

Deposition of a-Si by LPCVD at Low Temperatures from Monosilane-Atomic Hydrogen Mixtures

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A new method of deposition of a-Si by LPCVD from H-SiH₄ mixtures in the range of temperatures 440 ≤ T ≤ 540°C is described. The structural, optical and transport properties of the films are measured as a function of the deposition temperature.

Amorphous silicon prepared by thermal decomposition of monosilane (SiH₄) at atmospheric (APCVD) and low pressure (LPCVD) has been studied by several laboratories¹⁻⁴. Films of comparable quality to those prepared by plasma discharge of SiH₄ are obtained after a hydrogen plasma treatment² at 400°C. However, the deposition temperatures (T_D > 500°C) needed by these methods are incompatible with the unexpensive float glass substrates used in the large area applications of a-Si:H.

There is an increasing interest in a-Si:H deposited by CVD at temperatures lower than 500°C and several methods have been proposed :

1) Homogeneous CVD or HOMOCVD⁵ ; 2) Laser induced CVD⁶ ; 3) Mercury photosensitization of disilane⁷; 4) CVD from higher silanes⁸. The advantages of these techniques as compared to the standard plasma decomposition of SiH₄ are the following : firstly, the electrical properties of the films depend on a reduced number of deposition parameters (mostly deposition temperature) and are more reproducible. Secondly, a low density of spin defects are obtained by depositing at low temperature⁵ or by post-hydrogenated². Finally, negligible photo-induced instabilities (Staebler-Wronski effect) are observed at these low spin concentrations⁵.

We propose a different approach for low temperature deposition of a-Si:H : disilane (and probably higher silanes) is created "in situ" by reaction of monosilane with atomic hydrogen and is thermally decomposed. We present, here, the initial results of our study on the structural, electrical and optical properties of these films.

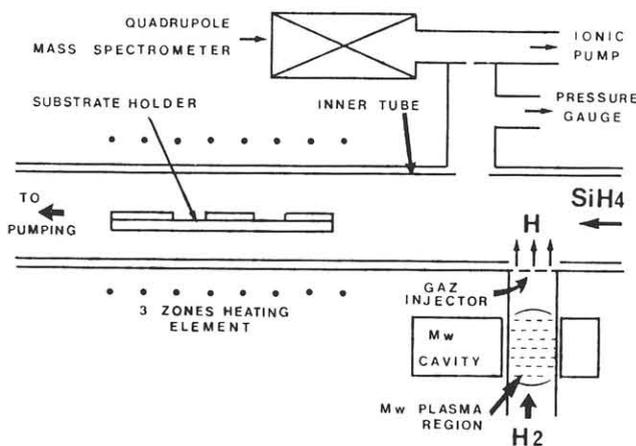


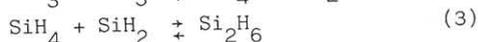
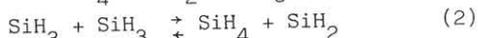
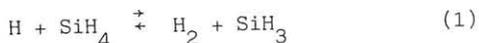
Fig. 1 : Schematic representation of the reactor

Fig. 1 shows a schematic representation of the reactor used for H-SiH₄ CVD. Molecular hydrogen is introduced in a quartz tube. Atomic

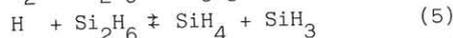
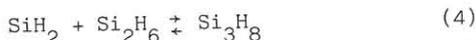
hydrogen is created from a plasma generated by microwaves at 2.45 GHz and is injected in a reaction chamber. This chamber is divided in two regions; in the first, H interacts with an incident flow of SiH_4 at room temperature; the second region, which includes a sample holder, is heated by Joule effect (440–540°C). Gases are evacuated by a rotary pump. The total pressures used are typically 2–5 Torr. Stable species are detected by a quadrupole mass spectrometer located between these two regions.

The formation of disilane is directly detected by the quadrupole mass spectrometer and the ratio $\text{Si}_2\text{H}_6 / \text{SiH}_4$ is optimized as a function of the total pressure, H_2 and SiH_4 flow rates and plasma power. We observe two types of deposits, one yellow-brown in the cold region and another more black in aspect only in the heated region. The first is a solid polymeric silicon hydride, the IR spectrum containing a strong pic at 2100cm^{-1} corresponding to the $(\text{SiH}_2)_n$ vibrations. The hydrogen content in the film is larger than 20%. The second type of film is amorphous silicon as we will discuss, in detail, later.

