

Some Physical Properties of Undoped Amorphous Silicon Prepared by a New Chemical Vapor Deposition Process Using Iodosilanes

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A new method of preparation of a-Si by thermal decomposition (hetero- and homo-CVD) of di- and triiodosilanes is described. The iodosilanes were prepared by the reaction of phenylsilanes with HI. Uniform films on glass and indium/tin oxide coated glass were prepared with thicknesses ranging up to 4.0 μm . Rutherford backscattering spectrometry (RBS) reveals only a slight amount of oxygen, which appears to be on the surface of the film. In addition RBS indicates the presence of a slight amount of iodine that has a density that decreases gradually as a function of depth. FTIR analysis also indicates a slight amount of oxygen and very little hydrogen.

Introduction

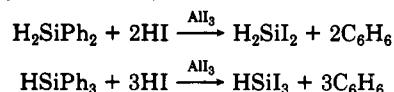
The need for inexpensive solar cells requires the development of thin films with large-area samples. In this regard amorphous silicon has received much attention because it is amenable to thin-film preparation. Furthermore, loss of momentum conservation in a-Si results in a much stronger optical absorption than that for c-Si. As a result the required film thickness for an effective solar cell for a-Si is very low (1 μm) compared to c-Si (300 μm). Chemical vapor deposition (CVD) methods are considered to be inexpensive and suitable for industrial scale production of thin films. Thin-film a-Si has been prepared by conventional CVD (low and high pressure)¹ as well as photo-CVD.² These methods are known as hetero-CVD methods because the chemical intermediates are produced by the decomposition of precursors on a hot substrate. In homo-CVD,³ the gas-phase chemical intermediates are produced by a furnace-heated reactor wall, and these intermediates diffuse to a cold substrate to produce a-Si. Films produced by hetero-CVD have a low concentration of hydrogen (less than 1 at. %)¹ and leave a large number of recombination centers (deep states) by not terminating the dangling bonds. On the other hand, homo-CVD films show higher hydrogen content.

The silane- or disilane-based CVD systems pose considerable technical problems due to the explosive nature of silane/oxygen mixtures⁴ and to vapor-phase nucleation (powdery film)⁵ unless the pressure is very low. It has been proposed⁶ that the chemical intermediates produced from the decomposition of halosilanes do not undergo vapor-phase polymerization, and a halosilane/air mixture is not an explosion hazard.

In this paper, we report the synthesis of diiodo- and triiodosilanes prepared from simple chemical reactions and the deposition of a-Si by hetero- and homo-CVD methods using a new type of reactor in an inductive furnace.

Experimental Section

Synthesis of Diiodo- and Triiodosilanes. Diphenylsilane and triphenylsilane both react smoothly with HI gas in the presence of AlI_3 catalyst to give diiodosilane (triiodosilane) with the following stoichiometry:



For these syntheses a slight molar excess of HI gas was slowly transferred from a lecture bottle (Matheson) to an evacuated high-pressure glass vessel (graduated) and condensed in a liquid N_2 bath. The HI contains some noncondensable gas phase impurities that were removed from time to time during the condensation process by connecting this vessel to the vacuum line. The condensed HI was slowly transferred as a gas to a liquid N_2 cooled high-pressure reaction vessel that contained diphenylsilane (24.8 g) or triphenylsilane (29.6 g, Aldrich) and AlI_3 (0.25 g). The reaction vessel was allowed to warm to ca. -40 °C in an acetonitrile/CO₂ slush bath for several hours. Upon completion of the reaction, unreacted HI and benzene were removed in vacuo. The purity of these iodosilanes was checked by ²⁹Si NMR. Triiodosilane contained 5.5% tetraiodosilane (Figure 1). The iodosilanes were then purified by fractional distillation: H_2SiI_2 at 38 °C (10 mmHg), bp₇₆₀ 149.5 °C,⁶ HSiI_3 at 44 °C (0.003 Torr), bp 220 °C.⁷ For diiodo- and triiodosilanes, no impurity resonances were detected, indicating less than 1% impurity. The compounds were stored under an inert atmosphere in the dark.

