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Liquid hydridosilane precursor prepared from cyclopentasilane via sonication at low temperatures without the action of light

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ABSTRACT

We report on a liquid hydridosilane precursor ink prepared via the ultrasonically induced ring-opening polymerisation of cyclopentasilane (Si_5H_{10}) without irradiation by ultraviolet light. The sonication is carried out in N_2 atmosphere at temperatures between 20 and 75 °C. We use size exclusion chromatography (SEC) to show polymer growth and estimate molecular mass with increasing sonication time. In combination with UV–vis transmission measurements, further SEC analysis is used to compare solutions subjected to either purely thermal or ultrasonic treatment at the same process temperature and for the same duration. Our findings provide strong evidence showing that the initiation of the polymerisation is sonocatalytic in nature and not thermic due to the macroscopic temperature of the solution. The liquid precursor is used to produce homogeneous hydrogenated amorphous silicon (a-Si:H) thin films via spin coating and pyrolytic conversion. The optoelectronic properties of the films are subsequently improved by hydrogen radical treatment. Fourier transform infrared spectroscopy (FTIR) is used to determine a compact film morphology and electrical conductivity measurements show that the layers attain a light-to-dark photosensitivity ratio of 2×10^3 making them suitable for application in optoelectronic devices.

1. Introduction

Since the seminal publication of Shimoda et al. [1] in 2006, work on solution-based silicon deposition technologies using liquid silicon hydrides has spread to numerous research groups around the globe. One of the major advantages of solution-based methods is that they can be used to fabricate doped and intrinsic semiconductor-grade amorphous and crystalline silicon layers without the aid of expensive high vacuum equipment. In addition, the liquid phase processing of the silicon precursor allows for high deposition rates using well-established techniques such as ink-jet printing, slot-die casting and aerosol coating. Applications include optoelectronic devices such as thin-film transistors [2,3], solar cells [4–6], and more recently, passivation layers in silicon heterojunction solar cells [7].

The conventional route for the preparation of high molecular weight silicon hydride polymers from a lower silane, the most prominent of which is cyclopentasilane (Si_5H_{10}, CPS), involves ring-opening photopolymerisation using ultraviolet (UV) light [1,8]. The resulting polymer is found to be a predominantly chain-like polydihydrosilane with generic formula $-(SiH_2)_n-$. The boiling point of oligosilanes consisting of roughly 9 Si atoms already exceeds the ~270 °C required to break Si-Si and Si-H bonds, which in turn enables the formation of an a-Si network upon pyrolytic conversion on a hot plate. However, the low volatility polymers used in the literature typically have a mass averaged molecular mass (M_w) in the range of 10^2–10^6 g/mol [9]. The M_w, along with the concentration and choice of solvent varies according to the precursor requirements for a given application, for instance, viscosity or desired film thickness. So far the high price for high-purity material and poor up-scaling of monomer synthesis has been an important drawback for the commercialization of printed silicon solar cells and electronics.

The present paper is concerned with the development of an alternative method of producing higher silicon hydrides of sufficiently low volatility of the form $-(SiH_x)_n-$, with $1 < x < 2$, via the ring-opening polymerisation of CPS by ultrasonic (US) irradiation. The US treatment of CPS monomer solutions takes advantage of the known sonochemical effects associated with acoustic cavitation [10–12]. These effects stem from cavitational collapse, a phenomenon which gives rise to short-lived "hot spots" possessing extremely high transient temperatures (of several thousand

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degree) and pressures (of several hundred atmospheres). The extreme conditions in the vicinity of these imploding microbubbles are proposed to be responsible for radical formation via the ring-opening of the CPS molecule and subsequent polymerisation in the bulk of the liquid.

