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**AIP Conference Proceedings**

Series Editor: Hugh C. Wolfe

**Number 73**

# **Tetrahedrally Bonded Amorphous Semiconductors**

(Carefree, Arizona, 1981)



**Editors**

**R.A. Street, D.K. Biegelsen, J.C. Knights**

**Xerox Palo Alto Research Center**



E8361462

**American Institute of Physics**

**New York**

**1981**

1650

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L.C. Catalog Card No. 81-67419  
ISBN 0-88318-172-X  
DOE CONF- 810331

# **Tetrahedrally Bonded Amorphous Semiconductors**

(Carefree, Arizona, 1981)



## PREFACE

A topical conference on Tetrahedrally Bonded Amorphous Semiconductors was held at the Carefree Inn, Carefree, Arizona, from the 12th to the 14th of March, 1981. The conference was sponsored by the American Physical Society, with financial support from the Solar Energy Research Institute, Xerox Corporation and the National Science Foundation. The conference concentrated on the basic physics of hydrogenated amorphous silicon, and was organized in response to the rapidly growing interest in the technological applications of this material.

The Organizing Committee consisted of: D. K. Biegelsen (Xerox); M. H. Brodsky (IBM); D. Carlson (RCA); H. Fritzsche (University of Chicago); J. Joannopoulos (MIT); J. C. Knights (Xerox); G. Lucovsky (North Carolina State University); W. Paul (Harvard); B. Seraphin (University of Arizona); J. Stone (SERI); R. A. Street (Xerox), conference chairman; J. Tauc (Brown University); P. C. Taylor (NRL). The members of the International Advisory Committee were: I. Solomon (France); W. Spear (UK); J. Stuke (W. Germany); K. Tanaka (Japan). The Program Committee comprised D. Carlson (RCA); H. Fritzsche (University of Chicago); G. Lucovsky (North Carolina State University); R. A. Street (Xerox), chairman; P. C. Taylor (NRL).

These proceedings have been organized into chapters which reflect the range of interest of the submitted papers:

Growth and Characterization of Films  
Atomic Structure and Bonding  
Electron States  
Electronic Transport  
Absorption and Recombination  
Surfaces and Interfaces

We are grateful to Violet Moffat, Erin Schreiner and Marilyn Tenney for their assistance in the organization of the conference and in the preparation of the proceedings. Our thanks also go to the projectionist, John Gill, and to the Carefree Inn and its staff for their contribution to the success of the conference.

R. A. Street  
D. K. Biegelsen  
J. C. Knights

Palo Alto, California  
April, 1981

## TABLE OF CONTENTS

### PREFACE

### CHAPTER I: Growth and Characterization of Films

Optical Emission Studies of Reactive Species in Plasma Deposition F. J. Kampas and R. W. Griffith .....	1
Deposition and Doping of a-Si:H from Si <sub>2</sub> H <sub>6</sub> Plasmas B. A. Scott, M. H. Brodsky, D. C. Green, R. M. Plecenik, E. E. Simonyi and R. Serino .....	6
New Insights on Growth Mechanism of a-Si:H from Optical Emission Spectroscopy M. Hirose, T. Hamasaki, Y. Mishima, H. Kurata and Y. Osaka .....	10
F-Etched a-Si Films V. L. Dalal, C. M. Fortmann and E. Eser .....	15
Experimental Evidence for a Kinetic Model for Hydrogen Incorporation into Sputtered a-Si Films T. D. Moustakas, T. Tiedje and W. A. Lanford .....	20
Comparison of a-Si:H Produced by rf Sputtering and Plasma Decomposition Methods G. Model, J. Blake, R. W. Collins, P. Viktorovitch, D. K. Paul, B. von Roedern and W. Paul .....	25
Growth Characterization of a-Si:H Films by <i>in Situ</i> Ellipsometry in a Silane Multipole Plasma B. Drevillon, J. Huc, A. Lloret, J. Perrin, G. de Rosny and J. P. M. Schmitt .....	31
Influence of Electric and Magnetic d.c. Fields on the Electronic Transport Properties of a-Si:H Alloys Produced by r.f. Glow Discharge R. Martins, A. G. Dias and L. Guimarães .....	36
The Role of RF Substrate Bias on the Growth and Properties of Plasma Deposited a-Si:H M. P. Rosenblum, M. J. Thompson and R. A. Street .....	42
The Growth and Properties of Bias-Sputtered a-Si:H D. P. Turner, I. P. Thomas, J. Allison, M. J. Thompson, A. J. Rhodes, I. G. Austin and T. M. Searle .....	47
Film-Plasma Interactions in Triode-Sputtered a-Si:H P. M. Martin and W. T. Pawlewicz .....	52
Bombardment Effects in a-Si:H Sputtered Films R. C. Ross and R. Messier .....	53
Properties of Amorphous Silicon Prepared at Different Temperatures by Pyrolytic Decomposition of Silane P. Hey, N. Raouf, D. C. Booth and B. O. Seraphin .....	58