Deposition of a-Si by Hetero-CVD. Amorphous Si thin films were deposited by hetero-CVD at temperatures ranging from 500 to 600 °C by using a specially designed double-wall quartz deposition system schematically shown in Figure 2. In an inert atmosphere inside a glovebag, the source material was fed into the sample holder by using a Becton Dickinson syringe, and the deposition unit was assembled. While continuously flowing argon through the unit, the carbon block, which rests on top of the substrate, was heated in the inductive furnace. The sample holder, which contains the liquid halosilane, can be moved up or down to vary the temperature and consequently the vapor pressure of the halosilane. As a result the substrate temperature and position of sample holder control the evaporation and deposition rates. Deposits were obtained on various substrates such as glass, graphite, and KBr. Films were obtained at a substrate temperature of 550 °C or below by using diiodosilane and close to 600 °C by using triiodosilane. Film thicknesses up to 4 μm were prepared (measured by a Sloan Dektak profilometer).

When this approach was used for indium tin oxide (ITO) coated glass substrates, the ITO film was etched away before Si deposition. Recently, reactive ion etching of ITO was shown to be

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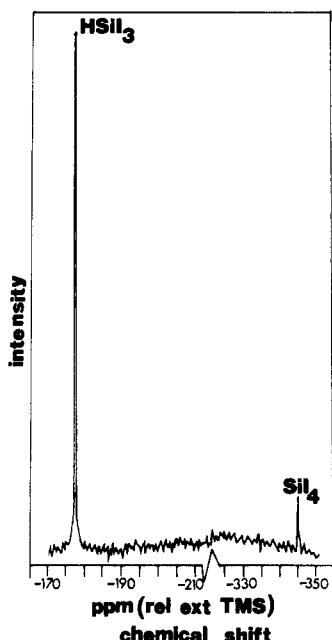


Figure 1. ^{29}Si NMR spectrum of HSiI_3 (in CHCl_3) with a small fraction of SiI_4 (5.5%). The ratio of HSiI_3 and SiI_4 was obtained from the integrated intensity of NMR spectrum.

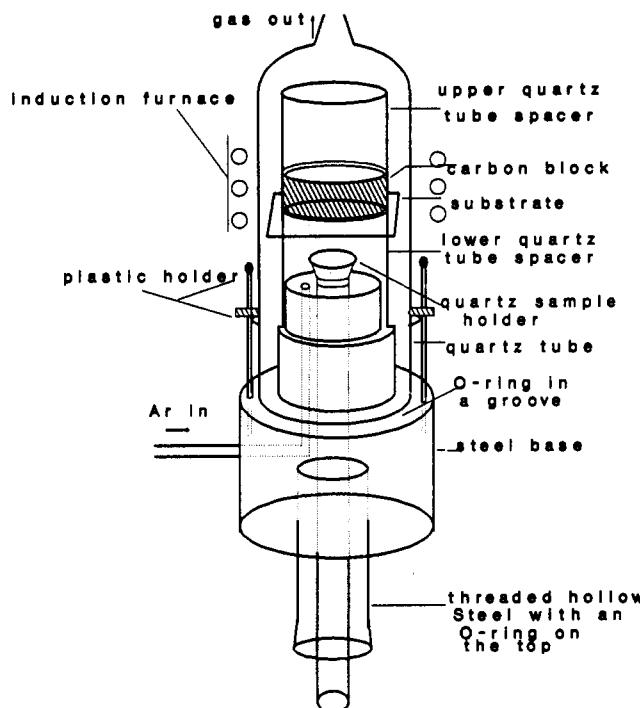


Figure 2. Schematic view of CVD unit for the preparation of a-Si. The rate of deposition can be controlled by the temperature of inductively heated substrate and the position of adjustable sample holder.