2. Materials and methods

Since CPS is pyrophoric in air, the preparation of the precursor solutions, the coating of the substrates and the pyrolytic conversion to hydrogenated amorphous silicon (a-Si:H) were carried out in the inert N_2 atmosphere of a glove box with residual traces of O_2 and H_2O of <1 ppm. The sonication of the precursor solutions was carried out using a *Hielscher UP200St* sonotrode mounted with a titanium acoustic horn with a 2 mm diameter tip. The operating frequency was 26 kHz, the amplitude (A) at the tip was between 35 and 63 μm with an ultrasonic intensity of 300–900 W/cm^2. A duty cycle per second (DC) of between 30% and 50% was used to avoid heating the solutions above ~75 °C during treatment when no active cooling of the solutions was undertaken. The sonication of CPS (~95% purity) was carried out in solution using cyclooctane (CO) as solvent. The solutions had volumes and concentrations of ~1.0 mL and 8–15 wt%, respectively. The process temperature (T) was measured using a type K thermocouple from *Thermocoax* in direct contact with the respective solutions. All samples were filtered with a 0.2 μm PTFE syringe filter prior to both SEC characterisation and spin coating.

Molecular weight distributions and the M_w were determined via size exclusion chromatography (SEC) using a Polymer Laboratories PL 220 SEC instrument equipped with a differential refractive index detector and a *PolyPore* column. The instrument was operated at a temperature of 30 °C at a flow rate of 1 mL/min. The SEC samples were diluted to about 0.3 wt% to avoid column overloading. Polystyrene (PS) standards were used as molecular weight references. Under these conditions the PS standards were found to be soluble in cyclohexene (CH), but not in CO. Two different measurement runs were therefore carried out, one using CH as SEC equipment solvent to estimate and follow changes in the M_w of sonicated solutions (*Section* 3.1) and another using CO as equipment solvent to study the difference between sonicated and pyrolysed solutions (*Section* 3.2). For the CH run, the sonication conditions were A = 42 μm, DC = 40%, T = 65–70 °C, and test samples for SEC analysis were taken from the untreated solution and after 90, 180, 220 and 270 min, respectively. For the CO run, two identical solutions were mixed, one intended for sonication and the other for purely thermal treatment (pyrolysis). Test samples were taken from an untreated solution and after 240, 390 and 625 min from the sonicated solution and after 625 min from the solution pyrolysed on a hot plate, respectively. The sonication conditions here were A = 35 μm, DC = 40%, T = 70–75 °C.

The optical transmission measurements were carried out on solutions in hermetic quartz tubes using a Lambda 950 spectrophotometer from PerkinElmer equipped with an integrating sphere in the UV–vis range from 220 to 740 nm. The solutions were sonicated and/or pyrolysed at T = 70–75 °C for 625 min.

The CPS-derived ink was cast on 15 × 15 mm^2 Eagle XG glass from *Corning* and on double-sided polished c-Si substrates via spin coating at 2000 rpm for 15 s. Intrinsic a-Si:H layers were subsequently produced by pyrolytic conversion on a hot plate at 440 °C for 1–3 min. The layer thicknesses vary from around 50–80 nm as measured using profilometry. After deposition and conversion, the layer properties were improved using hydrogen radicals generated via hot-wire in a high vacuum chamber fitted with tantalum filaments at 1300 °C fixed at a distance of 70 mm to the substrates, a substrate heater temperature of 400 °C, at a pressure of 0.05 mbar, with a H_2 flow of 50 sccm and for a treatment time of 120 min.

The ambient temperature synthesis of the precursor solution used to deposit the layers for the FTIR and electrical conductivity measurements required an ultrasonic treatment time of 875 min (A = 63 μm, DC = 50%) and was carried out at 20–25 °C using a home-made active cooling system consisting of Peltier coolers mounted on a copper block encasing the solution vial.

The FTIR measurements were carried out in N_2 atmosphere using a *Nicolet 5700* spectrometer. The electrical conductivity measurements were done using a halogen lamp under approximate AM 1.5 illumination conditions and two coplanar Ag electrodes with a width of 5 mm and a gap of 0.5 mm between them deposited onto a-Si:H on glass.