The chemical reactions to form Si_2H_6 from H- SiH_4 mixtures have been previously studied by Austin and Lampe¹⁰, from the mercury photosensitization of hydrogen (95%) – silane (5%) mixtures. The chemical reactions proposed are the following:



Other reactions decompose disilane creating, for example, higher silanes, trisilane is detected in our case :



Reactions 5 and 6 reduce the quantity of higher silanes available for deposition at low temperature. The same authors observe the same polymeric silicon hydride on the walls of the reactor and they suggest that this polymer enhances the

reaction of SiH_3 radicals on the walls. The consumption of SiH_3 by these reactions reduces the rate of formation of Si_2H_6 since they will compete with equation (2). We have observed, in fact, a reduction of the deposition rate by using dirty walls. Taking into account these facts we have chosen the conditions which reduce these deposits in the cold region and an inner quartz tube is introduced in the reaction chamber and cleaned systematically after deposition.

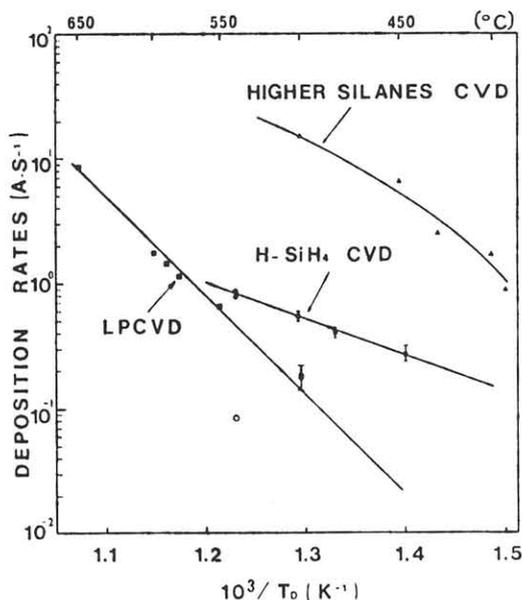


Fig. 2 : Deposition rates versus $10^3/T_D$.
 ▲ Higher silanes CVD. ■ LPCVD
 ● H-SiH₄ CVD (this work).
 ○ Contribution of SiH₄ (this work).

Fig. 2 shows the deposition rate of the H- SiH_4 CVD as a function of the deposition temperature. The total pressure was equal to 5 Torr and the silane to molecular hydrogen ratio was 4%. These results are compared with those obtained by CVD at 50 Torr⁸ of a higher silane mixture and by CVD of monosilane at $p = 500$ mTorr¹¹. At the lower temperature ($T_D = 440^\circ\text{C}$) the deposition rate is a factor of 20 lower than for higher silanes CVD but is ten times larger than for LPCVD of monosilane. This data clearly suggests that the deposition at this temperature is originated by the Si_2H_6 created "in situ" in our experiment

The calculated activation energy associated to the temperature dependence of the deposition rate is about 0.6eV which differs from the 1.7eV obtained from LPCVD of monosilane.

To determine the hydrogen content of the films the infrared absorption was recorded in the range $400\text{--}2500\text{cm}^{-1}$ on films deposited on crystalline Si substrates. For temperatures of 480°C or higher the density of SiH and SiH_2 bonds is too low for hydrogen content determination by this method. For the films deposited at 440°C the 2000 and 640cm^{-1} IR modes are observed and a total hydrogen content of 2% was estimated from the 640cm^{-1} mode. In fig. 3, we compare the hydrogen content as a function of the deposition temperature for films prepared by HOMOCVD⁵, higher silane CVD⁸, atmospheric pressure CVD^{2,3} and by H-SiH_4 CVD. The hydrogen concentration is a monotonic decreasing function of the deposition temperature and this independently of the method used for deposition.

