# Deposition of Silicon Films from Liquid Cyclopentasilane Precursors Using High Pressure Spray System

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## ABSTRACT

Si- films were deposited from liquid precursors, especially cyclopentasilane using a high pressure spray deposition system based on an electronically controlled piezo-injector in a inert gas atmosphere. This equipment might be applicable to other liquid precursors and targeted thin Si-films of importance. The thermal properties and reactivity with oxygen of pure liquid cyclopentasilane and its solutions in toluene are investigated by temperature dependent FTIR-Spectroscopy and Differential Scanning Calorimetry. The homogenous films of silicon in µm range thickness are deposited from pure liquid cyclopentasilane and its solutions in toluene on rigid carbon glass plates and on flexible carbon glass fiber substrates using a high pressure spray deposition system. The morphological and structural properties of the silicon films were investigated. These results and the chemical analysis of the films show that the annealed films are homogenous, adhesive and consist of pure polycrystalline silicon. The silicon films deposited from liquid cyclopentasilane in toluene solutions show cracks, whereas silicon films deposited from pure cyclopentasilane are cracks free over at least 400 cm$^2$ and might enable to develop large area solar cells.

*Keywords: Cyclopentasilane decomposition, Silicon films, High pressure spray, Solar Cells*

## 1. INTRODUCTION

Silicon semiconductor films are widely used in microelectronics, displays and photovoltaics. The films are deposited in various phases such as epitaxial, amorphous, nanocrystalline and polycrystalline depending on the required application using Chemical Vapour Deposition (CVD) and Physical Vapor deposition (PVD) techniques [1]. To form a p-n junction, the films are subsequently n- or p- doped using gases such as phosphine and borine etc. In general, CVD [1, 2] and Plasma Enhanced Chemical Vapour Deposition (PECVD) techniques [1, 3, 4] are used to deposit polycrystalline and amorphous silicon films, respectively. High quality films of silicon and of other materials can also be deposited using ion beam deposition technique [1, 4-8]. The grain size of the silicon films from nanocrystalline to polycrystalline is

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modified by annealing in vacuum or inert gas atmospheres or by surface annealing using lasers. The CVD technology has many drawbacks [1]. The source material is in gaseous state such as monosilane, which is highly toxic and reactive. Furthermore during the film formation, the gas phase reaction, diffusion and surface reactions are involved. The substrate is held at temperatures varying between 500 and 1200°C. Although in PECVD technique, the substrate temperature is lower (between 200 and 500°C) contamination of the film by particles in the processing environment limits the deposition rate in CVD technique. Expensive and large equipment such as high frequency generators and vacuum equipment are required. It is also difficult to deposit a film of uniform film thickness on a substrate of uneven surface [1].

The production costs are high due to expensive equipment and low film deposition rate. To reduce the cost of production of microelectronic components, displays and particularly solar cells, alternative efficient and low cost techniques for the deposition of silicon films are of utmost importance. The use of liquid silicon precursors would enable a continuous deposition of large surface area silicon films with high deposition rate on rigid as well as on flexible substrates. Various film deposition techniques may be used such as simple liquid spraying, spin coating or printing. The lower silicon hydrides such as monosilane $SiH_4$ under normal temperature and pressure (NTP) are gases, whereas higher silanes such as cyclopentasilane ($C_5H_{10}$) and cyclohexasilane ($C_6H_{12}$) are liquids under NTP. The research on liquid silanes goes back to as early as 1973 and the synthesis of liquid cyclopentasilane (CPS, $C_5H_{10}$) [9, 10] and cyclohexasilane ($C_6H_{12}$) [11] were described. A simplified way for synthesis of CPS was developed, recently [12]. CPS is liquid at NTP, has density of 0.973g/cm$^3$, melting point of -16.8°C and boiling point of 173.3 °C. This compound has a ring form structure, which is assumed to dissociate upon exposure to ultra violet radiation and heating above 500°C leading to the formation of polycrystalline silicon, details of decomposition, however, were not yet published. The research group of Shimoda [13-19] reported various methods to deposit Si film on substrates like UV assisted decomposition processing solutions and CPS diluted in Toluene, printing to form solar cells or Si thin film transistor etc. Further deposition method use lasers [20, 21]. The solution processed silicon thin-film transistors (TFTs) using a CPS based liquid precursor (10 percent CPS dissolved in toluene). Using this precursor, they deposited polycrystalline silicon (poly-Si) films by spin-coating and ink-jet printing, and fabricated the TFTs with electron and hole mobilities of 108 $cm^2 V^{-1} s^{-1}$ and 6.5 $cm^2 V^{-1} s^{-1}$ respectively. These mobilities are much larger than those achieved in solution-processed organic TFTs, and even exceed those of a-Si TFTs ($\leq$ 1 $cm^2 V^{-1} s^{-1}$). Ishihara *et al.* [20] reported the electron and hole mobilities of 391 and 111 $cm^2 V^{-1}s^{-1}$ in a single grain Si-TFT prepared by laser crystallization of a Silicon film obtained by spin coating of CPS solution. Therefore the deposition of Silicon films from liquid precursors offers a big potential for low cost deposition of semiconductor quality silicon films on rigid and flexible substrates for the microelectronics, displays and particularly microcrystalline film solar cell applications.

The techniques which so far have been used for the film deposition from the liquid precursors are solution processing, spin coating, laser induced coating and ink-jet printing [13-23]. For example spin coated films have considerable defects, it is difficult to deposit films of thickness more than 100 nm, although thicker films may be deposited by multiple coating. But thicker films are inhomogeneous, possess stress and show cracks after transformation to polycrystalline phase. In standard wafer based crystalline silicon photovoltaic technology, the films have thickness in micrometer range to achieve a conversion efficiency of 15 to 20 percent.