3. Results and discussion

3.1. Molecular weight estimates via size exclusion chromatography

In order to gain insight into the molecular mass distribution of treated and untreated CPS, various solutions were examined via SEC. In Fig. 1 we show several elugrams in cyclohexene of CPS solutions that illustrate the distribution and growth of higher silicon hydrides polymerised using ultrasound. The blue curve corresponds to untreated CPS which elutes at 10.1 min (peak cropped at top of plot). The additional signal between 8.5 and 9.75 min with peaks 1 (9.35 min) and 2 (9.0 min) indicates the presence of slightly higher molecular weight silanes other than CPS. These silanes are most probably by-products from the CPS synthesis or slow spontaneous oligomerisation products formed during storage in N_2 at ambient temperature.

As mentioned previously, we carry out the ultrasonic treatment of CPS in solution using CO as solvent. A measurement of pure CO (green elugram, likewise cropped at top of plot) reveals that it elutes concurrently with CPS monomer at 10.1 min. This has the drawback that we are unable to monitor changes in CPS concentration as sonication progresses. Nevertheless, we can still clearly observe the growth of higher molecular weight silicon hydrides with increasing sonication time from 90 to 270 min. This is evident

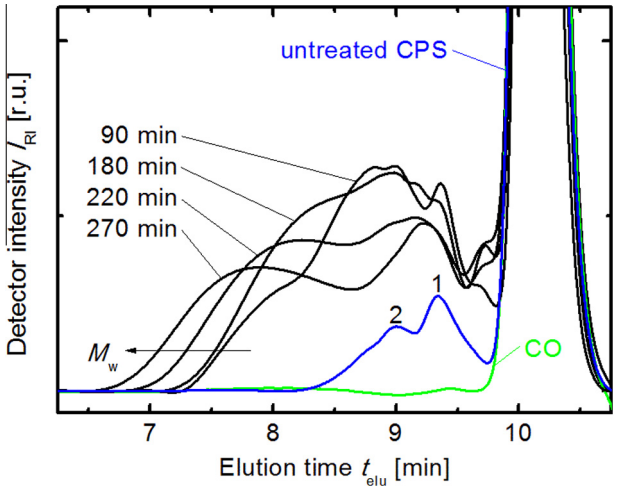


Fig. 1. SEC elugrams in cyclohexene of untreated CPS together with samples having undergone various sonication times. Included in the plot is an elugram for untreated CPS monomer (blue) and one for pure cyclooctane (CO, green), the solvent in which CPS is diluted prior to sonication. The arrow highlights the fact that progressively higher M_w species elute at an ever earlier elution time t_{elu} (see Fig. 2 for estimates of the actual M_w).

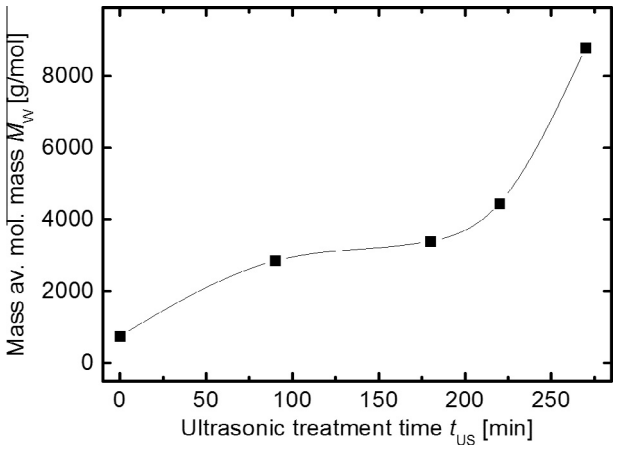


Fig. 2. Plot of the evolution of the mass average molar mass M_w as a function of ultrasonic treatment time t_{US} as estimated using the elugrams of Fig. 1 and polystyrene molecular weight standards. The line should serve as a guide to the eye.

