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PART I

Growth and Crystallization

Thermodynamic Study of Silane-hydrogen Chemical System

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ABSTRACT

The thermodynamic calculations of chemical equilibrium compositions of various species were performed for silane-hydrogen system at different temperatures [500-6000K], pressures [0.01-10 Torr], and mixing ratios [various silane fractions]. The effect of dopant impurities such as diborane and phosphine on equilibrium concentration profiles of various gaseous, ionic, and condensed species was also investigated. These data will be very useful in understanding the deposition chemistry of silane chemical systems and will be a valuable aid in optimization studies.

INTRODUCTION

Recently, hydrogenated amorphous silicon [a-Si:H] has become an increasingly attractive material for wide variety of applications such as solar cells, field effect transistors, photoreceptors, and imaging devices.[1] Plasma assisted chemical vapor depositon and etching are potentially important techniques for fabricating such novel devices and synthesizing various kinds of electronic materials. In order to understand the deposition chemistry, it is necessary to obtain a detailed knowledge of thermodynamic properties of a chemical system which in turn, permits one to calculate chemical equilibrium compositions for the system. A comprehensive thermodynamic study of the various ways of preparing silicon for photovoltaic applications, suggested that SiH_4 is probably the best raw material for obtaining high-purity silicon.[2]

The knowledge of thermodynamic properties of a chemical system permits one to calculate chemical equilibrium compositions for the system. A computer program capable of calculating equilibrium properites of plasmas [mixtures containing ionized species] was obtained from NASA Lewis Research Center.[3] This Fortran IV program was written for calculations such as: 1] Chemical equilibrium compositions for assigned thermodynamic states [T,P], [H,P], [S,P], [T,V], [U,V], or [S,V], 2] Theoretical rocket performance for both equilibrium and frozen composition during expansion, 3] Incident and reflected shock properties, and 4] Chapman-Jouguet detonation properties. A free energy minimization technique is used for the calculations of thermodynamic equilibrium compositions.

The program considers gaseous species as well as condensed species. Thus, it is ideal for calculating equilibrium compositions for complex mixtures in plasma at high temperatures for a given pressure. However, in performing these calculations, the plasma is considered ideal, i.e., no coulombic interactions are considered. Therefore, the results of these plasma calculations will be valid for

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systems with small ionic density so that coulombic effects are unimportant. To a great extent, this assumption is true of glow discharge plasmas. In equilibrium calculations, it is also assumed that gases obey ideal gas law, homogeneous mixing, and that the composition attains equilibrium instantaneously during expansion.

The program code uses all the species with known thermodynamic functions as available in its thermodynamic library. For species whose thermodynamic functions [such as heat capacity, enthalpy, entropy, and free energy] are not available, another Fortran IV Program [4] [PAC code] can be used to calculate the needed functions from spectroscopic constants.

These programs are used to obtain chemical equilibrium compositions of various gaseous, condensed, and ionic species at temperatures ranging from 500 to 6000K, and at various pressures from 0.01 Torr to 10 Torr, and for different mixing ratios of silanes and hydrogen. The effect of dopant impurities phosphine [PH_3] and diborane [B_2H_6] on the equilibrium compositions was also studied at various temperatures.

RESULTS AND DISCUSSIONS

Undoped SiH_4-H_2 system:

Typical equilibrium concentration profiles for various silicon and hydrogen containing species are plotted in Figures 1-3 as a function of temperature for silane to hydrogen ratio of 0.1 at total pressure of 1 Torr. The hydrogen atom concentration rises monotonically as a function of temperature and attains maximum above 3000K. Similarly, silicon atom concentration in gas phase attains maximum above 2000K, and slowly decreases above 5000K, probably forming polysilicons or polysilanes. Another very interesting feature to note is that all

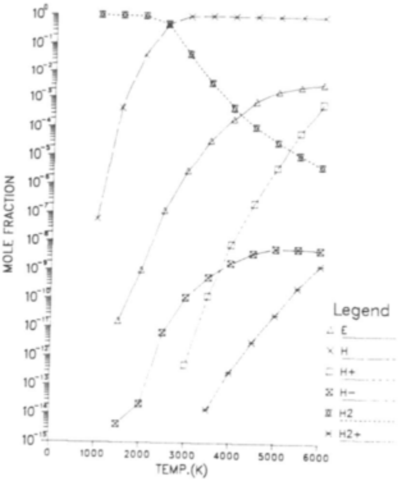

Figure 1

Temperature dependance of calculated equilibrium concentrations of electrons, H atom, H^+, H^-, H_2, and H_2^+ for SiH_4/H_2=0.1 and total pressure 1 Torr.