effective using HI, and the mechanism was suggested to involve ions and/or atoms.⁸ It is possible that a similar mechanism occurs after partial decomposition of the iodosilane. At any rate to avoid this problem, an alternate approach was employed. Thin films of a-Si were deposited on ITO by pyrolytic decomposition of iodosilane droplets in the following manner. A 450-W cartridge heater (Chromalox, USA) was embedded in a cylindrical carbon block, which was supported inside a vertical quartz tube using two narrow quartz tube holders. Power to the cartridge heater

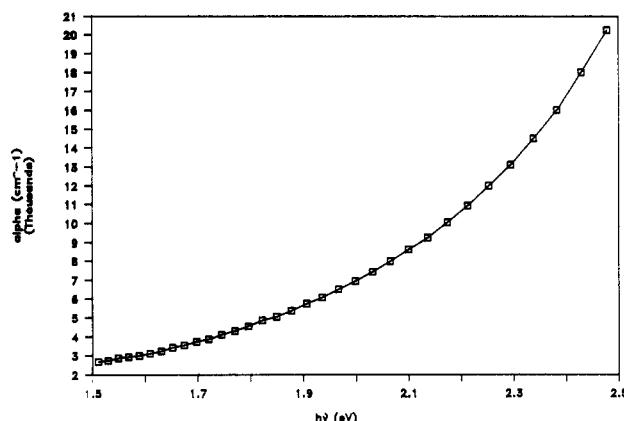


Figure 3. Optical absorption edge for a CVD film of a-Si prepared from the decomposition of diiodo monosilane at a substrate (glass) temperature of $550\text{ }^\circ\text{C}$. The amorphous nature of the film is indicated by the absence of absorption in the long-wavelength region.

was controlled by a variac while the quartz tube in the vicinity of the block was heated on the outside by a beaded resistive heater. The surface temperature of the substrate was monitored with a thermocouple. Iodosilane was added dropwise to a horizontal substrate on top of the carbon block by using a syringe protruding through a septum. Pyrolysis under an atmosphere of flowing Ar permitted the deposition of a-Si without etching away the ITO film from the substrate. Films were deposited on KBr and glass also. All films deposited by this method and by hetero-CVD were brown with a high reflectivity.

Deposition of a-Si by Homo-CVD. For this deposition method, the experimental arrangement was the same as that for hetero-CVD except that the substrate was kept at a lower temperature than the carbon block by placing it on top of a quartz tube spacer sitting on top of the carbon block heater (Figure 2). In this arrangement a hollow carbon block, heated to temperatures ranging from 500 to $600\text{ }^\circ\text{C}$, replaced the solid one shown in Figure 2 so that the evaporated source material was heated and partially decomposed as it passed through on its way to the substrate, which was held at temperatures ranging from 350 to $400\text{ }^\circ\text{C}$. A stream of argon was used to assist the mass transfer. Thus the deposition of a-Si occurred on a colder substrate than for hetero-CVD. The substrate temperature could be varied either by varying the power of the induction furnace or by changing the height of the quartz spacer tube. This type of deposition was carried out with an expectation of getting higher hydrogen content a-Si films.

Results and Discussion

The amorphous nature of the deposited films was confirmed by X-ray diffraction and optical absorption studies. The fact that no powder diffraction lines could be detected indicates that they are very broad and is consistent with an amorphous solid or crystallites that are very small. The absorption spectrum (Figure 3) is not consistent with polycrystalline silicon because it does not extend into the longer wavelength region. With use of a direct bandgap interpretation,⁹ the bandgap obtained by extrapolation varies from 1.6 to 1.8 eV , depending on the temperature of the substrate during preparation. For several films, electron spin resonance spectra give a resonance at $g = 2.0057$, a value consistent with those found previously for amorphous silicon, indicating the presence of dangling bonds.⁹ Consequently, the evidence supports the amorphous nature of the film.