Preparation of Amorphous Silicon Films by CVD of Higher Order  
Silanes for  $\text{Si}_n\text{H}_{2n+2}$   $n > 2$

S. C. Gau, B. R. Weinberger, M. Akhtar, Z. Kiss and A. G. MacDiarmid .....63

CHAPTER II: Atomic Structure and Bonding

NMR Studies of Sputtered and Glow Discharge Deposited a-Si:H  
W. E. Carlos, P. C. Taylor, S. Oguz and W. Paul .....67

Nuclear Spin-lattice Relaxation by Diffusion in Amorphous Si:H  
B. Movaghar and L. Schweitzer .....73

Proton Magnetic Resonance Studies of Plasma Deposited a-Si:H Films  
J. A. Reimer and J. C. Knights.....78

Characterization of the Protonic Distribution and Environment in  
Amorphous Silicon-Hydrogen Alloys Using Proton NMR and ESR  
F. R. Jeffrey, M. E. Lowry, M. L. S. Garcia, R. G. Barnes and D. E.  
Torgeson .....83

Relation Between Silicon-Hydrogen Complexes and Microvoids in  
Amorphous Silicon Films from IR Absorption  
D. E. Soule, G. T. Reedy, E. M. Peterson and J. A. McMillan.....89

Structural Inhomogeneities and the Interpretation of IR Absorption for  
a-Si:H Films  
G. Lucovsky and R. Rudder .....95

Chemical Bonding Effects on the Local Vibrations in Fluorinated and  
Hydrogenated Amorphous Silicon  
G. Lucovsky .....100

Behavior of Fluorine Atoms in a-Si:H:F Alloy Investigated by Gas  
Evolution  
S. Usui, A. Sawada and M. Kikuchi .....106

On the Structure of Fluorine Defects in Amorphous and Crystalline  
Silicon Studied by Hyperfine Interaction and Channeling Methods  
K. Bonde Nielsen, S. Damgaard, J. W. Petersen, W. Schou, I.  
Stensgaard and G. Weyer .....111

Small Angle Scattering Study of 2-Micron Hydrogenated Amorphous  
Silicon Films Deposited at 130°C and 250°C  
P. D'Antonio and J. H. Konnert.....117

Physicochemical Effect of Doping in Sputtered a-Si:H  
A. Deneuville, J. C. Bruyère, M. Toulemonde, J. J. Grob and P. Siffert ....120

CHAPTER III: Electronic Structure

Atomic Structure and Self-Consistent Electronic Structure of Periodic  
Models of Amorphous Hydrogenated Silicon  
C. Y. Fong and L. Guttman .....125

Electronic Densities of States in a-Si:H D. A. Papaconstantopoulos and E. N. Economou .....	130
Electronic Structure as a Probe of Bonding in Hydrogenated Amorphous Silicon D. C. Allan and J. D. Joannopoulos .....	136
A Theory of Impurities in Amorphous Semiconductors J. D. Dow and O. F. Sankey .....	141
Electronic Structure of Amorphous Silicon Alloys D. Adler and R. C. Frye .....	146
Electronic States of an Isolated Phosphorus Atom in an Amorphous Silicon Matrix W. Y. Ching and Chun C. Lin .....	151
Hole Conductivity Through Neighboring Si-H Bonds in Hydrogenated Silicon D. P. DiVincenzo, J. Bernholc, M. H. Brodsky, N. O. Lipari and S. T. Pantelides .....	156
Bonding Geometrics of Fluorine in a-Si:F. A Photoemission Study L. Ley, K. J. Gruntz and R. L. Johnson .....	161
Autocompensation in Doped Amorphous Silicon D. K. Biegelsen, R. A. Street and J. C. Knights .....	166
ESR and IR Studies on Sputtered Amorphous Si-C-H, Si-Ge-H and Ge- C-H T. Shimizu, M. Kumeda and Y. Kiriya .....	171
Changes in the Field Effect Density of States of a-Si:H with Annealing N. B. Goodman and H. Fritzsche .....	176