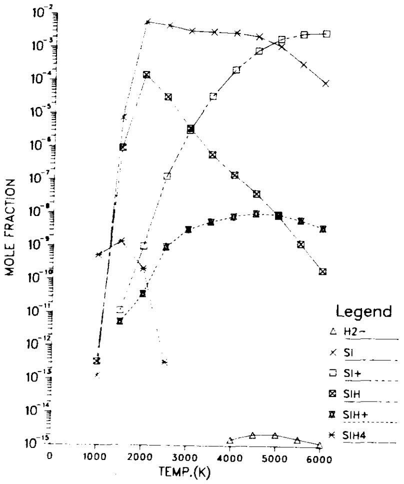

Figure 2.

Temperature dependance of calculated equilibrium compositions of H_2^-, Si atom, Si^+, SiH, SiH^+, and SiH_4 for SiH_4/H_2=0.1 and total pressure of 1 Torr.

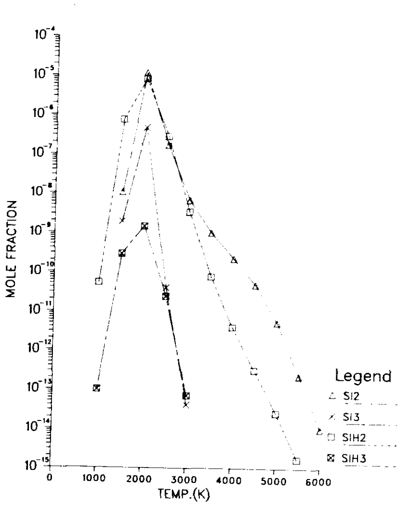

Figure 3.

Temperature dependance of calculated equilibrium compositions of Si_2, Si_3, SiH_2, and SiH_3 for SiH_4/H_2=0.1 and total pressure of 1 Torr.

are at maximum at 2000K. However, ionic species [Si^+, SiH^+, H^+, H_2+] increase monotonically above 2000K, thus contributing significantly only at high temperatures.

Similar concentration profiles were also obtained at different pressures and silane-hydrogen mixing ratios. For a silane-hydrogen system, pressure dependance on concentration profiles of various species is shown in Figure 4 at SiH_4/H_2 ratio of 0.1 and temperature of 2000K. Again all silicon containing species rise monotonically with pressure and reaches maximum at 5 Torr.

In order to optimize SiH_4/H_2 ratio, concentration profiles of silicon containing species were obtained for different silane fractions in hydrogen at a temperature of 2000K and total pressure of 1 Torr as depicted in Figure 5. Again, all silicon species show monotonically increasing function, reaching a maximum above 30% silane mixtures. Thus, if silicon containing species were to be maximized in a deposition system for higher deposition rate, then thermodynamic studies predict a system with $>$ 30% silane fraction in H_2 mixture at total pressure of 5 Torr and 2000K.

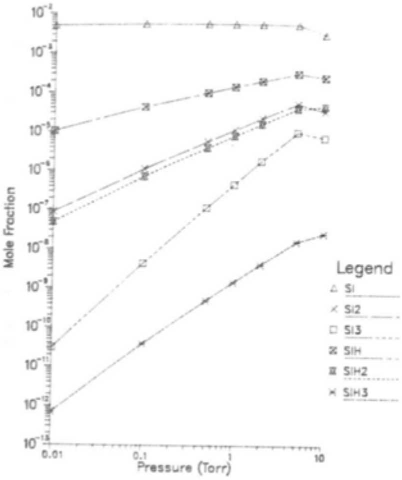

Figure 4.

Pressure dependance of calculated equilibrium compositions of Si, Si_2, Si_3, SiH, SiH_2, and SiH_3 for $SiH_4/H_2=0.1$ and T=2000K

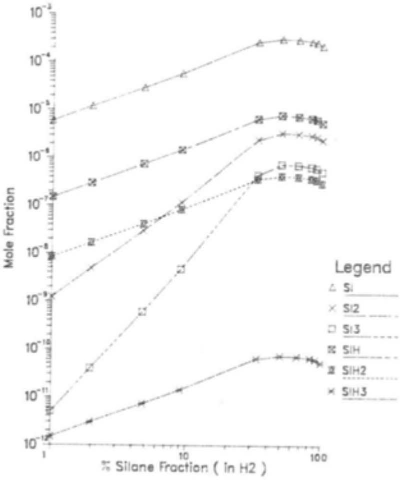

Figure 5.

Silane fraction dependance on equilibrium concentrations of Si, Si_2, Si_3, SiH, SiH_2, and SiH_3 at T=2000K and total pressure of 1 Torr.