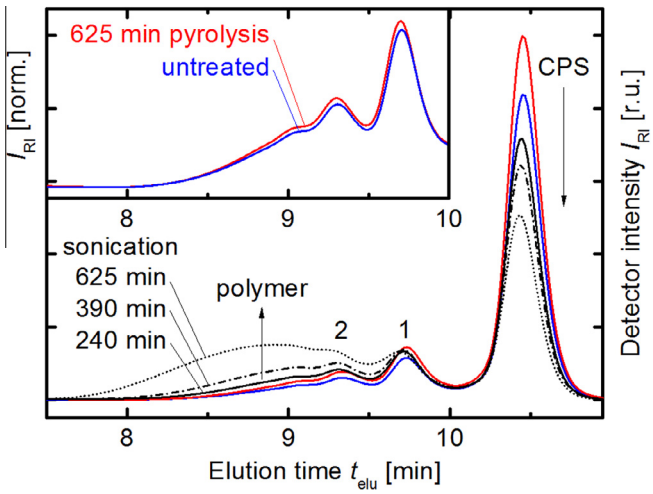


Fig. 3. SEC elugrams of CPS in cyclooctane depicting the evolution of larger molecular species with increasing sonication time (black lines) compared to purely thermally treated (red line) and untreated (blue) solutions. The decrease in CPS monomer at 10.35 min along with a corresponding increase in polymer signal for t_{elu} < 9.7 min demonstrates the sonocatalytically initiated polymerisation of CPS. On the other hand, the normalised inset shows that a similar solution thermally treated at the same process temperatures of 70–75 °C is found to be practically identical to the untreated solution, indicating that the polymerisation process is not macrothermally activated at these temperatures.

from the earlier elution time t_{elu} at which the progressively larger polymers begin to elute.

In Fig. 2 we estimate the mass average molar mass M_w of the dissolved polymer as a function of ultrasonic treatment time t_{US} using PS standards and the elugrams in Fig. 1. The M_w is seen to steadily increase up to >8000 g/mol with increasing t_{US}. We note that we expect the M_w of the samples with $\geqslant$220 min sonication times to be larger than those actually measured owing to the fact that the 220 min solution had already begun to turn slightly cloudy and the 270 min solution had already turned opaque white (see inset b) in Fig. 4). The turbidity indicates precipitation out of solution of the large M_w species which are not measurable using SEC.

3.2. Sonicated vs. pyrolysed CPS solutions

In the following we address the question as to whether the polymerisation process is initiated sonochemically due to hot spots generated by acoustic cavitation or simply activated "macrothermally" via pyrolytic bond cleavage as a result of the higher temperatures reached by solutions during sonication due to unintentional heating during sonication.

The process temperature of the solutions during sonication was generally found to increase with increasing amplitude (A), duty cycle (DC) and immersion depth (d_i) of the sonotrode in the solution. This is explained by the fact that the amount of ultrasonic power irradiated into the solution is proportional to A, the higher the DC, the shorter the idle time available for heat dissipation between ultrasonic bursts and finally, the deeper d_i is, the higher the contact area of the liquid with the hot sonotrode. In general, a steady-state process temperature without active cooling was reached after about 15 min of treatment and for the experimental conditions in this work was found to vary between 65 and 75 °C. To test and compare the effects, if any, of purely thermal treatment at the highest temperatures reached during sonication, identical solutions were prepared and treated pyrolytically or ultrasonically for a total of 625 min at 70–75 °C. The solutions were subsequently analysed via SEC and optical transmission measurements.

We shall address the SEC characterisation first. In Fig. 3 are depicted elugrams of an untreated CPS solution in blue, a CPS solution pyrolysed for 625 min in red and of CPS solutions after 240, 390 and 625 min of sonication in black. The main peak on the right at ca. 10.4 min corresponds to unreacted CPS monomer (with intensity I_{CPS}) and the signal for elution time t_{elu} < 10 min correspond to silicon hydride polymer (with intensity I_{poly}). Note that peak 1 at 9.7 and peak 2 at 9.3 min in the figure are the same as those at 9.35 and 9.0 min in Fig. 1 and correspond to either slightly larger silane by-products produced during CPS synthesis or to the CPS trimer and dimer, respectively. We see at once that pyrolysis at 70–75 °C has negligible chemical effect on the solution. This is most clearly seen in the normalised inset where the form and intensity of the curves for the untreated solution in blue and the pyrolysed solution in red are essentially the same. We therefore find no chromatographic evidence for the polymerisation of CPS due to thermally activated bond cleavage at solution temperatures up to 75 °C. The form of the curves for the sonicated solution is in stark contrast to that of the untreated and pyrolysed ones. Here a clear decrease in I_{CPS} with increasing sonication time is observed followed by corresponding increase in I_{poly}, from which the sonocatalytically initiated polymerisation of CPS is inferred.

