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Tetrahedrally Bonded Amorphous Semiconductors

(Carefree, Arizona, 1981)

Edited by
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American Institute of Physics

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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. Biegelesen (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

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OPTICAL EMISSION STUDIES OF
REACTIVE SPECIES IN PLASMA DEPOSITION*

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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 for-
mation 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 under-
stood. 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.[1,2] The species observed in emission from the silane glow
discharge are Si, SiH, H, and H_2. The potentially important species
SiH_2 and SiH_3 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_2.[3] The emission intensities of Si, SiH, H, and H_2
varied as the 0.84, 0.78, 1.92, and 1.85 power of the N_2 emission in-
tensity 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_2
require two electron-impact excitations. The following set of
energetically reasonable reactions is consistent with that conclusion:

$$e^- + SiH_4 \rightarrow SiH_4^* + e^- \tag{1}$$

$$SiH_4^* \rightarrow Si^* + 2H_2 \tag{2}$$

$$SiH_4^* \rightarrow SiH^* + H_2 + H \quad. \tag{3}$$
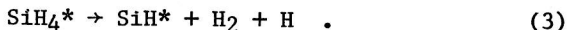
The excited states Si* and SiH* emit the detected photons. However, the excited states H* and H_2^* require another electron-impact excitation for their production. The anomalously high rotational and vibrational temperatures calculated from the SiH emission spectrum are explained by this mechanism.

A study of the photolysis of silane by 8.4 eV photons indicated that the primary products of silane photolysis are SiH_2 and SiH_3.[4] 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 Si, SiH, H, and H_2. The Si and SiH emission intensities are approximately one-tenth of their values for a monosilane discharge at the same pressure and rf power. The emission from H_2 and 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[5] that the electron-impact dissociation of disilane proceeds in the following way:

$$e^- + Si_2H_6 \rightarrow SiH_2 + SiH_4 + e^- \quad. \tag{4}$$
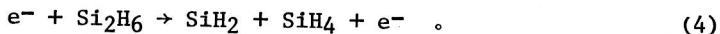
The fact that a-Si:H can be doped by the addition of PH_3 and B_2H_6 to the silane is central to photovoltaic applications. An understanding of the chemical reactions involved in doping would be useful for optimizing doping efficiency and reducing the number of defect states introduced in doping. We have found the species PH_2, PH, and P in the emission spectrum of a mixture of 1% PH_3 in 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[2] at some length the synergistic doping effect of N_2 and 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 N_2. Sensitivities for N_2 of 100 ppm in the silane are easily obtainable. When oxygen concentrations ∿0.1% are reached, emission from SiO appears in the spectrum.[1]

Another source of impurities is the process gas. A common impurity in silane is monochlorosilane (SiH_3Cl). We found that 1000 ppm SiH_3Cl in silane can result in a displacement of the Fermi level ∿0.2 eV downward in the bandgap of the deposited film. This concentration of SiH_3Cl is easily detectable as emission from 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 OH, CO, and N_2 is seen during an
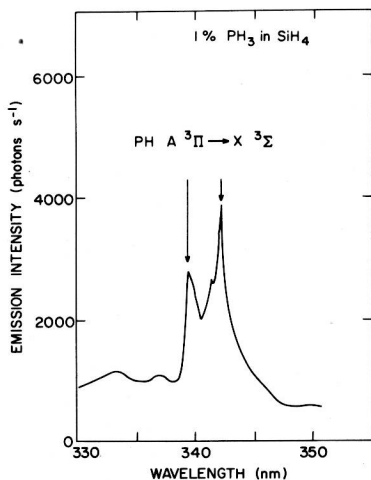
Fig. 1. Emission from PH in a 1% mixture of PH_3 in SiH_4.
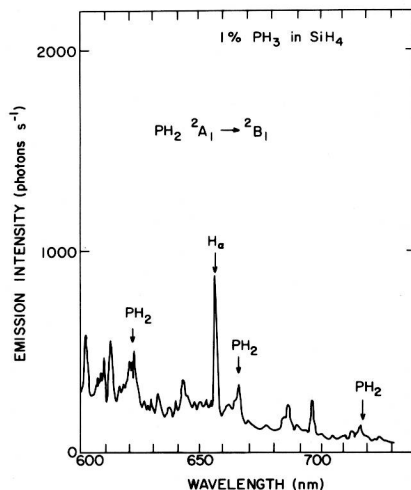
Fig. 2. Emission from PH_2. Bands not marked are due to H_2.