#### CHAPTER IV: Electronic Transport

Analysis of Conductivity and Thermoelectric Power Measurements on Amorphous Semiconductors P. Nielsen .....	181
Evidence for an Additional Conductivity Path in P-Doped a-Si:H from Schottky Barrier Height and Photoconductivity Temperature Dependence Measurements P. Viktorovitch, G. Model and W. Paul .....	186
High-Conductive and Wide Optical-Gap Boron-Doped Si:H Films A. Matsuda, M. Matsumura, K. Nakagawa, T. Imura, H. Yamamoto, S. Yamasaki, H. Okushi, S. Iizima and K. Tanaka .....	192
A Physical Interpretation of Dispersive Transport in Amorphous Silicon Hydride T. Tiedje, A. Rose and J. M. Cebulka .....	197



Anomalous Carrier Drift in a-Si Alloys T. Datta and M. Silver .....	202
Time of Flight Studies in Sputtered a-Si:H P. B. Kirby, W. Paul, P. Jacques and J. L. Brebner .....	207
Electronic Defect Levels in Plasma-Deposited Amorphous Silicon N. M. Johnson, M. J. Thompson and R. A. Street .....	212
Detailed Calculation of the density of Gap States obtained by DLTS measurements of doped a-Si:H Schottky Barrier Diodes J. D. Cohen, D. V. Lang and J. P. Harbison .....	217
Measurement of Free Carrier Mobility in Amorphous Silicon Using Traveling Waves D. Janes, S. Datta, R. Adler and B. J. Hunsinger .....	222
Study of Gap States in a-Si:H Alloys by Measurements of Photoconductivity and Spectral Response of MIS Solar Cells P. E. Vanier, A. E. Delahoy and R. W. Griffith .....	227
Spin Polarization Effects in the Photoconductivity of a-Si:H E. A. Schiff .....	233
Infrared Quenching of Photoconductivity: Recombination in a-Si:H P. D. Persans and H. Fritzsche .....	238

#### CHAPTER V: Absorption and Recombination

Optical Picosecond Studies of Carrier Thermalization in Amorphous Silicon Z. Vardeny, J. Tauc and C. J. Fang .....	243
Picosecond Time-Resolved Photoconductivity in Amorphous Silicon A. M. Johnson, D. H. Auston, P. R. Smith, J. C. Bean, J. P. Harbison and A. C. Adams .....	248
Relaxation of Photoinduced Sub-bandgap Absorption in a-Si:H S. Ray, Z. Vardeny, J. Tauc, T. Moustakas and B. Abeles .....	253
Photoacoustic Spectra of P-doped and Undoped GD a-Si:H Films S. Yamasaki, K. Nakagawa, H. Yamamoto, A. Matsuda, H. Okushi and K. Tanaka .....	258
Direct Measurement of the Absorption Tail of a-Si:H in the range of $2.1\text{eV} > h\nu > 0.6\text{eV}$ W. Jackson and N. M. Amer .....	263
Influence of Compression on Radiative Recombination in a-Si:H B. A. Weinstein .....	268
Super-Bandgap Radiation in a-Si B. A. Wilson .....	273

Photoluminescence Excitation Spectroscopy of Hydrogenated Amorphous Silicon	
S. G. Bishop, U. Strom, P. C. Taylor and W. Paul.....	278

Geminate and Non-Geminate Recombination in a-Si:H	
J. Mort, I. Chen, S. Grammatica, M. Morgan, J. C. Knights and R. A. Lujan.....	283

Studies on Primary Photocurrent of a-Si:H Using Xerographic and Vidicon Techniques	
I. Shimizu, S. Oda, K. Saito, H. Tomita and E. Inoue.....	288

Dispersive Diffusion Controlled Bimolecular Recombinations a-Si:H	
K. L. Ngai.....	293

Collection Efficiency of Photogenerated Carriers in Silicon Hydride a-SiH <sub>x</sub> MIS Solar Cell Structures	
B. Abeles, C. R. Wronski, Y. Goldstein, H. E. Stasiewski, D. Gutkowitz-Krusin, T. Tiedje and G. D. Cody.....	298