Finally, by assuming that the sensitivity of the differential RI detector to the various silanes (of similar refractive index) in the limited retention time range from about 7–10 min remains approximately constant, we can make a rough estimate of the amount of unreacted CPS monomer remaining in the processed solution by monitoring the intensities (integrated areas) of I_{CPS} and I_{poly}. Defining the CPS concentration as $c_{CPS} = I_{CPS}/(I_{CPS} + I_{poly})$, we estimate that the ready-to-use ink consists of ~30% unreacted CPS monomer. Despite the high price of CPS, the presence of residual unreacted monomer in the ink is necessary since it significantly increases the solubility of the silicon hydride polymer. More cost-effective alternative solvents are currently being searched for.

In order to corroborate the aforementioned conclusions drawn from the SEC analysis that the initiation of the polymerisation is sonocatalytic and not macrothermal in nature, additional optical transmission measurements were conducted on treated and untreated solutions. Shown in Fig. 4 are the transmission spectra from 220 to 740 nm of an untreated CPS solution (blue), a solution pyrolysed at 70–75 °C for 625 min (red), a solution sonicated at this same process temperature for 625 min (black, dashed), and of the same sonicated solution after filtering (black). As was found in the chromatographic analysis, the fact that the blue and red curves again overlap demonstrates that the solution remains essentially unchanged after pyrolysis. This suggests that no

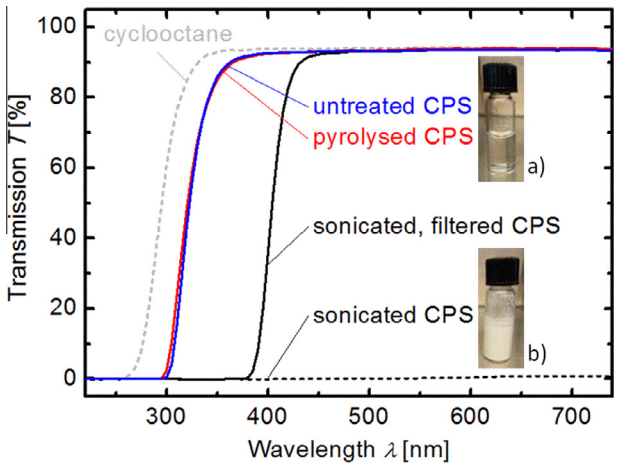


Fig. 4. Optical transmission measurements of various CPS solutions in cyclooctane (dashed grey curve). The blue curve corresponds to untreated CPS and the red curve shows that the pyrolysis of CPS at 70–75 °C results in essentially no changes in optical behaviour (solution remains transparent as evident from inset a)). On the other hand, the dashed black line and the photograph in inset b) reveal that sonication at the same process temperature results in an opaque white solution with practically zero transmission. As evident from the solid black curve, the solution becomes significantly more transparent after filtering (0.2 μm filter).