This paper reports in detail the deposition of Si-films by a high pressure spray system designed and built at IVT- Esslingen, Germany. This system enables to deposit high quality

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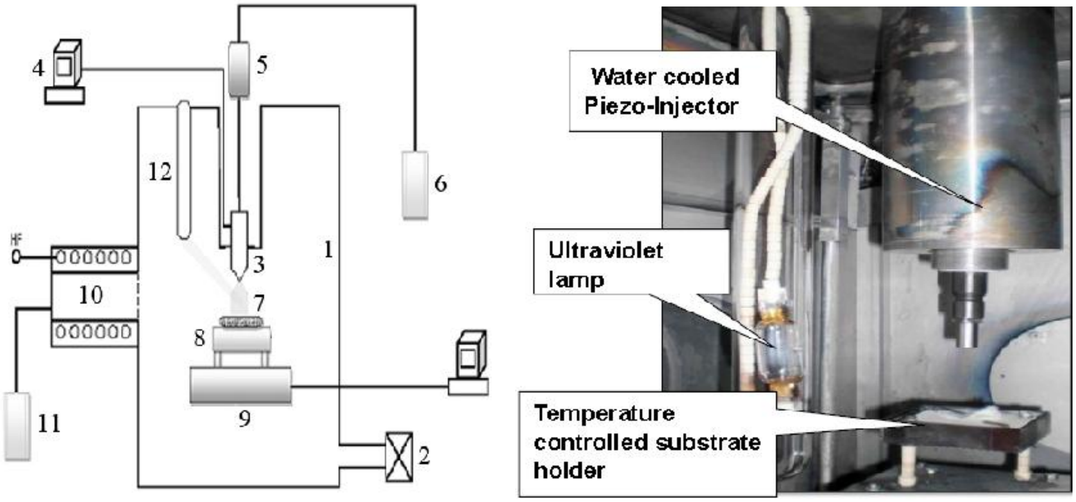
e.g. homogenous, stress and defect free silicon films in µm range with high deposition rate from the liquid precursors such as pure cyclopentasilane and its solutions in toluene. The films cover on rigid and flexible substrates e.g. rigid carbon glass plates and flexible carbon glass fabrics, respectively. The thermal properties of CPS and it´s reaction with various oxygen concentrations in inert gases like nitrogen or argon are not known in detail and are studied safe CPS.

## 2. EXPERIMENTAL DETAILS

### 2.1 High Pressure Spray Film Deposition System

Fig.1a shows the working principle of the film deposition system by high pressure spraying with all the components. The system consists of a recipient 1 connected to a vacuum pumping system 2. The recipient can be evacuated to a pressure of 10-6 mbar and filled with inert gases such as Ar to desired pressures. On the top of the recipient is a high pressure piezo-injector 3 fitted to spray the liquid precursors. This piezo-injector is connected to the electronic control system 4, water cooled liquid (CPS or it´s solutions in toluene) holder 5 and high pressure argon gas bottle 6. The substrates 7 for the film deposition are placed on a temperature controlled substrate holder 8. The substrate holder is capable of heating up to 1200°C and is connected to a temperature controller 9. A H.F. ion beam source 10 with Ar gas bottle 11 is also attached to the recipient. The ion beams of inert gases such as Ar as well as electron beams can be generated up to energies of 6 keV by ion beam source. This ion beam source is used to ion etch the substrate surfaces and also to affect the dissociation of CPS and it´s solutions during spraying on the substrates. There is an ultraviolet lamp 12 to dissociate the CPS molecules in the sprayed aerosol.



(a) (b)

**Fig. 1: (a) Schematic diagram of the high pressure spray film deposition system; 1. Recipient, 2. Pumping system, 3. Piezo-injector,4. Electronic control system, 5. Water cooled CPS container, 6. Argon gas bottle, 7. substrate, 8. X/Y table, 9. Substrate holder, 10. H.F. Ion beam source, 11. Ar-gas bottle,12. Ultraviolet lamp, (b) Realized equipment.**

A gas purifier is also connected to the recipient. This gas purifier supplied from Pure Guard, by Johnson Mathey works at 470°C. This purifier removes the gases like oxygen, nitrogen, hydrogen and also water from the circulating gases. During the spraying and dissociation of

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CPS and it´s solutions in toluene, the atoms of silicon, hydrogen, and carbon are produced and the argon gas in the recipient is contaminated. Therefore, the gas from the recipient is circulated through this purifier to remove the carbon and hydrogen and to keep the argon gas atmosphere in the recipient clean. To be safe, the content of the recipient gas atmosphere is analyzed using a quadrupole mass spectrometer.

Fig. 1b shows a high pressure piezo-injector fitted on top inside the recipient to spray the CPS solutions on the substrates placed on a X/Y moveable and temperature controlled substrate holder. The substrates can be heated up to 1200°C. The UV lamp of 500 W and emitting wavelengths between 300 and 500 nm in the recipient dissociates the CPS during spraying. The high piezo-injector is a Bosch HDEV4 and is enclosed in a water cooled steel cylinder. The cooling is necessary to avoid the dissociation of CPS in the injector. The inlet of the injector is connected to an Ar gas bottle (gas pressure 200 bar), CPS holder and the piezo-injector is connected to an electronic controller supplied by Genotech. The electronic controller regulates the spraying conditions such as piezo trigger voltage, injecting pressure and opening time of the injector. In this way, the pressure of the liquid in the injector, spraying time, number of pulses,pulse duration and pulse interval are precisely regulated.The homogeneity of the deposited silicon film also depends on the distance between the spraying nozzle and the substrate. The angle of the aerosole cone ejecting from the nozzle depends on the Ar gas pressure, opening and closing of the injector (no. of pulses), the pulse duration and the pulse interval and the type of nozzle. The typical parameters used for the deposition of Si films from CPS and solutions are the following:
Argon gas pressure in the recipient: $10^{-3}$- to$10^{-4}$ mbar
Argon gas pressure on the CPS holder: 10 to 30 bar
Number of voltage pulses on injector: 5 to 10
Pulse duration: 260 µs
Pulse interval: 8500 to 9000 µs
Piezo-injector Voltage: 85 to 90 Volt

The aerosol ejected from the nozzle was recorded by a high speed video camera by varying injector parameters and changing the distance between the spraying nozzle to obtain a homogenous silicon film. The optimum distance between the nozzle and substrate was found to be 30 mm. Homogenous silicon films of thicknesses from nm to µm range may be achieved by adjusting above mentioned parameters. The aerosol cones ejected from two different nozzles (left-narrow cone nozzle, right-wide cone nozzle) are shown in Fig. 2.