Effects of Geminate Recombination on Photovoltaic Efficiency of a-Si:H Solar Cells	
I. Chen and J. Mort.....	302

## CHAPTER VI: Surfaces and Interfaces

Surface Chemical Reactivity of Plasma-Deposited Amorphous Silicon	
D. E. Aspnes, B. G. Bagley, A. A. Studna, A. C. Adams and F. B. Alexander, Jr. ....	307

Effect of Thermal Annealing on the Structural and Electrical Properties of Pd-a-Si:H Interfaces	
C. C. Tsai, R. J. Nemanich and M. J. Thompson.....	312

Diffusion Length of Holes in a-Si:H by the Surface Photovoltage Method	
J. Dresner, D. J. Szostak and B. Goldstein.....	317

Problems Regarding the Conductance in a-Si:H Films	
H. Fritzsche and M. Tanielian.....	318

A Study of Amorphous Si:H:F Alloys Using MIS Tunnel Junctions	
I. Balberg and D. E. Carlson.....	323

Thickness Dependence of the Resistivity of Amorphous Hydrogenated Silicon on Various Substrates	
G. O. Johnson, J. A. McMillan and E. M. Peterson.....	329

Interference Fringe Analysis of a-Si:H Schottky Barrier Cells	
D. L. Staebler.....	334

OPTICAL EMISSION STUDIES OF  
REACTIVE SPECIES IN PLASMA DEPOSITION\*F. J. Kampas and R. W. Griffith  
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## ABSTRACT

Optical emission studies of the glow-discharge deposition of a-Si:H alloys reveal the presence of reactive species derived from process gases and impurities. Studies of the dependences of emission intensities upon deposition parameters elucidate the mechanisms of formation of these species. Effects of impurities detected by emission spectroscopy upon a-Si:H film electronic properties are discussed. A model of the chemical reactions involved in film growth is presented.

## INTRODUCTION

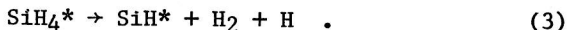
Although the plasma deposition of a-Si:H is now common practice, the chemical reactions involved in film growth are not well understood. The two techniques commonly used for studying the chemistry of a-Si:H film deposition are optical emission spectroscopy and mass spectrometry. In this paper we shall discuss the results of studies of the optical emission from silane and disilane glow discharges and also speculate about the nature of the chemical reactions responsible for a-Si:H film growth.

## RESULTS AND DISCUSSION

We have studied the silane glow discharge in great detail. In this section we summarize results which are presented more completely elsewhere.<sup>1,2</sup> The species observed in emission from the silane glow discharge are Si, SiH, H, and H<sub>2</sub>. The potentially important species SiH<sub>2</sub> and SiH<sub>3</sub> have no known emission spectrum. In order to determine the origin of the emitting species we studied the power dependences of the emission intensities of the four species along with a small amount of added N<sub>2</sub>.<sup>3</sup> The emission intensities of Si, SiH, H, and H<sub>2</sub> varied as the 0.84, 0.78, 1.92, and 1.85 power of the N<sub>2</sub> emission intensity over a range of 10-100 W rf power. It was concluded that the emitting excited states of Si and SiH are produced by one electron-impact excitation, whereas the emitting excited states of H and H<sub>2</sub> require two electron-impact excitations. The following set of energetically reasonable reactions is consistent with that conclusion:



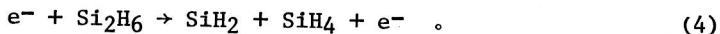
\*Work performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.



The excited states  $\text{Si}^*$  and  $\text{SiH}^*$  emit the detected photons. However, the excited states  $\text{H}^*$  and  $\text{H}_2^*$  require another electron-impact excitation for their production. The anomalously high rotational and vibrational temperatures calculated from the  $\text{SiH}$  emission spectrum are explained by this mechanism.

A study of the photolysis of silane by 8.4 eV photons indicated that the primary products of silane photolysis are  $\text{SiH}_2$  and  $\text{SiH}_3$ .<sup>4</sup> While these species were not detected directly, higher silanes produced by subsequent reactions were detected mass spectrometrically. That study is not inconsistent with our own work. The reactions given in Eqs. 2 and 3 may account for only a small part of the glow discharge decomposition of silane.

