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Pyrolytic transformation from polydihydrosilane to hydrogenated amorphous silicon film

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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.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) films have received considerable interest because of their immense potential for various applications 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 gasses. 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 the 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 a 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 gasses (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 synthesized 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.

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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<1 ppb, 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 by the 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 the 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 a photographic image of Sol.P films with a thickness of 50 nm, coated on a quartz substrate 2×2 cm^2 in size and pyrolyzed at temperatures between T_p=270 and 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 pyrolyzed 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 Section 3.2.1, we study the T_p-dependence of Raman spectra of amorphous phonon bands to confirm the formation of the three-dimensional amorphous silicon network. In Section 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

Fig. 3(a) and (b) shows 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

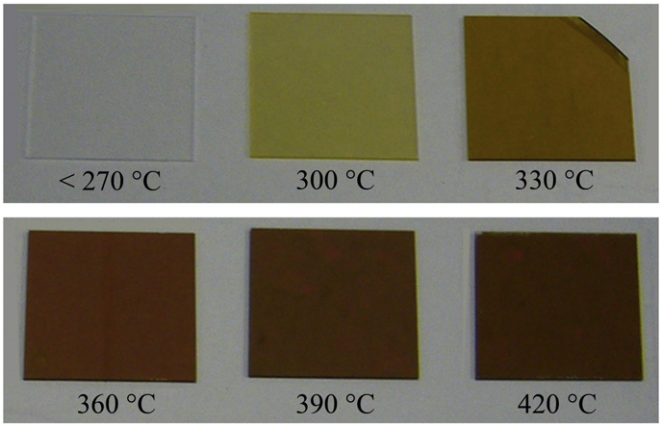

Fig. 1. Photographic image of Sol.P films coated on quartz substrate. The films were pyrolyzed at T_p=270–420 °C. Substrate size is 2×2 cm^2.

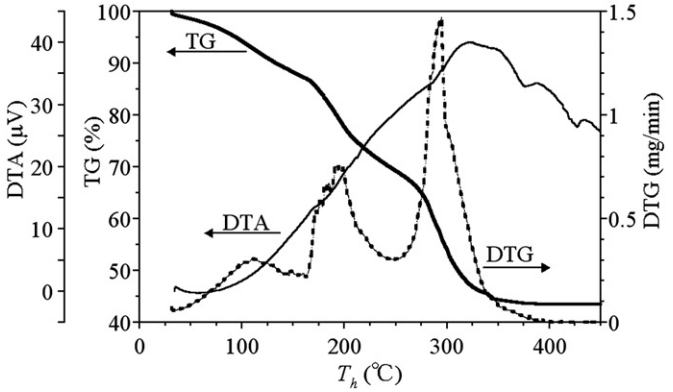

Fig. 2. TG (bold solid line), DTA (thin solid line), and DTG (dashed line) curves of polydihydrosilane as a function of heating temperature.