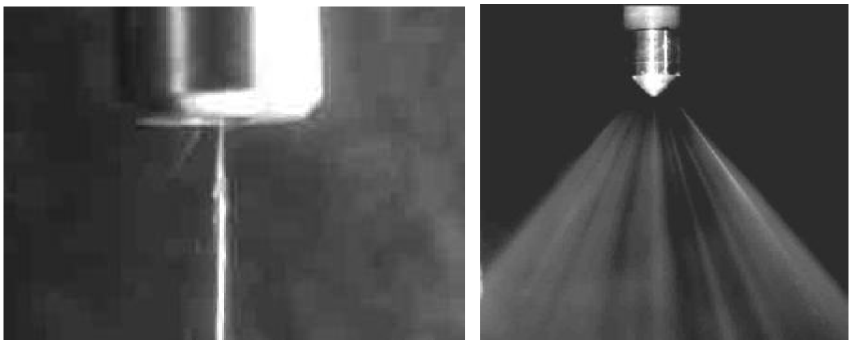

**Fig. 2: Photographs of the ejecting aerosoles from the nozzle of high pressure injector under two different conditions.**

The silicon films were deposited on rigid and flexible substrates from CPS solutions in toluene and pure CPS using high pressure spray system. The morphology, thickness and

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lattice structures of the films were investigated using techniques such as scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDXA), optical microscopy and glanzing incident X-ray diffraction using Cu Kα radiation.

## 2.2 Thermal Properties of Cyclopentasilane

The molecular structure of consists of a ring structure. Cyclopentasilane (CPS) was synthesized for the first time in 1973 by Hengge and Bauer [9, 10]. A simplified way for synthesis of CPS has been developed, recently by Lee *et al*. [12]. Liquid polysilanes are more stable compared to $SiH_4$ gas but CPS is still pyrophoric. The pyrophoric nature is only weakly attenuated by diluting it in organic liquids such as toluene. Therefore, the substance has to be handled under inert gas atmosphere, because the limits of oxygen traces causing the explosive reaction are not known in detail, but are investigated here. The UV irradiation of CPS causes the photopolymerization to polysilanes and Si atoms and the formation of Si film takes place [13]. The liquid CPS is commercially now available but not at the time of the research at high quality. To conduct the present research work, the pure and diluted CPS solutions were obtained from research institutions. One source was ETH-Zürich, Switzerland. The thermal behavior and reaction with oxygen of pure CPS and it´s solutions in toluene were investigated by using techniques such as Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR). The CPS or its solution was introduced in a closed gold plated DSC-pan in an inert Ar gas atmosphere using a glove box, It was then heated to 500 $^{o}$C, similar like the method to study metal organics [24]. Additional experiments were performed with DSC-pan cover pierced to enable the access of air into it during heating to analyze the reaction kinetics with air depending on. The results were used to estimate the limit of oxygen concentration not leading to explosion, or the time to explosion. The analysis of the evolved gas on heating occurred in a heatable cell in an Ar atmosphere by FTIR [25]. Heating the cell from 30 to 270$^{o}$ C in steps of 5$^{o}$ C, IR-spectra were recorded at each step.

## 3. RESULTS AND DISCUSSION

### 3.1 Decomposition of Pure CPS and 20 percent CPS solution in toluene

An IR-spectrum of CPS at 30°C is shown in Fig. 3, as derived after the subtraction of the toluene IR-spectrum from the spectrum of the CPS solution. The bands at wave numbers of 2150, 902 und 716 cm$^{-1}$ correspond to pure CPS, and agree roughly with the literature values [9, 10, 12]. The IR-spectra of the CPS solution recorded in steps of 5° C during heating from 30°C to 270° C are shown in Fig.4. The main effects observed are the increase of the absorbance of both the evaporation of toluene and CPS, a strong rise of the background, especially the growth of new bands in the medium and low wavenumber ranges. The rise of background occurs below 100°C slowly and continues strongly above 150-160$^{o}$C. The new bands are narrow ones especially that at 2188 cm$^{-1}$ close to the 2150 cm$^{-1}$ CPS band. Other bands arise between 1050 - 1150 cm$^{-1}$ and 725 – 975 cm$^{-1}$. Traces of water are also present, indicated by the noise-like bands between 4000 and 3500 cm$^{-1}$. The IR-spectrum of CPS solution after subtracting the toluene IR-spectrum at the end of heating (270°C) is plotted in Fig 3 and the detailed evolution of the bands in Fig. 4. These figures show the bands corresponding to CPS as well as some new bands. The bands between 2000 and 2300 cm$^{-1}$ can be assigned to Si-H bonds, those at 1050 - 1150 cm$^{-1}$ mainly to Si-O bonds and those between 725 and 975 cm$^{-1}$ also to Si-H, but including some Si-O bands [26-34]. They are similar to those observed for polysilanes and for thins films of -Si:H, Si/$SiO_2$ and $SiO_2$. The spectra of pure CPS are quite similar to those of Fig. 3, however without the residues of toluene spectra subtraction.