The emission spectrum of a disilane discharge also reveals the presence of  $\text{Si}$ ,  $\text{SiH}$ ,  $\text{H}$ , and  $\text{H}_2$ . The  $\text{Si}$  and  $\text{SiH}$  emission intensities are approximately one-tenth of their values for a monosilane discharge at the same pressure and rf power. The emission from  $\text{H}_2$  and  $\text{H}$  are reduced by a similar factor compared to a monosilane discharge despite the fact that the deposition from disilane occurred at five times the rate as the deposition from monosilane. These facts imply that monosilane is a product of the disilane discharge. This supports the hypothesis of the IBM group<sup>5</sup> that the electron-impact dissociation of disilane proceeds in the following way:



The fact that a-Si:H can be doped by the addition of  $\text{PH}_3$  and  $\text{B}_2\text{H}_6$  to the silane is central to photovoltaic applications. An understanding of the chemical reactions involved in doping would be useful for optimizing doping efficiency and reducing the number of defect states introduced in doping. We have found the species  $\text{PH}_2$ ,  $\text{PH}$ , and  $\text{P}$  in the emission spectrum of a mixture of 1%  $\text{PH}_3$  in  $\text{SiH}_4$ . See Figs. 1 and 2.

In studying the electronic properties of any material one must consider the unavoidable presence of impurities. We have described<sup>2</sup> at some length the synergistic doping effect of  $\text{N}_2$  and  $\text{O}_2$  in the plasma, as might be introduced by a small leak in the deposition system. Small air leaks can be detected quite easily by the emission from  $\text{N}_2$ . Sensitivities for  $\text{N}_2$  of 100 ppm in the silane are easily obtainable. When oxygen concentrations  $\sim 0.1\%$  are reached, emission from  $\text{SiO}$  appears in the spectrum.<sup>1</sup>

Another source of impurities is the process gas. A common impurity in silane is monochlorosilane ( $\text{SiH}_3\text{Cl}$ ). We found that 1000 ppm  $\text{SiH}_3\text{Cl}$  in silane can result in a displacement of the Fermi level  $\sim 0.2$  eV downward in the bandgap of the deposited film. This concentration of  $\text{SiH}_3\text{Cl}$  is easily detectable as emission from  $\text{SiCl}$  (281 nm) and results in 600 ppm incorporated Cl.

Outgassing of the deposition system is a third source of impurities. Emission from the species  $\text{OH}$ ,  $\text{CO}$ , and  $\text{N}_2$  is seen during an

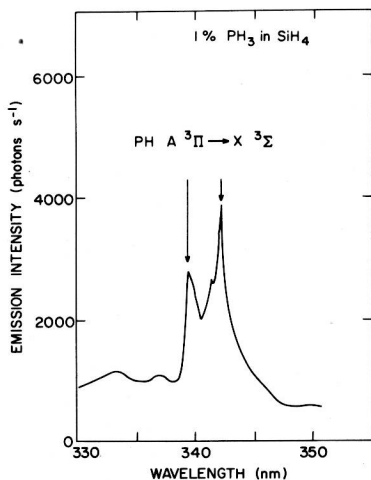


Fig. 1. Emission from PH in a 1% mixture of  $\text{PH}_3$  in  $\text{SiH}_4$ .

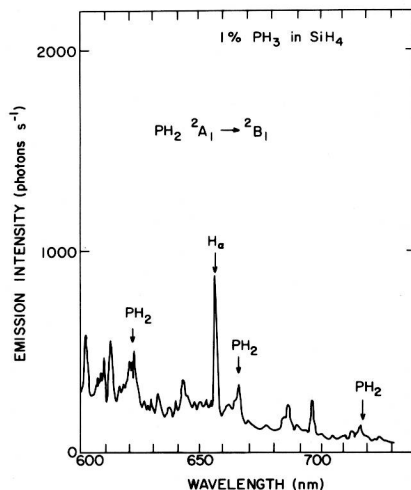
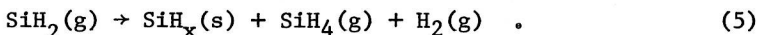


Fig. 2. Emission from  $\text{PH}_2$ . Bands not marked are due to  $\text{H}_2$ .