Doped SiH_4-H_2 System:

Phosphorous doped impurities:

For n^+ materials, phosphorous is used as a dopant. Typical experimental conditions involved in making n^+ microcrystalline materials are $SiH_4/H_2=0.01$, $PH_3/SiH_4=2\%$ and total pressure of 1 Torr. Figure 6 shows concentration profiles of phosphorous containing species as a function of temperature in above mentioned conditions. Silicon and hydrogen containing species [including all ionic species] show similar trends as mentioned in undoped materials. The Phosphorous concentration reaches a maximum at 2000K and remains at this constant value, however, PH goes through a maximum at 2000K. Thus, if PH has a deleterious effect on material properties then by operating above 3000K, only phosphorous atoms can be selectively doped.

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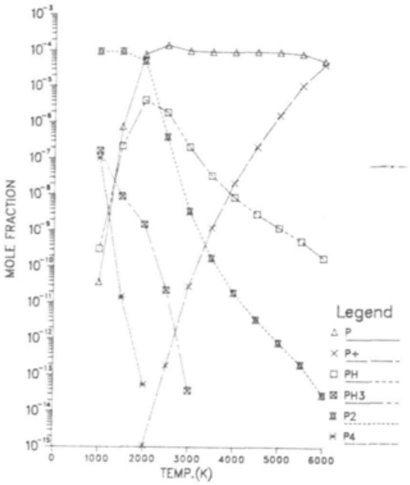

Figure 6.

Temperature dependance of equilibrium compositions of P, P^+, PH, PH_3, P_2, and P_4, for $SiH_4/H_2=0.01$, P=1 Torr and $PH_3/SiH_4=2\%$.

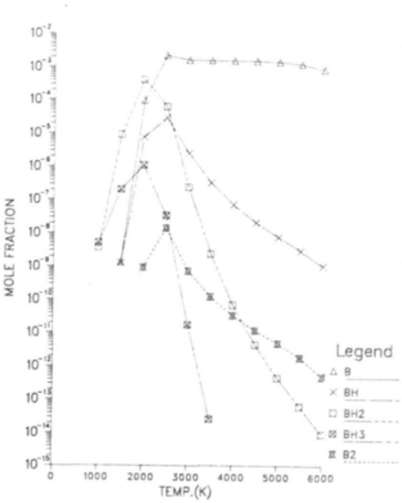

Figure 7

Temperature dependance of equilibrium compositions of B, BH, BH_2, BH_3, and B_2 for $SiH_4/H_2=0.1$, P=1 Torr, and $B_2H_6/SiH_4=2\%$

Boron doped impurities:

For p^+ materials, diborane is used as a source for boron dopant. The equilibrium compositions for boron containing species are plotted in Figure 7 as a function of temperature. Concentation profiles were obtained under usual conditions of $SiH_4/H_2=0.1$, $B_2H_6/SiH_4=2\%$, and total pressure of 1 Torr. Again, atomic boron concentration rises rapidly and reaches a maximum at 2500K, while BH and BH_3 goes through a maximum at 2500K and BH_2 at 2000K. However, BH, BH_2 and BH_3 drop off quickly above 2500K. Thus, knowledge of concentration - temperature profiles will be a valuable aid in optimization studies for selective doping.

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SUMMARY

The thermodynamic calculations of chemical equilibrium compositions at various temperatures, pressures, and silane fraction were performed for the silane-hydrogen system. The effect of dopant impurities on concentration profiles was also investigated. These data will be very valuable in understanding plasma behavior of chemical systems, qualitatively. The plasma system does not attain thermodynamic equilibrium instantaneously, but may reach a steady state and thus coupling kinetics studies will give actual concentration profiles. However, understanding the system in thermodynamic sense gives us baseline knowledge of the species concentration present in a given system. Thus, thermodynamics can be used as a guide line for establishing general process parameters.

ACKNOWLEDGEMENT

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ELECTRICAL AND OPTICAL PROPERTIES OF PECVD AMORPHOUS SILICON GROWN AT LOW FREQUENCIES.

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ABSTRACT

The semiconducting properties of a-Si are ideally suited for making a switch to control the matrix addressing of an array of liquid crystal pixels. This investigation explores the differences between a-silicon deposited by plasma enhanced chemical vapor deposition at 13.56MHz and at 60KHz. The bonded hydrogen concentration, the index of refraction and the optical band gap of a-Si have been measured. The device used to explore the field effect mobility of a-Si is an inverted staggered FET fabricated on a glass substrate with conventional photolithography.