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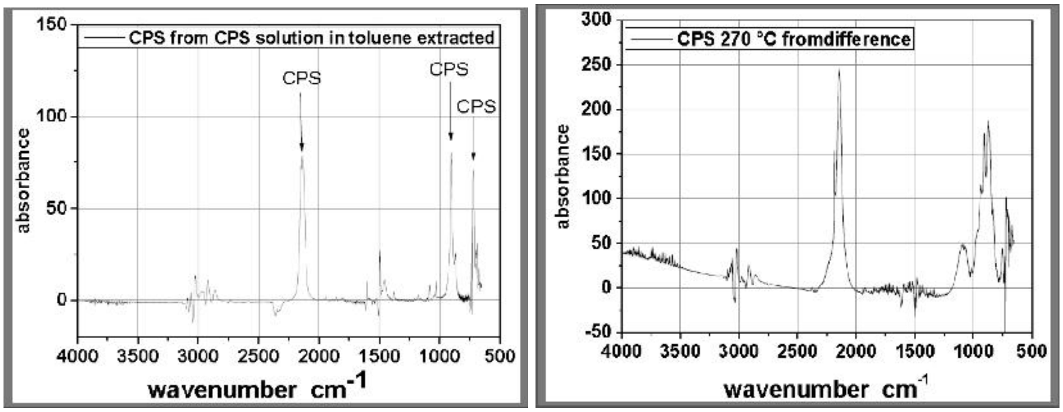
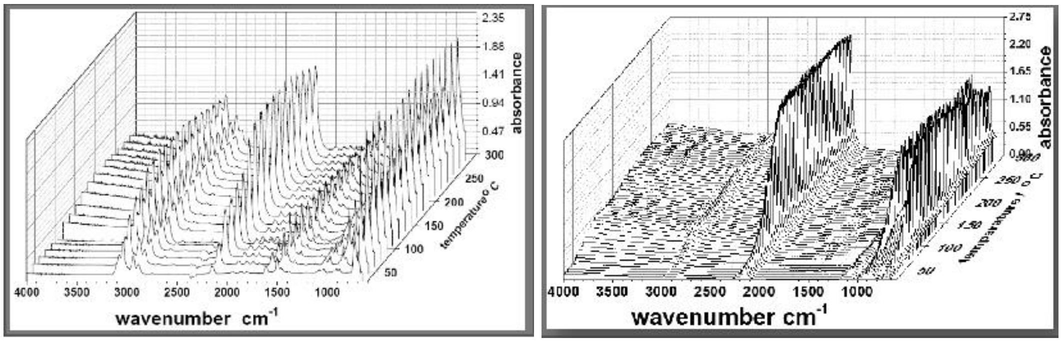


**Fig. 3: Infrared spectrum of the 20% CPS solution in toluene after subtraction of the infrared spectrum of toluene (left 30°C, right – heated to 270$^{o}$C ).**

CPS evaporates below 100$^{o}$C which is indicated by the increase of intensity of the CPS bands. The increase of the base lines with increasing temperature of the FTIR-spectra shown in Fig. 3 and 4 is interpreted as formation of particle of Si or Si-H from CPS in the gas phase of the cell. The rise of the IR spectra between 30 and 130 $^{o}$C was extracted from the spectra of Fig. 4 (omitting the bands). Applying Mie-Theory the particle size distribution can be estimated by a least squares fit procedure [35]. Details of the particle size evaluation which resulted in sub-micron diameters are given in earlier publications [36, 37].



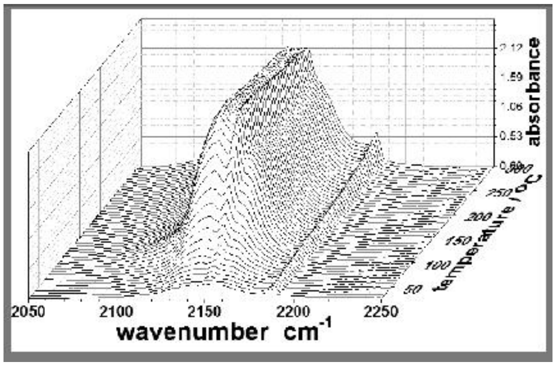


**Fig. 4: The infrared spectra of CPS pure (right) and 20% CPS solution in toluene (left) recorded during heating the solution in steps of 5°C up to 270°C. Peaks between 2050 and 2250 cm$^{-1}$ (bottom) which increases strongly for both types of CPS samples.**

Fig. 5 shows the DSC curve with closed gold (should avoid reactions but could obviously not) pan from room temperature to 500°C. The broad endothermic peak below 250°C.

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corresponds to the evaporation of CPS and toluene. The endothermic peak at 368°C on 2$^{nd}$ heating and 333 °C ob cooling is related to the melting point of $Au_{94}Si_6$ [38, 39]. This alloy was obviously formed by the reaction of CPS on deposition onto the DSC pan with its Au layer on heating. The evidence of scattering by particles in the IR-spectra in the heatable cell (rise of the background on temperture increase) and the increase of the sharp endothermic DSC peak on temperature cycling may indicate the formation of Si particles or Si-H-clusters in the gas phase and the sub-sequent formation of the alloy on precipitation on the gold cladding of the DSC pan. Thermal decomposition is similar to that of polysilanes and CPS from solid state [38,39].

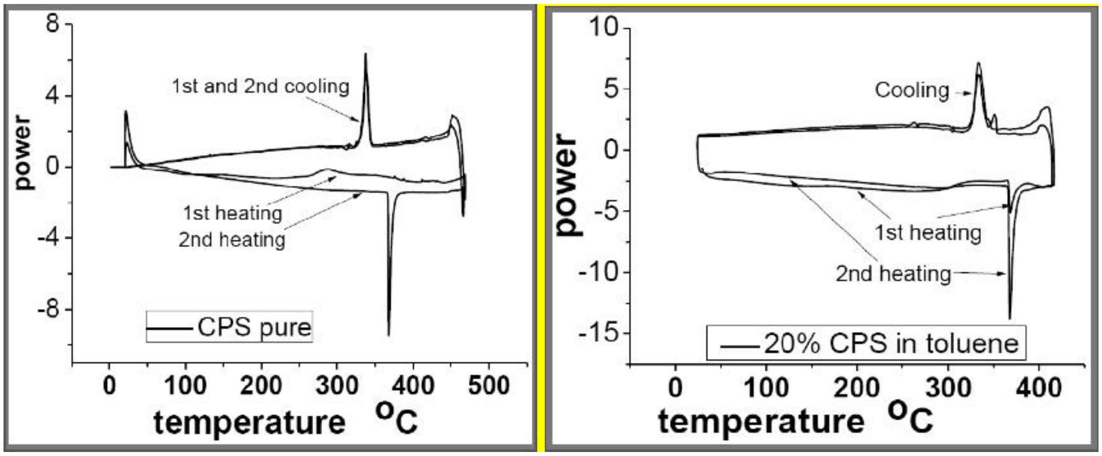

**Fig. 5: The differential thermal analysis (DSC) curves from room temperature to 500°C of a 20% CPS solution in toluene and pure CPS. The Si reacts with the gold cladding of the when deposited from the gas phase.**