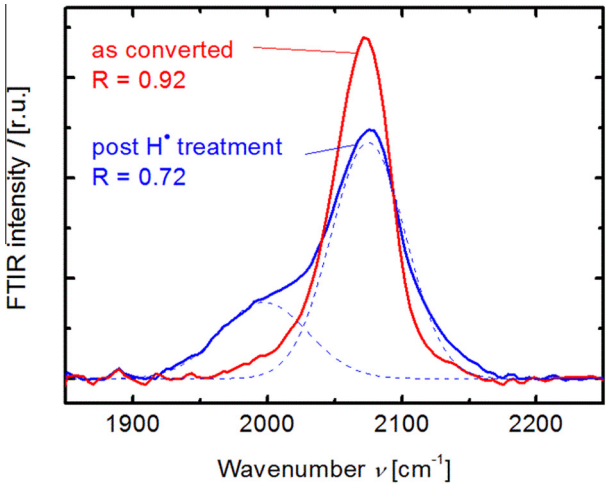
polymerisation via thermally activated bond cleavage has taken place. As seen in inset a) the solution remains transparent in the whole visible range, consistent with an absorption edge at about 320 nm. On the other hand, as evident from inset b) the sonicated solution prior to filtering has become milky white and its transmission spectrum indicates that it is almost completely opaque. After filtering out the precipitated polymer, the solid black line shows that the solution appears transparent once more. However, the absorption edge has now shifted to about 400 nm indicating that higher silicon hydrides have been formed [13].

Interestingly, after filtering or shortly before becoming turbid, careful observation shows that solutions sonicated at 65–75 °C take on a light-brown/beige colour, while solutions sonicated at room-temperature or below have frequently been observed to take on a clear yellow colour. The former colour has been reported to correspond to a silicon hydride of the form $(SiH_2)_n$ [14] and the latter is associated with a branched silicon sub-hydride of the generic form $(SiH_x)_n$, with $1 < x < 2$ [15,16]. A more detailed study of these temperature effects is currently being pursued.

3.3. Film properties

The aforementioned description of the sonocatalytic polymerisation method enables the preparation of a printable ink which we now show can be used to spin coat polymer thin films that are convertible into a-Si:H upon pyrolytic conversion on a hot plate. We remark for completeness that spin coating using untreated and/or pyrolysed CPS solutions yield almost entirely dewetted films upon coating and no film is discernible on the substrate upon curing on the hot plate (see a) in Fig. 5 (Right)).

In the following we use FTIR to study the microstructure and hydrogen-silicon bonding configuration of the films deposited using our CPS-derived ink. Shown in Fig. 5 (Left) are FTIR spectra as a function of wavenumber of two a-Si:H thin films deposited on c-Si substrates before (red) and after (blue) hydrogen radical ($H^{\cdot}$) treatment. The spectra exhibit absorption peaks in the two expected regions associated with a-Si:H, namely the Si-H and Si-H_2 stretching modes in the range 2000–2100 cm^{-1} and the Si-Si wagging mode at about 630 cm^{-1} (not shown). The stretching mode at 2000 cm^{-1} is associated with Si-H bonds where the hydrogen passivates a silicon dangling bond located in a dense amorphous matrix [5]. On the other hand, modes between 2075 and 2100 cm^{-1} are attributed to Si-H/Si-H_2 vibrational modes at the internal surface of hollow regions or microvoids [17]. As evident from the spectra, the films prepared from our ink exhibit a dominant peak in the latter range, indicating a void-rich microstructure. The infrared microstructure factor, defined as $R = I_{2075}/(I_{2075} + I_{2000})$, with I_{2075} and I_{2000} corresponding to the intensities of the components at 2075 and 2000 cm^{-1}, respectively, provides a measure of the morphology of the material with larger values indicating higher microvoid densities. The converted film yields a value of R of around 0.92 which compares favourably to previously reported values of around 0.9 for similarly prepared layers with photopolymerised precursors [18]. After $H^{\cdot}$ treatment, we observe a significant amount of tetragonally coordinated silicon with hydrogen-saturated dangling bonds at 2000 cm^{-1} associated with the Si-H mode of state-of-the-art PECVD a-Si:H. This indicates that hydrogen has diffused into dense regions in the bulk of the film and has been incorporated into lattice sites previously



