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Author(s)	Masuda, Takashi; Matsuki, Yasuo; Shimoda, Tatsuya
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Description	

Pyrolytic Transformation from Polydihydrosilane to Hydrogenated Amorphous Silicon Film

Takashi Masuda [a], Yasuo Matsuki [a,c], Tatsuya Shimoda [a,b]

[a] Japan Science and Technology Agency, ERATO, Shimoda Nano-Liquid Process Project, 2-13 Asahidai, Nomi, Ishikawa, 923-1211, Japan

[b] School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa, 923-1292, Japan

[c] Yokkaichi Research Center, JSR Corporation, 100 Kawajiri-cho, Yokkaichi, Mie, 510-8552, Japan.

Abstract

The 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. Using a solution process, we coated substrates with polydihydrosilane solution and studied the pyrolytic transformation of the material into hydrogenated amorphous silicon (a-Si:H). From thermal gravimetry and differential thermal analysis data a significant reduction in weight of the material and a construction of Si-Si bonds are concluded for the pyrolysis temperature T_p = 270 to 360 °C. The appearance of amorphous silicon phonon bands in Raman spectra for films prepared at $T_p \geq 330$ °C suggests the construction of a three-dimensional amorphous silicon network. Films prepared at $T_p \geq 360$ °C exhibit a hydrogen content near 10 at.% and an optical gap near 1.6 eV similar to device-grade vacuum processed a-Si:H. However, the infrared microstructure factor, the spin density, and the photosensitivity require significant improvements.

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

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) films have received considerable interest because of their immense potential for various application in large-area electronic devices such as solar cells and thin-film transistors [1,2]. To date, a-Si:H films are deposited using expensive vacuum-based equipment and high amounts of dangerous and expensive silicon-based gases. These are factors making cost reduction and large-area film deposition difficult. If a-Si:H films can be deposited using liquid state silicon materials and inexpensive vacuum-free equipments, this situation might change drastically. Previously, we have reported on synthesis of silicon precursor 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 spin-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 polydihydrosilane followed by a spontaneous formation of a three-dimensional silicon network releasing a high amount of gases (H_2 and SiH_x). Pyrolysis experiments of silicon containing polymers with a purpose to fabricate efficient emitters in the UV to IR spectral range for light emitting diodes have been reported recently [5]. However, systematic studies for the Sol.P a-Si:H films were not reported so far. The aim of the present research is the study of the pyrolytic transformation from a polydihydrosilane liquid film to an a-Si:H solid film by changing the pyrolysis temperature T_p from 270 to 420 °C employing a fixed heating time of 15 min. To examine the pyrolytic transformation, thermal gravimetry (TG) and differential thermal analysis (DTA), Raman scattering, Fourier-transform infrared spectroscopy (FT-IR), and secondary ion mass spectroscopy (SIMS) measurements are applied. To characterize the electrical properties of Sol.P films, transmittance and reflectance spectroscopy in the UV–visible range (UV–VIS TR), electron spin resonance (ESR), and photoconductivity/dark conductivity measurements are carried out.

2. Experiment

2.1 Preparation of Sol.P films

Polydihydrosilane was synthesised by a photo-induced ring-opening polymerization process of cyclopentasilane (Si_5H_{10};CPS) [6] employing the Kipping method [7,8]. The polydihydrosilane dissolved in cyclooctane at the concentration of 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 films on various solid substrates. The pyrolysis of the polydihydrosilane was carried out at T_p = 270 to 420 °C using a fixed heating time of 15 min. The samples were set on a hot plate in a glove box filled with nitrogen gas in order to avoid reaction with air, as 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.

2.2 Characterization

The thermal analysis of polydihydrosilane was carried out using TG/DTA (EXTAR TGDTA6200 by Seiko Instruments Inc.) which was installed in the glove box. Inactive Al_2O_3 was selected as a sample pan. Approximately 20–30 mg of polydihydrosilane was added dropwise on the pan. To prevent as much oxidation as possible during the measurement, the purge gas was purified via a gas purifier (by Pureron 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 temperature 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 $100 mW/cm^2$ 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.

3. Results and discussion

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

Fig. 1 shows photographic image of Sol.P films with a thickness of 50 nm, coated on quartz substrate 2 × 2 cm^2 in size and pyrolysed at temperatures between $T_p < 270$ and $T_p = 420$ °C. The films prepared at $T_p \leq 270$ °C are transparent, and a drastic change from transparent to yellow color appears when T_p is increased from 270 to 300 °C. This change 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 corresponds to an insulator material whereas the yellow and brown color of films pyrolysed at T_p = 300–420 °C indicates the presence of semiconductor materials. From this, a transformation from a polymer to an amorphous semiconductor can be concluded to occur near $T_p = 270$ °C.

