) program of Japan Science and Technology Agency.

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- 306



Fig. 1 Photographic image of Sol.P films coated on quartz substrate. The films were pyrolysed at $T_p = 270-420$ °C. Substrate size is 2×2 cm².



312 Fig. 2 TG (bold solid line), DTA (thin solid line), and DTG (dashed line) curves of





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



319 Fig. 4 FT-IR absorbance spectra at (a) 1950–2200 cm^{-1} and (b) 550–750 cm^{-1} for Sol.P

films prepared at $T_p = 270-420$ °C on single crystalline silicon substrates.





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Fig. 5 Hydrogen and oxygen content versus T_p . The closed circles and squares give the hydrogen and oxygen concentrations, respectively, from SIMS measurements. The open circles give the hydrogen content estimated from the IR absorption data analyzing the wagging mode near 640 cm⁻¹.



Fig. 6 (a) Tauc plot of the Sol.P films on a quartz substrate. The films were prepared at $T_p = 300-420$ °C. (b) Plot of E_g versus T_p .



329

330 Fig. 7 Conductivity and spin density in Sol.P films prepared at $T_p = 300-420$ °C. The

value of σ_d and σ_p at room temperature and of N_S are depicted by closed circles, closed squares, and open triangles, respectively.