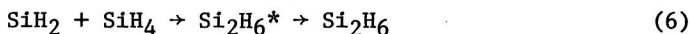
argon discharge used to clean the substrates. These species arise from  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{N}_2$  adsorbed onto the electrodes and chamber.

Metallic impurities are potentially very deleterious to the electronic properties of semiconductors. The argon cleaning discharge mentioned earlier shows emission from Mg and Zn when the substrate temperature is about 350 C. Emission from Zn is seen also in the silane discharge under these conditions. However, SIMS analysis of the deposited films show less than 0.2 ppm of Zn in the film bulk, 0.2 ppm being the sensitivity of the SIMS measurement. Thus emission spectroscopy of the discharge is more sensitive than SIMS for detecting Zn.

We turn now to the question of the chemical species involved in the growth of the a-Si:H film. Knights has stated that the species involved in film growth are probably  $\text{SiH}_2$  and  $\text{SiH}_3$ .<sup>6</sup> As stated earlier, the reaction given in Eq. 4 has been advanced to explain the higher deposition rate in a disilane glow discharge. A rapid surface reaction was postulated to account for the fact that a-Si:H films have a smaller H to Si ratio than  $\text{SiH}_2$ , and the following reaction was proposed:<sup>5</sup>

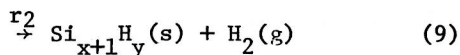
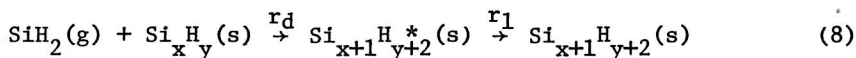


Lampe has proposed the following gas-phase reaction to explain results obtained in the photolysis of silane:<sup>4</sup>



The species  $\text{Si}_2\text{H}_6^*$  is a disilane molecule with an internal activation energy of 2.1 eV. We propose that hydrogen elimination during film

deposition occurs through an analogous reaction:



The quantities  $r_d$ ,  $r_1$ , and  $r_2$  are the rates of the deposition, deactivation, and hydrogen elimination reactions, respectively. The ratio of the rates,  $r_2/r_1$ , can be calculated from the atomic hydrogen content of the film,  $c_H$ :

$$r_2/r_1 = 2c_H^{-1} - 3 \quad (10)$$

This result follows from the fact that the film gains  $r_1 + r_2$  silicon atoms per second but gains only  $2r_1$  hydrogen atoms per second. An Arrhenius plot of  $r_2/r_1$  versus  $1000/T_s$ , where  $T_s$  is the substrate temperature, should give the difference in activation energy between the two rates. In Fig. 3 we have made such a plot using values of hydrogen concentration versus  $T_s$  taken from the literature.<sup>7,8</sup> The points fall close to straight lines for  $T_s$  less than 300 C. At 300 C, other mechanisms of hydrogen elimination, such as those that occur in the annealing of already deposited films, become important.

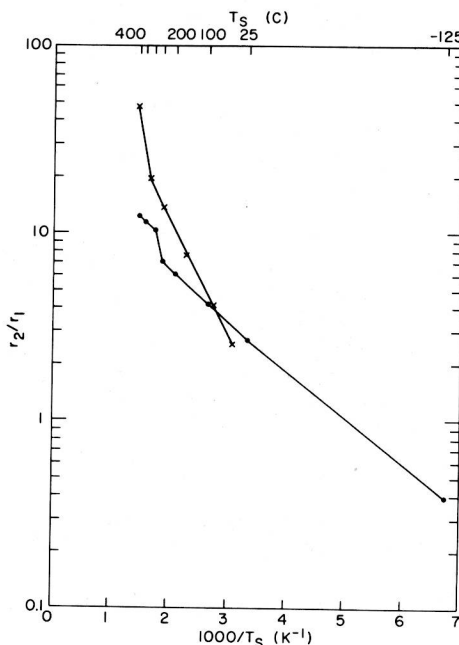


Fig. 3. Plot of  $\log r_2/r_1$  versus  $1000/T_s$ . o ref. 7; x ref. 8.

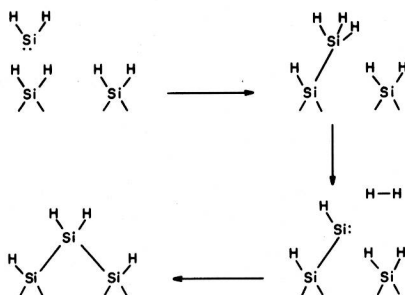


Fig. 4. Proposed mechanism of film growth, hydrogen elimination and cross-linking at film surface.