### 3.2 Safety Analysis of CPS Handling

The reaction of CPS which is hazardous [40, 41] with air was investigated by DSC technique by heating it in a pierced pan at a heating rate of 5°C /min. The DSC curves were evaluated by the kinetic model of two competitive reactions an endothermic (evaporation) and exothermic (reaction with oxygen) one. The derived kinetic parameters were introduced into an adiabatic self-heating model. It was estimated that pure CPS would explode in air in 0.7 s and 20% solution in toluene within 5 s both at room temperature. These data enable the estimation that safe handling of pure CPS is only possible at lower oxygen concentrations than of the order of magnitude of 0.00001 and that of diluted CPS (in toluene) at 0.00002-0.00003. Details of the evaluation are published elsewhere [36, 37].

### 3.3 Silicon Film Deposition from 20% CPS Solution in Toluene

A high pressure CPS holder was filled with 20% CPS solution in toluene in a glove box under Ar gas atmosphere and connected to the high pressure injector and Ar gas bottle as described in section 2. A carbon glass plate of 20x10x3 mm3 was placed on the temperature controlled substrate holder. The recipient was evacuated to a pressure of the order of $10^{-6}$ mbar and filled with argon gas to a pressure of $10^{-4}$ mbar. The gas purifier was activated and the UV lamp was turned on. The electronic controller of the high pressure injector was turned on and adjusted to the following parameters for spraying the CPS solution:

| | |
|---|---|
| - Argon gas Pressure in the recipient: | 2. $10^{-4}$mbar |
| - Argon gas pressure in CPS holder: | 10 bar |

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- Number of pulses: 5 to 10
- Pulse duration: 260 µs
- Pulse interval: 8500 µs
- Piezo-injector Voltage: 90 V

After spraying, substrate was heated to a temperature of 700 °C for a period of 20 minutes in the recipient. Fig. 6 shows the SEM image of the silicon film. The substrate was completely covered by a smooth, homogenous and adhesive Si film. Some spherical shaped bubbles are on the surface. They might have occurred due to the evaporation of gas dissolved in the film on annealing. The thickness was measured from the cross section of Si film/substrate by SEM and has a value of 2 µm. 2 µm thickness is a value already challenging to be deposited without faults. An EDXA-spectrum of the Silicon film was recorded and is shown in Fig.7. This spectrum confirms that film consists of pure Si without any impurities.

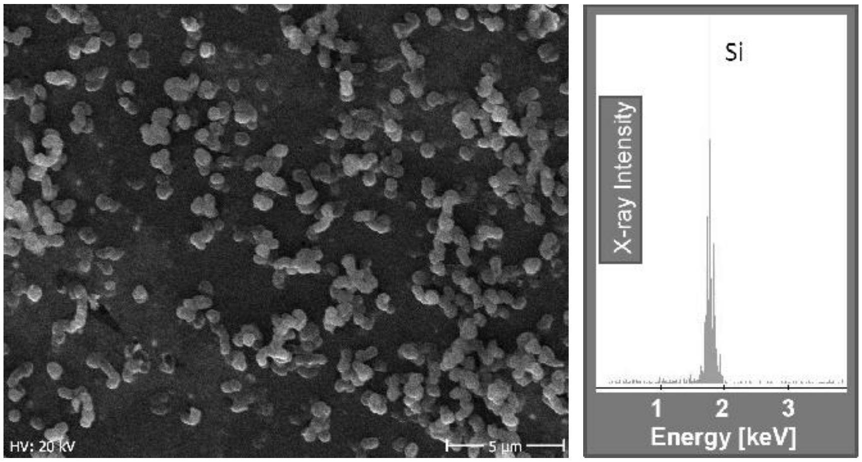

**Fig. 6: (a) SEM image of a Si particles of deposited on a carbon glass plate from 20% CPS solution and annealed at 700 °C for 20 min, the particle size corresponds to the size obtained by thermal decomposition, (b) The related EDXA curve.**

Fig. 7 shows the glanzing incident X-ray diffraction pattern of the silicon film on the carbon glass substrate at a x-ray incident angle of 2°. This method gives information on the crystallite sizes and cell sizes and can confirm thickness. Diffraction pattern shows the broad diffraction lines corresponding to the carbon glass substrate and narrow lines correspond to polycrystalline silicon. The lattice parameter of the diamond cubic lattice of silicon film was calculated from the X-ray diffraction pattern and the value is 0.5407 nm. The cell volume is 1.58.10-22 $cm^3$ and the density of silicon atoms is 5.06.1022 atoms/ $cm^3$ .The lattice parameter of pure silicon is 0.5430 nm.

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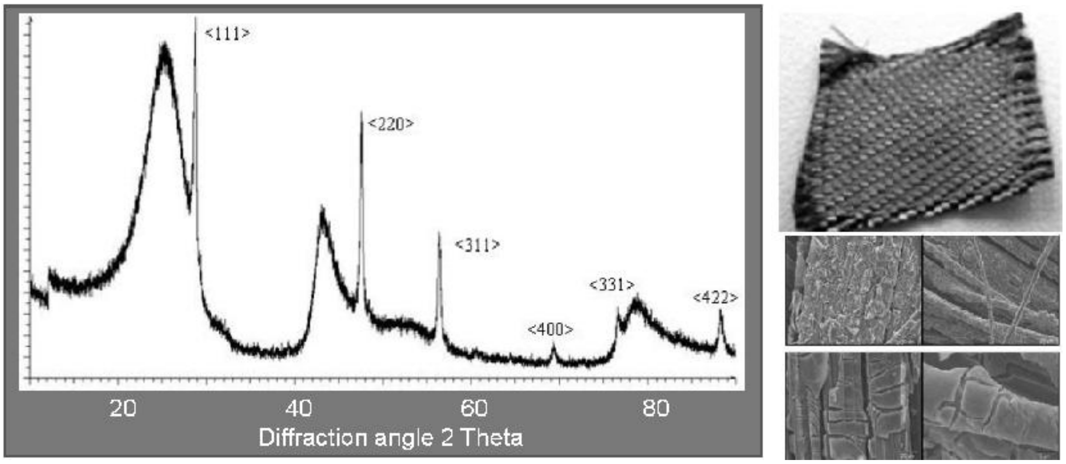