The composition of the film was investigated by using FTIR spectroscopy and Rutherford backscattering spec-

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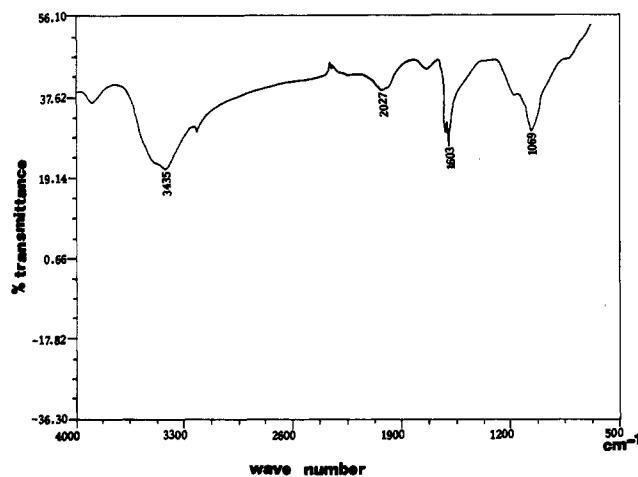


Figure 4. Infrared spectrum of a-Si deposited on KBr crystal by the decomposition of diiodosilane in CVD. The spectrum is characterized by the presence of Si-H, Si-O, and Si-OH vibrational modes.

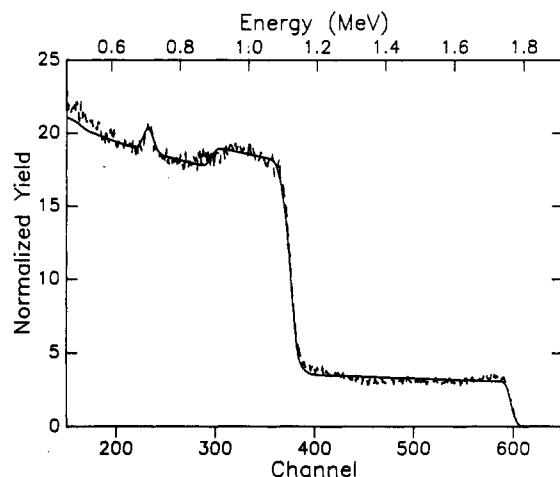


Figure 5. RBS spectrum of a-Si deposited on graphite disk by decomposition of diiodosilane in CVD. The spectrum is characterized by the presence of abundant silicon, a small amount of oxygen at the surface, and iodine throughout the bulk.

trometry (RBS) to be described in detail in a subsequent paper. The FTIR spectrum in Figure 4 was obtained for a film deposited on KBr using diiodosilane at 550 °C. The lines at 2027, 1069 and 3435, and 1603 cm⁻¹ indicate the presence of H, O, and OH, respectively. Although the phenyl group has a line at 1069 cm⁻¹, it cannot be responsible for the line in Figure 4 because the ²⁹Si NMR spectrum of the iodosilane precursor gives no evidence of a phenylsilane impurity. Consequently, the assignments seem reasonable; however, a more detailed study is needed. The oxygen presumably results from oxidation of the surface upon exposure to air after preparation. Evidence for this conclusion is found in the RBS data below. The band for Si-H is weak, indicating that percentage incorporation is low.¹⁰ Unfortunately, the film was too thin to determine its thickness by using the profilometer in our laboratory. Consequently the atom percent of hydrogen in the film could not be estimated. Since the Si-I stretching frequency falls beyond the window limit of KBr, the presence of iodine was checked by RBS.

The RBS spectrum (Figure 5) clearly indicates that silicon is the most abundant element in the film. The

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Table I. Composition^a of Silicon Film Determined by Rutherford Backscattering Spectrometry

sublayer	thickness/nm	silicon	iodine	oxygen
1	70	1.00	0.020	0.670
2	400	1.00	0.013	
3	500	1.00	0.013	
4	300	1.00	0.013	
5	370	1.00	0.005	

^a Mole ratio.