argon discharge used to clean the substrates. These species arise from H_2O, CO, and 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 SiH_2 and SiH_3.[6] 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 SiH_2, and the following reaction was proposed:[5]

$$SiH_2(g) \rightarrow SiH_x(s) + SiH_4(g) + H_2(g) \quad . \tag{5}$$
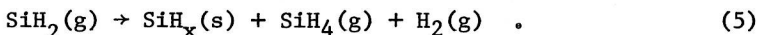
Lampe has proposed the following gas-phase reaction to explain results obtained in the photolysis of silane:[4]

$$SiH_2 + SiH_4 \rightarrow Si_2H_6^* \rightarrow Si_2H_6 \tag{6}$$

$$\rightarrow H_2 + SiH_3SiH \tag{7}$$
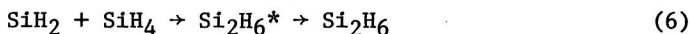
The species $Si_2H_6^*$ is a disilane molecule with an internal activation energy of 2.1 eV. We propose that hydrogen elimination during film

deposition occurs through an analogous reaction:

$$\text{SiH}_2(g) + \text{Si}_x\text{H}_y(s) \overset{r_d}{\to} \text{Si}_{x+1}\text{H}^*_{y+2}(s) \overset{r_1}{\to} \text{Si}_{x+1}\text{H}_{y+2}(s) \tag{8}$$

$$\overset{r_2}{\to} \text{Si}_{x+1}\text{H}_y(s) + \text{H}_2(g) \tag{9}$$
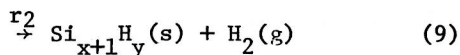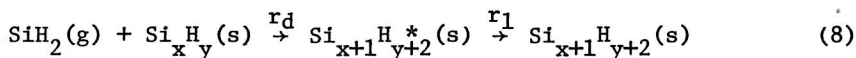
The quantities r_d, r_1, and r_2 are the rates of the deposition, deactivation, and hydrogen elimination reactions, respectively. The ratio of the rates, r_2/r_1, can be calculated from the atomic hydrogen content of the film, c_H:

$$r_2/r_1 = 2c_H^{-1} - 3 \tag{10}$$

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 Arhennius 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.[7,8] 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.
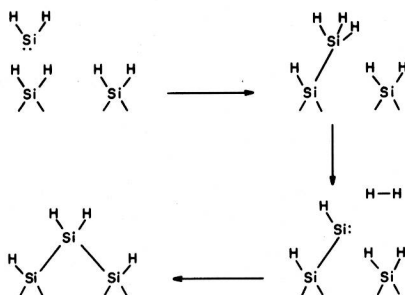
Fig. 4. Proposed mechanism of film growth,
hydrogen elimination and cross-linking at
film surface.

A model with 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 in-
serts across a nearby Si-H bond, a well-known reaction.[9] The entire
mechanism is shown in Fig. 4. The model we have presented is incom-
plete in that is 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$_2$H$_6$ PLASMAS

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ABSTRACT

Compared to SiH$_4$, the plasma deposition of amorphous hydrogenated silicon from Si$_2$H$_6$ 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$_2$H$_6$-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$_3$), the distribution coefficient is C$_{eff}$<1 for Si$_2$H$_6$ plasmas, compared to C$_{eff}$>1 for depositions from SiH$_4$, yet film electrical properties are comparable. On the p-type side, much smaller differences are observed with B$_2$H$_6$ 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$_4$, including higher deposition rates and/or lower temperature growth. This is related to the lower stability of the higher hydrides, due more to kinetic[1] 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$_4$-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[2,3].