**(a)** **(b)**

**Fig.7: (a) The glanzing incident X-ray diffraction pattern of silicon film deposited from 20% CPS in toluene solution and annealed at 700°C. (b) Micrograph and SEM images of the samples.**

A silicon film was also deposited on flexible carbon glass fiber substrate from 20% CPS solution in toluene under similar deposition conditions as for rigid carbon glass plate as described above. The substrate was heated at 950°C for 10 minutes. Fig. 7 shows the optical micrograph (a) and SEM images (b) of the silicon films deposited on flexible carbon glass fiber substrate. The substrate is completely covered by an adhesive silicon film of 2 µm thickness. There are some cracks in the film. They might be due to stress in the film. An EDXA-spectrum of the Silicon film was taken as shown in Fig.6. This spectrum confirms that film consists of pure silicon without any impurities. The glanzing incident X-ray diffraction patterns of the Si film on the flexible carbon glass fiber at a X-ray incident angle of 2° shows diamond cubic structure as also observed in the case of rigid carbon glass plate, too.

## 3.4 Si Film Deposited from pure CPS

The CPS solution holder was filled with pure CPS under argon atmosphere in a glove box and connected to the injector as described in the case of 20% CPS solution, the film depositing conditions were similar as well. Fig. 8 shows the optical micrograph (a) and the SEM images (b) with different magnifications taken from different areas of the deposited silicon film on the flexible carbon glass fiber substrate. The silicon film is about 1 µm thick and is adhesive to the substrate, is homogenous, and it is without cracks in contrast to the film deposited using 20% CPS solution in toluene.

An EDXA-spectrum of the Silicon film was taken as shown in Fig.8. This spectrum confirms that the film consists of pure Si without any impurities.

A comparison of the SEM images (Fig. 7 and 8) of Si films deposited from 5 percent CPS in toluene, 20 percent CPS in toluene and pure CPS on carbon glass fiber shows that Si films deposited from pure CPS has no cracks. It may be concluded from these results that the origin of the cracks in Si films may be due to residual toluene in the precipitating CPS which evaporates when forming the Si-layer.

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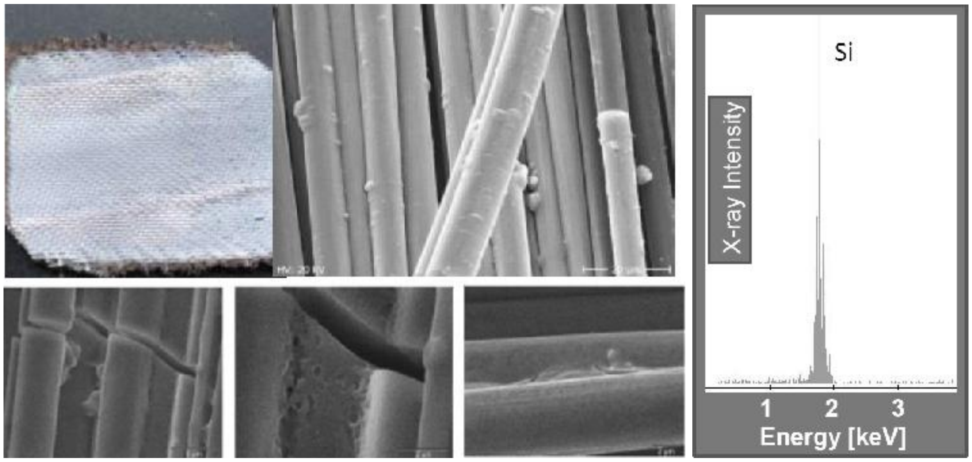

(a) (b)

**Fig. 8: (a) Photograph (left) and SEM images (right) of a silicon film of 2 µm thickness deposited on a carbon glass fiber substrate and the fibers from pure CPS solution and annealed at 950 °C for 10 minutes. (b) The related EDXA curve.**

Fig. 9 shows the glanzing incident X-ray diffraction pattern of the silicon film deposited using pure CPS on the flexible carbon glass fiber at x-ray incident angle of 2°. The diffraction patterns show the broad diffraction lines corresponding to the carbon glass fiber and narrow lines with indices correspond to polycrystalline diamond cubic structure Si as also observed in the case of rigid carbon glass plate. The mobilities and and conducting properties are typical to thin films of the same thickness and purity. The X-ray diffraction pattern of the Carbon glass substrate is also shown in the figure.

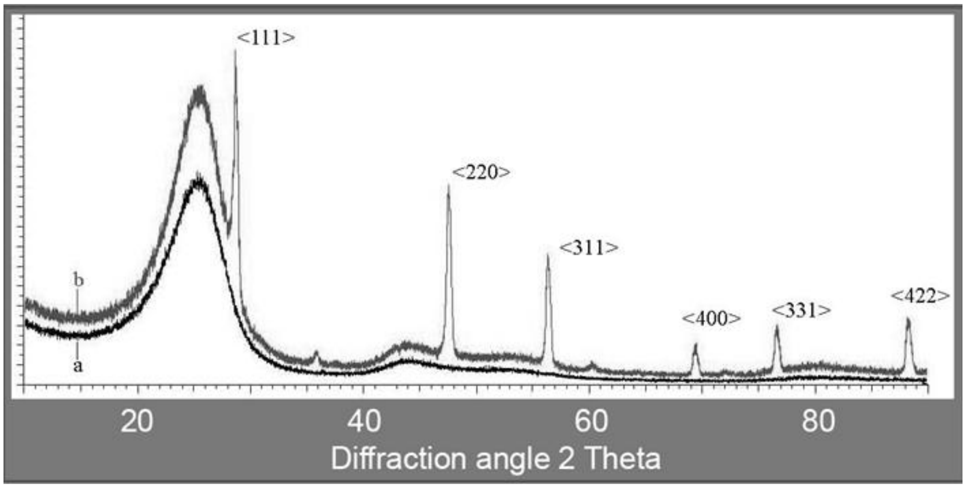

**Fig.9. The glanzing incident x-ray diffraction patterns of silicon film deposited on carbon glass fiber from pure CPS and annealed at 950°C for 10 minutes. Curve with indices - polycrystalline diamond cubic structure Si**

Comparing the morphological, compositional and structural investigations of the Si films deposited from pure and 20% CPS in toluene solution, it is demonstrated that thick ( µm range ) pure polycrystalline crystalline, homogenous and crack free films of Si can be deposited from pure liquid CPS using our high pressure spray deposition system. The spray

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technic of CPS and the ion beam assisted degradation opens applications at industrial scale of manufacturing thin films of various sizes and thicknesses.