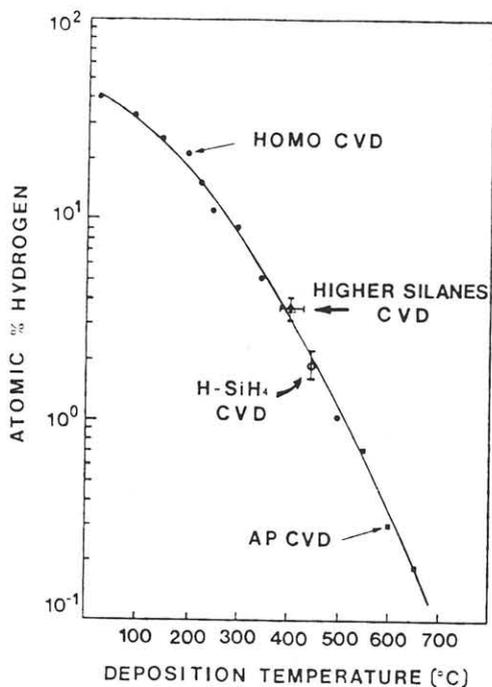


Fig. 3 : Hydrogen concentration versus T_D
 ● HOMOCVD (ref.5). ■ APCVD (ref.2-3)
 ▲ Higher silanes CVD (ref.8)
 ○ H-SiH_4 CVD (this work).

The structure of the films deposited in the temperature range $440\text{--}540^\circ\text{C}$ is amorphous : no crystalline peaks were detected by X-ray diffraction in a standard $\theta\text{--}2\theta$ geometry. The optical gap was determined by a $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot for films of $0.5\text{--}0.8\mu\text{m}$ thick, where α is the absorption coefficient in cm^{-1} and $h\nu$ is the photon energy. The optical gap is between 1.55

and 1.6 eV and increases slightly with decreasing temperature. These values are in qualitative agreement with the values of 1.5 to 1.65 eV of the optical gap for higher silanes deposited in the temperature range $375\text{--}475^\circ\text{C}$ ⁸. No significant differences are observed with the optical gap of APCVD a-Si:H (1.55 eV) deposited at 600°C ^{2,3,12}.

The dark conductivity at room temperature decreases from $5 \times 10^{-8} (\Omega\text{cm})^{-1}$ for undoped films at $T_D = 540^\circ\text{C}$ to $3 \times 10^{-10} (\Omega\text{cm})^{-1}$ at $T_D = 440^\circ\text{C}$. An Arrhenius plot is shown on fig. 4 for samples deposited at different temperatures.

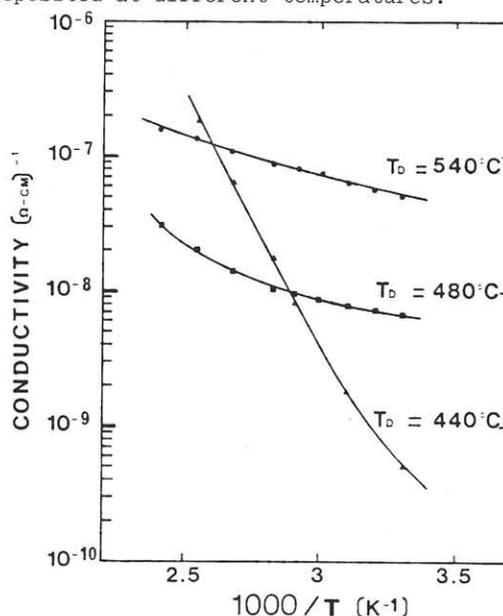


Fig. 4 : $\text{Log } \sigma$ versus $1000/T$ for different deposition temperature

Activation energy of the curves changes from 0.12 eV at $T_D = 540^\circ\text{C}$ to 0.7 eV at 440°C . This can be interpreted by two different transport mechanisms : in films deposited at high temperatures conduction is by hopping at the Fermi level such as in the case of atmospheric pressure CVD a-Si deposited at 600°C ; in films deposited at the low temperature (440°C) the conductivity is by activation to the band and this indicates a lower density of gap states related with the higher concentration of hydrogen into the film. The AMI photoconductivity ($100\text{mW}/\text{cm}^2$) is $10^{-7} (\Omega\text{cm})^{-1}$ for the films deposited at this temperature. No measurable photoconductivity was obtained for films deposited at higher temperatures in agreement with the previous discussion.

In conclusion, we have deposited amorphous silicon from Si_2H_6 created "in situ" by reacting H-SiH_4 mixtures in the range of temperatures 440-540°C. This method produces clean Si_2H_6 and could be used for CVD or plasma discharge deposition at lower temperatures, if the creation of disilane and the deposition rates are optimized. At the lower deposition temperature (440°C), amorphous silicon containing about 2% of bonded hydrogen and a density of states lower than in standard CVD is obtained.

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