INTRODUCTION

Since plasma-enhanced chemical vapor deposition (PECVD) entails a synergistic combination of free radical chemistry in the plasma and the physical deposition of kinetic energy at the growth surface, it is quite reasonable to expect that significant differences in the properties of deposited materials might occur below a transition frequency which permits constant acceleration between collisions as ions penetrate the plasma sheath. Other system parameters such as power and concentration of bonded hydrogen are of course also significant.

The semiconducting properties of a-Si are ideally suited to the system requirements of a FET switch used to control the matrix addressing of an array of liquid crystal pixels [1]. Response time, saturation on-current, contact voltage drop, threshold voltage and off-current are all important device parameters that are dependent upon bulk a-Si properties and on interface characteristics. Previous reports have described a-Si FETs fabricated with PECVD done at high frequency (13.56MHz). We have earlier reported FETs fabricated from amorphous silicon and silicon nitride grown in a low frequency plasma discharge [2]. This investigation explores whether there exist any differences between material deposited at 13.56MHz and that obtained in a plasma generated at 60KHz.

EXPERIMENTAL PROCEDURE

The plasma depositions were done in two commercially available reactors both of which are capacitatively coupled, Reinberg-configured chambers. Each is configured with circular, parallel electrodes. The bottom electrode is heated and grounded and the top electrode is powered and temperature controlled with circulating coolant. Gas flow is radially inward. On both machines the electrode spacing was set at 25mm. The Technics PlasmaEtch II reactor has an electrode diameter of 20cm and the PlasmaTherm PD3011 reactor has electrodes 70cm in diameter. Each machine could be powered with an ENI PL-1 at 60KHz or with properly matched and shielded power supplies at 13.56MHz. All of the depositions reported here were made at a platen temperature of 300°C and a counterelectrode temperature of 60°C. The chamber gas for the a-Si was 10% silane diluted with argon. All gases were of electronic grade purity. Depositions were made at a power level of 30mw/cm^2 in the smaller chamber and at 12 mw/cm^2 in the bigger chamber. Gas residence time was about three seconds in each reactor.

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Measurements to determine the bonded hydrogen content of the films were made on a Nicolet Fourier transform IR spectrometer. The hydrogen concentration [H] was calculated by integrating under the bond-wagging mode at 620 cm^{-1} first identified by Brodsky et al.[4].

$$[H] = A_{\omega} \int \alpha(\omega)/\omega \, d\omega \qquad (1)$$

The calibration constant, $A_{\omega} = 1.6x10^{19} cm^{-2}$, determined by Fang et al.[5], is used in this paper.

Measurements to determine the optical band gap and index of refraction were made on a Cary14 spectrophotometer. Films of a-Si were deposited on 22mil thick wafers of Corning 7059 glass. Film thicknesses ranged from 0.2 to 1.2 microns. Data was analyzed using the standard equations for transmission through a thin film on a transparent substrate [3].

The FET device structure is shown in Fig. 1. After a thin layer of gate metal was patterned on Corning 7059 glass a triple layer of amorphous materials was plasma deposited in single pumpdown. The gate dielectric was 150nm of silicon nitride, the intrinsic a-Si layer was 200nm thick and the n^+ layer 50nm thick. N^+ material was obtained by mixing silane and phosphene to yield a source-drain contact layer with a bulk conductivity of about 10^{-2}/ohm-cm. A layer of Mo was deposited to contact the n^+ layer after which the Mo and n^+ were patterned back to form the FET structure. After plasma etching a thickness of 100 nm of a-Si remained in the channel. Channel lengths of 5 and 25 microns were fabricated which varied in width from 20 to 1000 microns. Gate to source and drain overlap in these research devices was large enough to insure the absence of overlap limited behavior [2].

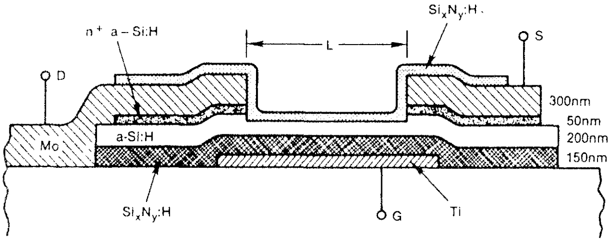

Fig.1. Cross-section of a inverted, staggered gate FET.

The field effect effective mobility was measured in two ways. At low drain bias voltage,we have assumed the validity of

$$I_d = \mu_e C (W/L) (V_g - V_t) \qquad (2)$$

and in the saturation region the usual square law model

$$I_d = \mu_e C (W/2L) (V_g - V_t)^2 \qquad (3)$$

is employed where C is the gate insulator capacity per unit area, W and L the channel dimensions, and V_g and V_t are the gate and threshold voltages.