## 4. CONCLUSIONS

A high pressure spray film deposition system, to deposit films from liquid precursors is developed. The thermal properties and reactivity with oxygen of pure liquid CPS and it´s solutions in toluene are investigated by temperature dependent FTIR-Spectroscopy and Differential Scanning Calorimetry (DSC). It was estimated that pure CPS would explode in air latest in 0.7 s and 20% solution in toluene within 5 s at room temperature. It was estimated that safe handling of pure CPS is only possible at lower oxygen concentrations than of the order of magnitude of 0.00001 and that of diluted CPS at 0.00002-0.00003. Silicon films are deposited on rigid and flexible (fabric) carbon glass fiber substrates from pure CPS and CPS in toluene solutions using this system. The investigations of the morphological, compositional and structural properties of the films shows that homogenous, crack free and µm range thick Si films can be deposited from pure CPS. The thicknesses up to some micron and the size of some cm$^2$ is of an advantage over small electronics as in most publications. The system can be scaled up to deposit large surface area Si films continuously on flexible substrates using several piezo-injectors analogue to the common rail technology used in high pressure fuel injection well introduced in automotive industries. Our common rail high pressure spray deposition system would enable large scale industrial Si deposition plants. The continuous deposition of Si films from liquid silanes as well as n- and p-doping and synthesis of antireflection coatings are in progress.

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## REFERENCES

1. Frey H, Khan HR. Handbook of thin film technology. Springer Berlin Heidelberg; 2015.
2. Furusawa T, Kojima T, Hiroha H. Chemical vapor deposition and homogeneous nucleation in monosilane pyrolysis within interparticle spaces-application of fines formation analysis to fluidized bed CVD. Chem. Eng. Sci. 1988;43(8): 2037-2042.
3. Cuomo JJ, Rossnagel SM, Kaufman HR. Handbook of ion beam processing technology. Park Ridge, NJ (USA); Noyes Publications; 1989
4. Guo L, Kondo M, Fukawa M, Saitoh, K, Matsuda A (1998). High rate deposition of microcrystalline silicon using conventional plasma-enhanced chemical vapor deposition. Jpn. J. Appl. Phys. 1998;37(10A),:L1116
5. Silier I, Gutjahr A, Banhart F, Konuma M, Bauser E, Schöllkopf V, Frey H. Growth of multi-crystalline silicon on seeded glass from metallic solutions. Mater. Lett. 1996;28:87-91.
6. Silier I., Konuma M, Gutjahr A, Bauser E Banhart F, Zizler C, Schöllkopf V, Frey H. In: Proceedings 25th IEEE Photovoltaic Specialists Conference, Washington; 1996, pp681
7. Khan HR, Frey H, Bernhardt F. Structural, morphological, electrical and luminous properties of undoped micro/nanocrystalline silicon films deposited by ion-assisted beam deposition techniques Nucl. Instrum. Methods Phys. Res., Sect. B 1996; *112*(1-4):289-293.
8. Khan HR, Frey H. Ion beam deposition of crystallographically aligned nano-crystalline silicon films. Surf. Coat. Technol. 1999;472:116-119,

E-mail address: ne@online.de.