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 consequently only 42 % of the material remained in the form of hydrogenated amorphous silicon. In agreement with thermal desorption spectroscopy (TDS) measurements [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, 200, and 300 °C. A broad exothermal peak is found in the DTA signal extending from 80 to 450 °C with a maximum near 320 °C. These results suggest that the transformation from a polymer to a cross-linked amorphous silicon network (i.e. Si-Si bond construction) is particularly active between 300 and 360 °C and that the amorphous network becomes more stable at higher temperature.

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.

3.2.1 Raman scattering

Figs. 3(a) and 3(b) show the first-order Raman spectra of the Sol.P films prepared at T_p in the range of 270–330 °C and 330–420°C, respectively. The Raman data were averaged over 10 measurements for each sample in a back scattering geometry using a He-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 peaks corresponding to the amorphous silicon phonon bands. In literature, the a-Si:H Raman phonon bands at 476, 387, 288, and 154 cm^{-1} have been assigned to transverse optical (TO), longitudinal optical, longitudinal acoustic, and transverse acoustic band, respectively. Fig. 3(b) shows the Raman spectra of the Sol.P films prepared at T_p = 330, 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).

The appearance of amorphous silicon phonon bands for films prepared at $T_p \geq$ 330 °C suggests construction of the three-dimensional amorphous silicon network near the temperature T_p = 330 °C. Indeed, the Raman spectra for the Sol.P films prepared at $T_p \geq$ 330 °C are quite similar to typical Raman spectra for vacuum-processed (Vac.P) a-Si:H films [13,14]. Thus one may term the Sol.P films prepared at $T_p \geq$ 330 °C Sol.P a-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 indicates the improvement of short-range tetrahedral ordering because of its sensitivity to the bond-angle fluctuations [14], so that the pyrolysis at $T_p \geq$ 330 °C induces a modification of the amorphous network from a more distorted to a more ideal tetrahedral configuration, in addition to the amorphous silicon network construction.

3.2.2 FT-IR and SIMS

Figs. 4(a) and 4(b) show the IR absorption coefficient $\alpha(\omega)$ in the wavenumber range of 1950–2200 cm^{-1} and 550–750 cm^{-1}, respectively, for the Sol.P films prepared at T_p = 270–420 °C. The absorption peaks near 2000 and 2070–2090 cm^{-1} at $T_p \geq$ 360 °C are assigned to the stretching modes of Si-H bonds embedded in bulk material and to the stretching modes of Si-H/Si-H_2 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] which is known to have a vibrational frequency near 640 cm^{-1}. Only the sample prepared at 270 °C deviates significantly from this value. As is seen in Fig. 4(a), the Si-H stretching modes of our material are all centered near 2080 cm^{-1} except for the samples prepared at the rather low temperatures of 270 and 300 °C which show a Si-H stretching absorption shifted to higher wavenumber.

As mentioned above, the 2070–2090 cm^{-1} peaks at $T_p \geq 330$ °C are related to the vibration of Si-H/Si-H_2 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],

$$R = \mathrm{I}_{2090}/(I_{2000}+I_{2090}). \qquad (1)$$

Here, 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 from 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. Large 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 local environment of the Si-H dipole [16,17]. This suggests that the films prepared at $T_p \leq 330$ °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 concentration values of 9.2–10.6 at.% (by SIMS) in films prepared at $T_p \geq 360$ °C 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 $T_p \geq 360$ °C is presumably due to the three-dimensional shrinkage related to the weight loss. With regard to oxygen, the high concentration of it for the films prepared at $T_p \leq 330$ °C means that the construction of the amorphous silicon network is not dense enough so that it oxidises rather easily in air.

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. 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) between 270 and 360 °C suggests a release of high amounts of H_2 and SiH_x due to the thermal decomposition of molecules via the breaking of Si-H and Si-Si bonds. The broad 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 hydrogen. The construction of the three-dimensional amorphous silicon network and the strong 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.

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

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

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

where α is the optical absorption coefficient, E is the photon energy in eV, B is a constant, and E_g is the optical gap (called “Tauc gap”). The fitting procedure yields E_g = 2.40, 1.92, 1.64, 1.64, and 1.64 eV for the film prepared at T_p = 300, 330, 360, 390, and 420 °C, respectively, as shown in Fig. 6(b). The parameter B is found to be 5.7×10^5 and 7.7×10^5 $\text{eV}^{-1}\text{cm}^{-1}$ for T_p = 300 and 330 °C, and 6.7×10^5 $\text{eV}^{-1}\text{cm}^{-1}$ for $T_p \geq$ 360 °C. It is known that E_g in Vac.P a-Si:H films varies with the hydrogen content [2]. Accordingly, 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 absorption is no longer dependent on the hydrogen content, and gives E_g = 1.64 eV. This is consistent with E_g = 1.5–1.6 eV observed in Vac.P unhyrogenated amorphous silicon films [2,20].