A model with  $\text{SiH}_4$  elimination was also investigated using a set of equations analogous to Eqs. 8 and 9. In that case, straight lines were not obtained. The fact that straight lines were obtained from Eqs. 8 and 9 encouraged us sufficiently to consider the chemistry of the cross-linking step, which must follow hydrogen elimination. We propose that the divalent silicon atom resulting from hydrogen elimination inserts across a nearby Si-H bond, a well-known reaction.<sup>9</sup> The entire mechanism is shown in Fig. 4. The model we have presented is incomplete in that it does not explain the effect of electrode bias upon hydrogen content. Work on that problem is in progress.

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DEPOSITION AND DOPING OF a-Si:H FROM Si<sub>2</sub>H<sub>6</sub> PLASMAS

B. A. Scott, M. H. Brodsky, D. C. Green, R. M. Plecenik, E. E. Simonyi and R. Serino

IBM T. J. Watson Research Center, Yorktown Heights, NY 10598

## ABSTRACT

Compared to SiH<sub>4</sub>, the plasma deposition of amorphous hydrogenated silicon from Si<sub>2</sub>H<sub>6</sub> results in compositionally similar films, deposited at rates at least an order of magnitude higher. The films also display larger dark and photoconductivities, a result related directly to higher  $E_f$  in the intrinsic Si<sub>2</sub>H<sub>6</sub>-prepared material. The effect is structural, not impurity-dominated. Dopant incorporation is also found to be strongly influenced by the silicon source, as is the doping efficiency. For a given gas phase concentration of n-type dopant (PH<sub>3</sub>), the distribution coefficient is  $C_{eff} < 1$  for Si<sub>2</sub>H<sub>6</sub> plasmas, compared to  $C_{eff} > 1$  for depositions from SiH<sub>4</sub>, yet film electrical properties are comparable. On the p-type side, much smaller differences are observed with B<sub>2</sub>H<sub>6</sub> doping of the two sources. Finally, a-Si:H plasma deposition chemistry is examined within the context of a neutral radical model and hydrogen etching experiments.

## INTRODUCTION

The use of higher silanes for various CVD silicon processes offers potential advantages over SiH<sub>4</sub>, including higher deposition rates and/or lower temperature growth. This is related to the lower stability of the higher hydrides, due more to kinetic<sup>1</sup> than thermodynamic factors. We have been investigating the deposition of amorphous hydrogenated silicon (a-Si:H) by plasma decomposition of higher silanes to determine whether the resulting compositional, structural and transport properties differ from SiH<sub>4</sub>-deposited material. In addition, studies using such source compounds can lead to insight concerning the important chemical mechanistic questions of a-Si:H film growth<sup>2,3</sup>.

## FILM PREPARATION

Disilane was synthesized by the reduction of hexachlorodisilane with LiAlH<sub>4</sub>, using a modification of the method reported by Bethke and Wilson<sup>4</sup>. Small quantities of Si<sub>2</sub>H<sub>6</sub> were also synthesized by the electric discharge technique for comparison purposes<sup>5</sup>. Since Si<sub>2</sub>H<sub>6</sub> boils at 259 K, purification was performed in a series of low temperature distillation steps, followed by analysis using gas chromatography/mass spectroscopy<sup>5</sup>. Purities >99.9% were obtained exclusive of higher silanes, which are always present at ~ 1% levels. Depositions were carried out in an inductively-coupled plasma apparatus described elsewhere<sup>6</sup>.

## INTRINSIC a-Si:H

In earlier work<sup>2</sup> we found two major differences between disilane- and monosilane-prepared films. First, deposition from Si<sub>2</sub>H<sub>6</sub> occurs at rates over an order of magnitude larger than those obtained with SiH<sub>4</sub> under comparable conditions. Secondly, we have consistently observed higher dark and AM1 photoconductivities in Si<sub>2</sub>H<sub>6</sub>-prepared films (substrate temperature  $T_s = 300^\circ\text{C}$ ). In a subsequent section we examine possible mechanistic reasons for the deposition rates observed from SiH<sub>4</sub> and Si<sub>2</sub>H<sub>6</sub>. The difference in transport properties can be ascribed to the results shown in Fig. 1. Here the activation energies for intrinsic Si<sub>2</sub>H<sub>6</sub>-deposited films generally fall below those of SiH<sub>4</sub>-prepared films deposited at the same  $T_s$ . This would make  $E_c - E_F$  smaller and thus  $E_F$  lies higher in



the gap. Using the Anderson-Spear model<sup>7</sup>, a higher  $E_F$  implies a lower number of positively-charged recombination centers.