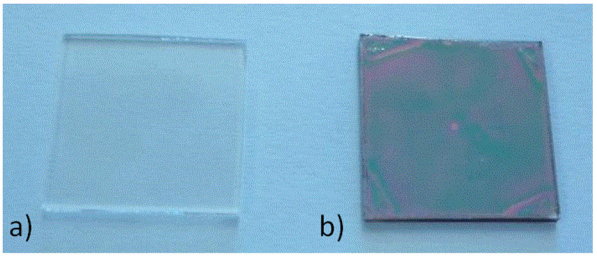


Fig. 5. (Left) Typical FTIR spectra of a-Si:H depicting the Si-H/Si-H_2 stretching modes between 2000 and 2075 cm^{-1}. The microstructure factor, R, is calculated to be 0.92 and 0.72 prior to and after H radical treatment, respectively. The dashed curves are the deconvoluted component modes comprising the signal of the treated sample. (Right) Photographs of glass substrates after pyrolytic conversion on the hot plate previously spin coated with a purely thermally treated solution a) and with a sonocatalytically treated ink b).

Table 1
Summary of electrical conductivity performance of spin coated a-Si:H thin films before and after hydrogen radical treatment.

Material	Photoconductivity σ_{ph} [S/cm]	Dark conductivity σ_d [S/cm]	Photoresponse σ_{ph}/σ_d
Untreated	1×10^{-8}	9×10^{-10}	$<10^2$
H-passivated	2.4×10^{-8}	1.1×10^{-11}	2×10^3

containing Si dangling-bond defects. The weakening of the 2075 cm^{-1} peak and growth of the 2000 cm^{-1} mode after passivation (dashed blue curves) suggests a partial reconstruction into a material of more compact morphology possessing an improved R of around 0.72.

Finally, in order to characterise the thin films in terms of optoelectronic performance, dark (σ_d) and photoconductivity (σ_{ph}) measurements were performed. From these measurements, the light-to-dark photosensitivity ratio or photoresponse defined as $\sigma_{PR} = \sigma_{ph}/\sigma_d$ is calculated and used as a figure of merit for the optoelectronic quality of the material. A higher σ_{PR} indicates a lower defect density in the film, which in turn means better suitability for application in optoelectronic devices [5].

As summarised in Table 1, the σ_d and σ_{ph} values for untreated films are typically of the order of 9×10^{-10} and 1×10^{-8} S/cm, respectively. This gives σ_{PR} of $<10^2$. After undergoing the hot-wire H· treatment, the σ_d decreases to 1.1×10^{-11} S/cm and the σ_{ph} increases to 2.4×10^{-8} S/cm, resulting in $\sigma_{PR} = 2.2 \times 10^3$ for our best film to date. Our attained values of σ_{ph} prior to and after H· treatment lag behind known literature photoconductivities for spin coated films using CPS monomer in the range $2–0.6 \times 10^{-7}$ and $9–5 \times 10^{-6}$ S/cm, respectively [4,19]. This may be due to poor densification upon cross-linking during pyrolytic conversion, suboptimal passivation parameters or point to impurities in our CPS monomer batch.

4. Conclusions

We have demonstrated a novel sonocatalytic route for the ring-opening polymerisation of cyclopentasilane that does not require the action of light and is not thermally activated by the temperature of the solution. Our method employs 26 kHz ultrasound and the synthesis is routinely carried out in the temperature range from 20 to 75 °C.

Through a comparison of sonicated and pyrolysed solutions via size-exclusion chromatography, optical transmission measurements and spin coating we rule out that the polymerisation is pyrolytically initiated by the macroscopic temperature of the solution itself, and conclude that hot spots generated upon cavitational collapse are the driving force responsible for the observed polymer growth.

The utility of the precursor ink is demonstrated by spin coating a-Si:H thin films exhibiting similar properties to layers fabricated from photolytically prepared cyclopentasilane-based polydihydrosilane precursors found in the literature. Fourier transform infrared spectra of untreated a-Si:H layers reveal a microvoid-rich morphology which is significantly improved after exposure to H radicals. The microstructure factor after passivation is calculated to be 0.72, constituting the lowest value reported thus far for films spin coated from cyclopentasilane derived inks. The dark and photoconductivity are likewise improved to 1.1×10^{-11} and 2.4×10^{-8} S/cm, respectively, giving a photoresponse of 2.2×10^3 for our best films.

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