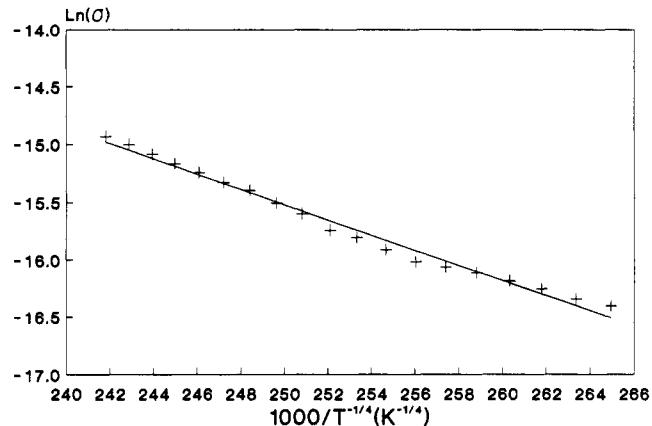


Figure 6. Plot of $\ln \sigma$ versus $T^{-1/4}$ for a silicon film deposited at 500 °C by using diiodosilane. The least-squares fit is indicated by the line through the points.

shape of the iodine response indicates that it occurs throughout the film, but its density decreases somewhat with film depth. On the other hand the oxygen response is peaked, indicating that oxygen does not extend into the film very far. Consequently, the oxygen may result from oxidation of the surface upon exposure of the film to air. These conclusions are based on the simulation¹¹ of the RBS spectrum indicated by the smooth curve in Figure 5. Because of the variation in the composition of iodine with thickness, the simulation is based on five sublayers that have thicknesses presented in Table I. Accordingly, the oxygen-rich layer comprises only 70 nm of a film that is 1640 nm thick. On the other hand, iodine is present throughout the film, but never exceeds a composition of 2%. For this simulation the sensitivity to iodine composition is $\pm 0.1\%$.

The temperature dependence of the conductivity (σ) of the film was measured in vacuum as described earlier.¹² Plots of $\ln \sigma$ versus $1/T$ deviate from linearity and suggest a hopping conduction mechanism.^{10,13} According to the variable range hopping model proposed by Mott,^{10,14} $\ln \sigma$ is linearly dependent on $1/T^{1/4}$ as has been found for our films (Figure 6). Similar behavior has been found for thin-film a-Si:H prepared by vacuum evaporation.¹⁰ On the basis of a fit of the data in Figure 6 to the model, the density of states at the Fermi level is $6.3 \times 10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$, which compares well with the value¹⁰ ($5 \times 10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$) measured for a vacuum-evaporated film of nearly identical resistivity ($4 \times 10^6 \Omega \text{ cm}$) at 25 °C.

On the basis of the composition of the film deduced from FTIR and RBS data, a tentative mechanism for the decomposition of diiodo- and triiodosilane can be presented. The low composition of H and I that results in the film

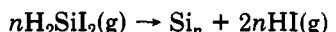
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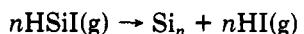
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is consistent with removal of HI, especially in the case of the diiodosilane. Furthermore, it was observed that H_2SiI_2 decomposes below 550 °C but $HSiI_3$ does not. Thus



More than one molecule is presumed to be involved because the reaction seems to occur more easily for higher fluxes of molecules. This mechanism is also consistent with the fact that little evidence of I_2 formation is observed during decomposition of the diiodosilane.

For triiodosilane, iodine formation is observed, and the higher temperature required for decomposition may be indicative of another mechanism. One possibility is



Another reaction known to occur is



and decomposition of the diiodosilane would lead to amorphous silicon.

The presence of a small amount of iodine in the film is consistent with the need for more than one molecule in the decomposition reaction. Thus, trapping of a partially dehydrohalogenated silane would account for the incorporation of the iodine.

Summary

Another possible way of depositing a-Si from iodosilanes by thermal decomposition is demonstrated by using the experimental setup shown in Figure 2. Due to the absence of vapor nucleation of chemical intermediates produced from decomposed iodosilanes and due to the nonexplosive nature, iodosilane precursors emerge as new sources for the deposition of a-Si.

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Registry No. a-Si, 7440-21-3; H_2SiI_2 , 13760-02-6; $HSiI_3$, 13465-72-0.

Additions and Corrections

1990, Volume 2

Walter Torres and Marye Anne Fox*: Rectifying Bilayer Electrodes: Layered Conducting Polymers on Platinum.

Page 310. The captions for Figures 5 and 6 should be reversed.