3.4.2. Conductivity and spin density

Typical 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 drastic decrease at T_p = 360 °C, and attains 5.1×10^{-11} S/cm at T_p = 420 °C, while σ_p is of the order of 10^{-7} S/cm, except for the minimum at T_p = 360 °C. The value of N_S starting from 2.5×10^{16} cm^{-3} exhibits a maximum in a film prepared at T_p = 360°C, and attains 2.8×10^{17} cm^{-3} for the high-T_p films. Since the paramagnetic spin density 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 T_p = 300 to 360 °C is attributed mainly to the increase of dangling bonds due to the breaking of the Si-H and Si-Si bonds. In contrast, the decrease of N_S in the range from T_p = 360 to 420 °C suggests that the high T_p serves as an annealing effect to reduce the number of dangling bonds (See also the FWHM data in Fig. 3(c)). A photosensitivity (i.e. ratio of σ_p to σ_d) of Sol.P films prepared at $T_p \geq 360$ °C exhibits the order of 10^3, 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 $T_p \geq 360$ °C. Note that device-grade Vac.P a-Si:H films are known to have $N_S < 10^{16}$ cm^{-3} [2].

4. Conclusion

In this study, we have emphasized that the pyrolytic transformation from polydihydrosilane 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 = 300 and 330 °C give evidence for the construction of a three-dimensional amorphous silicon network in this temperature range, as supported also by the TG/DTA results. The electrical 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 [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 stretching modes indicates a void-rich material. Further work appears necessary to improve the Sol.P a-Si:H material with the aim of fabrication of a-Si:H solar cells from liquid phase precursors.

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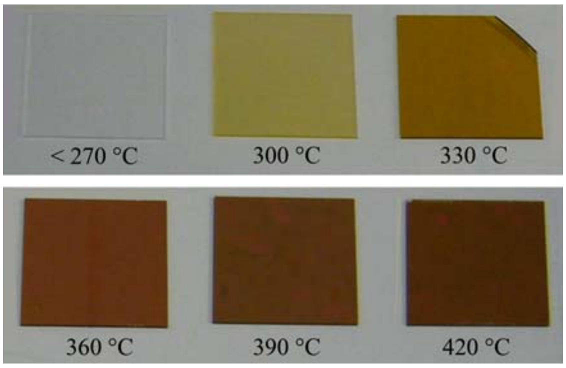

Fig. 1 Photographic image of Sol.P films coated on quartz substrate. The films were pyrolysed at $T_p = 270–420$ °C. Substrate size is 2×2 cm^2.

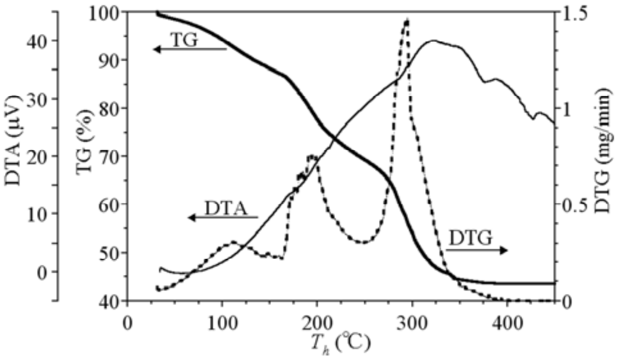

Fig. 2 TG (bold solid line), DTA (thin solid line), and DTG (dashed line) curves of polydihydrosilane as a function of heating temperature.

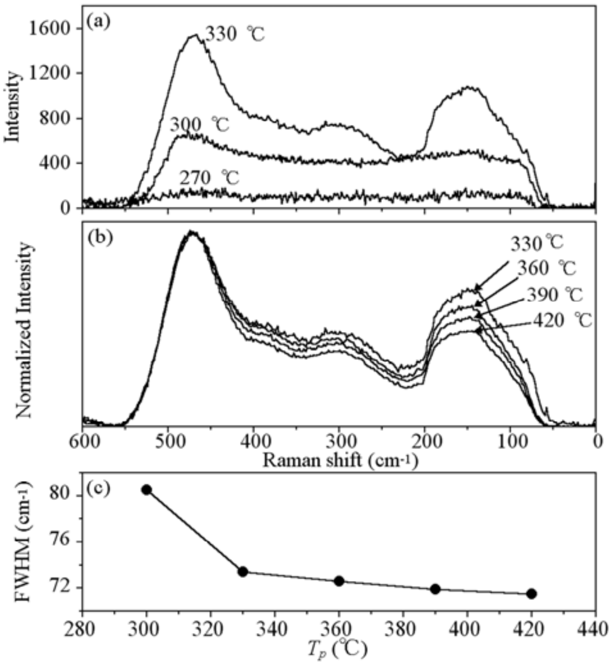

Fig. 3 (a) Raman spectra from the Sol.P films prepared at T_p = 270, 300, and 330 °C. (b) Raman spectra from the films prepared at T_p = 330, 360, 390, and 420 °C. The intensity was normalized to the same TO height. (c) FWHM of the TO Raman band versus T_p.