FILM PREPARATION

Disilane was synthesized by the reduction of hexachlorodisilane with LiAlH$_4$, using a modification of the method reported by Bethke and Wilson[4]. Small quantities of Si$_2$H$_6$ were also synthesized by the electric discharge technique for comparison purposes[5]. Since Si$_2$H$_6$ boils at 259 K, purification was performed in a series of low temperature distillation steps, followed by analysis using gas chromatography/mass spectroscopy[5]. 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[6].

INTRINSIC a-Si:H

In earlier work[2] we found two major differences between disilane- and monosilane-prepared films. First, deposition from Si$_2$H$_6$ occurs at rates over an order of magnitude larger than those obtained with SiH$_4$ under comparable conditions. Secondly, we have consistently observed higher dark and AM1 photoconductivities in Si$_2$H$_6$-prepared films (substrate temperature T$_s$=300°C). In a subsequent section we examine possible mechanistic reasons for the deposition rates observed from SiH$_4$ and Si$_2$H$_6$. The difference in transport properties can be ascribed to the results shown in Fig. 1. Here the activation energies for intrinsic Si$_2$H$_6$-deposited films generally fall below those of SiH$_4$-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[7], a higher E_F implies a lower number of positively-charged recombination centers.
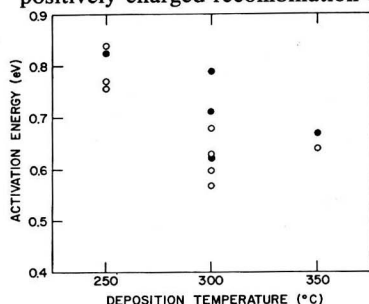

Fig. 1: Dark conductivity activation energy for SiH_4 (●) and Si_2H_6 (○) deposited films.

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 a 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-neglible amounts of impurities are present, photoconductivity is lowest. Si_2H_6-prepared samples with the lowest inpurity levels show the greatest enhancements over SiH_4-deposited material. Hence, we conclude that there exist subtle but nevertheless real structural differences leading to the somewhat higher photoconductivities observed for Si_2H_6-prepared films.

Table I. COMPARISON OF DISILANE-PREPARED INTRINSIC a-Si(H) FILMS[†]

| Sample | Log(ohm•cm) | | | ΔE_{dark} (eV) | ΔE_{pc} (eV) | Comments |
	ρ_{pc}	ρ_{dark}	ρ_o			
507(2.0)	3.37	6.77	−3.97	0.63	0.15	Si_2H_6 from electric discharge
659(1.2)	3.65	6.33	−3.25	0.57	0.13	Oxygen <200 ppm Chlorine <60 ppm
509(2.0)	3.85	7.73	−3.73	0.68	0.16	Si_2H_6 from electric discharge
704(1.2)	4.35	7.78	−2.48	0.60	0.12	Oxygen 800 ppm; Chlorine 70 ppm

[†]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 PH_3, AsH_3 and B_2H_6 mixed into the SiH_4 and Si_2H_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 $(N_{dopant}/N_{Si})_{gas} = 1\%$. Also shown is the dopant/Si ratio in the solid and the distribution coefficient, C_{eff}[8]. For the n-type dopants we have the following significant results. Although there is little difference between the room temperature conductivities of SiH_4- and Si_2H_6-prepared films using 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 SiH_4-prepared films to attain a comparable conductivity. The doping efficiency is therefore much less for n-doped SiH_4-deposited films. An even lower doping efficiency is observed for AsH_3/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 B_2H_6-doping: comparably high conductivities are achieved with somewhat less boron actually incorporated in 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.