9. Hengge E, Bauer G. Cyclopentasilan, das erste unsubstituierte cyclische Siliciumhydrid. Angew. Chem. 1973;85(7):304-305 German.
10. Hengge E, Bauer G. Darstellung und Eigenschaften von Cyclopentasilan. Monatshefte für Chemie/Chemical Monthly 1975;106(2):503-512 German.
11. Hengge E, Kovar E. Darstellung und Charakterisierung von Cyclohexasilan Si6H12. Z. Anorg. Allg. Chem. 1979; 459(1):123-130 German.
12. Lee DW, Park YAW, Han JS, Yoo BR. Dephenylation of decaphenylcyclopentasilane with HCl catalyzed by aluminum chloride: facile synthetic route to cyclopentasilane. Bull. Korean Chem. Soc., 2009:3;2443.
13. Shimoda I, Furusawa M, Aoki T, Yudasaka I, Tanaka H, Iwasawa H, Wang D, Miyasaka M, Takeuchi Y. Solution-processed silicon films and transistors. Nature. 2006;440(7085):783-786.
14. Masuda T, Sotani N, Hamada H, Matsuki Y, Shimoda T. Fabrication of solution-processed hydrogenated amorphous silicon single-junction solar cells. Appl. Phys. Lett. 2012;100:253908
15. Ohdaira K, Guo C, Takagishi H., Masuda T, Shen Z, Shimoda, T. Si heterojunction solar cells with a-Si passivation films formed from liquid Si. In *Photovoltaic Specialists Conference (PVSC), 2016 IEEE 43rd* 2016: 0694-0697). IEEE.
16. Zhang J, Trifunovic M, van der Zwan M, Takagishi H, Kawajiri R, Shimoda T, *et al.* Single-grain Si thin-film transistors on flexible polyimide substrate fabricated from doctor-blade coated liquid-Si. Appl. Phys. Lett. 2013;102(24): 243502.
17. Murayama H, Ohyama T, Yoshida I, Terakawa A, Masuda T, Ohdaira K, Shimoda T. Photo-stability of a-Si solar cells fabricated by "Liquid-Si printing method" and treated with catalytic generated atomic hydrogen. Thin Solid Films. 2015;575:100-102.
18. Trifunovic M, Sberna PM, Shimoda T, Ishihara, R. Polycrystalline silicon TFTs on a paper substrate using solution-processed silicon. In Electron Devices Meeting (IEDM), 2016, IEEE International (pp. 32-3). IEEE.
19. Guo C, Ohdaira K, Takagishi H, Masuda T, Shen Z, Shimoda T. Formation of amorphous silicon passivation films with high stability against postannealing, air exposure, and light soaking using liquid silicon. *Japanese Journal of Applied Physics*, 2016;*55*(4S):04ES12.
20. Ishihara R, Zhang J, Trifunovic M, Derakhshandeh J, Golshani N, Mofrad DMT *et al*. Single-Grain Si Thin-Film Transistors for Monolithic 3D-ICs and Flexible Electronics. IEICE Transactions on Electronics. 2014;97(4): 227-237.
21. Ishihara R, van der Wilt PC, van Dijk BD, Burtsev A, Metselaar JW, Beenakker CIM. Advanced excimer-laser crystallization process for single-crystalline thin film transistors. Thin Solid Films, 2003;427(1):77-85.
22. Bedini AC, Muthmann S, Allgaier J, Bittkau K, Finger F, Carius R. Liquid hydridosilane precursor prepared from cyclopentasilane via sonication at low temperatures without the action of light. Ultrason. Sonochem. 2017;*34*:289-293.
23. Iyer GR, Hobbie E K, Guruvenket S, Hoey JM, Anderson KJ, Lovaasen J *et al*. Solution-based synthesis of crystalline silicon from liquid silane through laser and chemical annealing. ACS Appl. Mater. Interfaces, 2012;4(5):2680-2685.
24. Fischer TS, Eisenreich N, Pfeil A. Kinetic parameters of the thermal decomposition of trimethylindium by DSC. Thermochim. Acta. 1999;339(1):35-40.
25. Krause H, Eisenreich N, Pfeil A. Kinetics of evaporation and decomposition of isopropyl nitrate by rapid scan IR spectroscopy. Thermochim. Acta. 1989;149:349-356
26. Kim S, Lee CY, Jin MHC. Fourier-transform infrared spectroscopic studies of pristine polysilanes as precursor molecules for the solution deposition of amorphous silicon thin-films. Sol. Energy Mater. Sol. Cells. 2012;100:61-64.
27. Brodsky MH, Cardona M, Cuomo JJ. Infrared and Raman spectra of the silicon-hydrogen bonds in amorphous silicon prepared by glow discharge and sputtering. Phys. Rev. B. 1977;16(8):3556.

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28. John P, Odeh IM, Thomas MJK, Tricker MJ, Wilson JIB, England JBA, Newton D. Determination of the hydrogen content of a-Si films by infrared spectroscopy and 25 MeV α-particle elastic scattering. J. Phys. C: Solid State Phys., 1981;14(3):309.
29. He L, Inokuma T, Kurata Y, Hasegawa S. Vibrational properties of SiO and SiH in amorphous SiOx: H films (0≤ x≤ 2.0) prepared by plasma-enhanced chemical vapor deposition. J. Non-Cryst. Solids.185(3):249-261.
30. Han SM, Aydil ES. Detection of combinative infrared absorption bands in thin silicon dioxide films. Appl. Phys. Lett. 1997;70(24): 3269-3271.
31. Liu PT, Chang TC, Sze SM, Pan FM, Mei YJ, Wu WF *et al*. The effects of plasma treatment for low dielectric constant hydrogen silsesquioxane (HSQ). Thin Solid Films. 1998;332(1):345-350.
32. Lambers J, & Hess P. Infrared spectra of photochemically grown suboxides at the Si/SiO2 interface. J. Appl. Phys. 2003;94(5):2937-2941.
33. Kaiser RI, Osamura Y. Infrared spectroscopic studies of hydrogenated silicon clusters-Guiding the search for Si $\ mathsf {_2} $ H $\ mathsf {_x} $ species in the Circumstellar Envelope of IRC+ 10216. Astron. Astrophys. 2005;432(2):559-566.
34. Li CP, Li XJ, Yang JC. Silicon Hydride Clusters Si5H n (n= 3−12) and Their Anions: Structures, Thermochemistry, and Electron Affinities. J. Phys. Chem. A. 2006;110(43):12026-12034.
35. Guschin V, Becker W, Eisenreich N, Bendfeld A. Determination of the nanoparticle size distribution in media by turbidimetric measurements. Chem. Eng. Technol. 2012;35(2):317-322.
36. Hadjiev H, Frey H, Schubert J, Koleczko A, Neutz J, Eisenreich N. Decomposition and oxidation of cyclopentasilane diluted in toluene Proc. 42nd Int. Ann. Conf. of ICT, June 28 - July 01, 2011, Karlsruhe, Germany, P103
37. Hadjiev H, Khan HR, Frey H, Schubert J, Koleczko A, Neutz J, Eisenreich N. Decomposition and oxidation of cyclopentasilane in Proc. 43rd Int. Ann. Conf. of ICT "Energetics Materials-Modelling, Simulation and Characterization of Pyrotechnics, Propellants and Explosives", 26-29th June 2012, Karlsruhe, Germany
38. Schülli U, Daudin R, Renaud G, Vaysset A, Geaymond O, Pasturel A. Substrate-enhanced supercooling in AuSi eutectic droplets. Nature. 2010; 464(7292):1174-1177.
39. Lambracht P. Materialwissenschaftliche Aspekte bei der Entwicklung bleifreier Lotlegierungen, Ph.D Thesis, Technische Universität Darmstadt, Germany 2002, German
40. John P, Cowie BC, Odeh IM. Thermal dehydrogenation of polysilane. Phil. Mag. B. 1984;49(6):559-564.
41. Schmidt D, Böhme U, Seidel J., Kroke E. Cyclopentasilane $Si_5H_{10}$: First single crystal X-ray structure of an oligosilane $Si_xH_y$ and thermal analysis with TG/MS. Inorg. Chem. Commun. 2013;35:92-95.

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