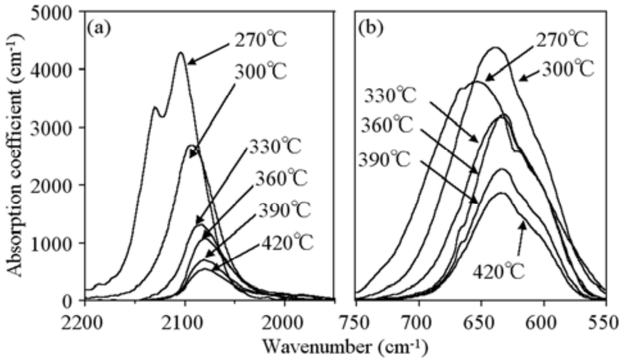

Fig. 4 FT-IR absorbance spectra at (a) 1950–2200 cm^{-1} and (b) 550–750 cm^{-1} for Sol.P films prepared at T_p = 270–420 °C on single crystalline silicon substrates.

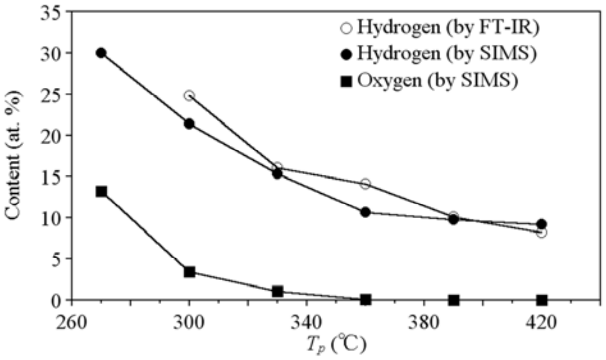

Fig. 5 Hydrogen and oxygen content versus T_p. The closed circles and squares give the hydrogen and oxygen concentrations, respectively, from SIMS measurements. The open circles give the hydrogen content estimated from the IR absorption data analyzing the wagging mode near 640 cm^{-1}.

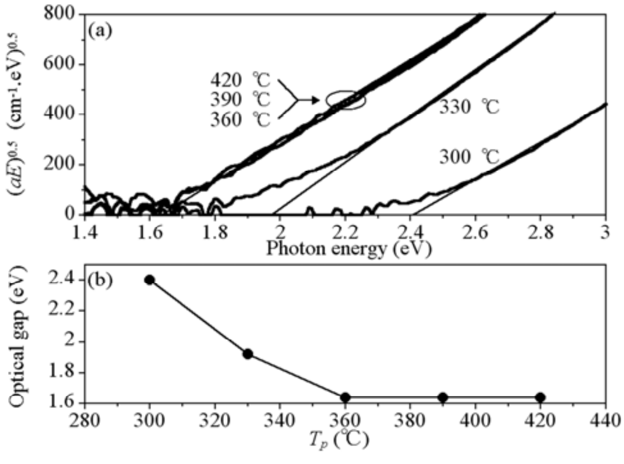

Fig. 6 (a) Tauc plot of the Sol.P films on a quartz substrate. The films were prepared at T_p = 300–420 °C. (b) Plot of E_g versus T_p.

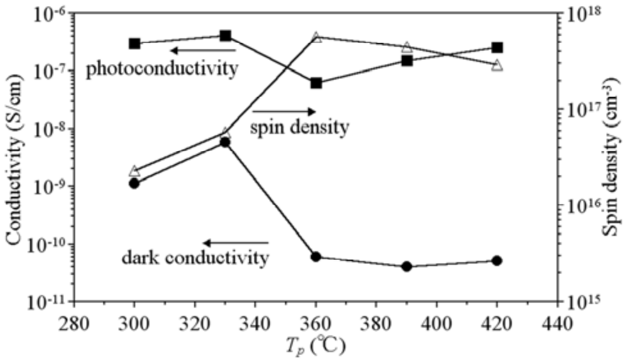

Fig. 7 Conductivity and spin density in Sol.P films prepared at T_p = 300–420 °C. The value of σ_d and σ_p at room temperature and of N_S are depicted by closed circles, closed squares, and open triangles, respectively.