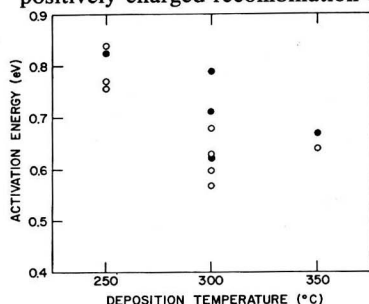


Fig. 1: Dark conductivity activation energy for  $\text{SiH}_4$  (●) and  $\text{Si}_2\text{H}_6$  (○) deposited films.

Although greater  $E_F$  could be due to n-type impurities, we have carried out extensive chemical analysis by electron microprobe on the film series shown in Table I. Impurities such as P and As were not observed. Their electrical effects on a-Si:H are known to occur at levels well within microprobe sensitivity limits. We find, in fact, that where non-negligible amounts of impurities are present, photoconductivity is lowest.  $\text{Si}_2\text{H}_6$ -prepared samples with the lowest impurity levels show the greatest enhancements over  $\text{SiH}_4$ -deposited material. Hence, we conclude that there exist subtle but nevertheless real structural differences leading to the somewhat higher photoconductivities observed for  $\text{Si}_2\text{H}_6$ -prepared films.

Table I. COMPARISON OF DISILANE-PREPARED INTRINSIC a-Si(H) FILMS<sup>†</sup>

Sample	$\rho_{pc}$	$\rho_{dark}$	$\rho_o$	$\Delta E_{dark}$ (eV)	$\Delta E_{pc}$ (eV)	Comments
507(2.0)	3.37	6.77	-3.97	0.63	0.15	$\text{Si}_2\text{H}_6$ from electric discharge
659(1.2)	3.65	6.33	-3.25	0.57	0.13	<u>Oxygen</u> <200 ppm <u>Chlorine</u> <60 ppm
509(2.0)	3.85	7.73	-3.73	0.68	0.16	$\text{Si}_2\text{H}_6$ from electric discharge
704(1.2)	4.35	7.78	-2.48	0.60	0.12	<u>Oxygen</u> 800 ppm; <u>Chlorine</u> 70 ppm

<sup>†</sup>Substrate temperature 300°C; r.f. power given in ( )

#### DOPED a-Si:H

A detailed series of experiments were carried out with n- and p-type dopants  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{B}_2\text{H}_6$  mixed into the  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$  source gases. The main results of this study are illustrated in Table II, where the room temperature conductivity is presented for a series of monosilane and disilane films prepared under identical plasma conditions at a gas phase doping ratio  $(N_{\text{dopant}}/N_{\text{Si}})_{\text{gas}} = 1\%$ . Also shown is the dopant/Si ratio in the solid and the distribution coefficient,  $C_{\text{eff}}$ <sup>8</sup>. For the n-type dopants we have the following significant results. Although there is little difference between the room temperature conductivities of  $\text{SiH}_4$ - and  $\text{Si}_2\text{H}_6$ -prepared films using  $\text{PH}_3$ , the actual amount of phosphorus incorporated in each case differs significantly. Over an order of magnitude more phosphorus must be incorporated in the  $\text{SiH}_4$ -prepared films to attain a comparable conductivity. The doping efficiency is therefore much less for n-doped  $\text{SiH}_4$ -deposited films. An even lower doping efficiency is observed for  $\text{AsH}_3/\text{SiH}_4$ . The conductivity is nearly two orders of magnitude poorer, yet films show the largest actual incorporation of n-type dopant. On the other hand, essentially the opposite result is observed for  $\text{B}_2\text{H}_6$ -doping: comparably high conductivities are achieved with somewhat less boron actually incorporated in  $\text{SiH}_4$ -deposited a-Si:H. Note that with neither source gas are dark conductivities above  $10^{-2} (\Omega\text{-cm})^{-1}$  attained on the n- or p-doped side.