MASTER

HYDROGEN IN AMORPHOUS SILICON*

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ABSTRACT

The structural aspects of amorphous silicon and the role of hydrogen in this structure are reviewed with emphasis on ion implantation studies. In amorphous silicon produced by Si ion implantation of crystalline silicon, the material reconstructs into a metastable amorphous structure which has optical and electrical properties qualitatively similar to the corresponding properties in high-purity evaporated amorphous silicon. Hydrogen studies further indicate that these structures will accommodate $\lesssim 5$ at.% hydrogen and this hydrogen is bonded predominantly in a monohydride (SiH_1) site. Larger hydrogen concentrations than this can be achieved under certain conditions, but the excess hydrogen may be attributed to defects and voids in the material. Similarly, glow discharge or sputter deposited amorphous silicon has more desirable electrical and optical properties when the material is prepared with low hydrogen concentration and monohydride bonding. Results of structural studies and hydrogen incorporation in amorphous silicon are discussed relative to the different models proposed for amorphous silicon.

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I. INTRODUCTION

During the past few years, there has been increasing interest in the study of amorphous semiconductors.¹ This interest is perhaps most evident in the case of amorphous silicon (a-Si). Motivations for the study of a-Si and hydrogenated a-Si (a-Si:H) range from interest in the properties of a single element amorphous semiconductor, which can in principle, reveal basic information concerning the ideal amorphous state, to interest in device fabrication. In the crystalline state Si is perhaps the most thoroughly understood semiconductor, and it was hoped that information available from studies of crystalline Si could be applied to help understand the amorphous state. Furthermore, since a-Si is a metastable phase of Si, investigations of a-Si also offer the possibility of observing new phenomena associated with metastability which do not exist in crystalline Si.

Many of the earlier studies of a-Si were motivated by a desire to understand the properties of an ideal amorphous structure; however, the observation by Spear and Le Comber² that incorporation of hydrogen into a-Si allowed the electrical properties to be controlled by dopants opened totally new areas of investigation. High purity a-Si displays intrinsic conductivity which is largely unaffected by dopants. Several studies have shown that, with the inclusion of hydrogen and more recently fluorine,^{3,4} the room temperature conductivity can be varied orders of magnitude with conventional n- or p-type dopants.⁵

The control over the electrical properties afforded by hydrogenation has stimulated a large amount of research in device applications of a-Si:H. Device structures from a-Si:H which have been demonstrated to date include MOS devices,⁶ vidicon arrays,⁷ and photovoltaics.⁸ Indeed, the possibility of producing large area, low cost solar cells has been largely responsible

for the recent growth in the research and development effort in a-Si:H and related amorphous materials.

II. PREPARATION METHODS

High purity a-Si can be prepared by a variety of techniques. Initial studies of a-Si were performed on films evaporated under high vacuum conditions.⁹ The techniques of sputter deposition¹⁰ and ion implantation¹¹ have also been used to prepare films of high purity a-Si. Although films prepared by these different techniques have qualitatively similar properties, variations in material properties are observed not only for films prepared by different techniques but also for films prepared by a given technique under different deposition conditions.¹² These variations have been attributed to variations in the a-Si structure that result from variations in substrate temperature and deposition rate as well as from variations in impurity content. For most cases, the high purity a-Si films have room temperature conductivities $\sim 10^{-3}$ to $10^{-4} (\Omega \text{ cm})^{-1}$ with the conductivity dominated by electronic states in the energy gap that are generally attributed to dangling Si bonds. These gap states effectively pin the Fermi level and thus prevent control of the electrical properties by the use of conventional dopants.

Optical measurements reveal that pure a-Si does not have a well-defined optical band gap but shows a broad absorption edge which extends into the ir.¹³ This absorption is attributed to defect and dangling-bond states noted above; additional information concerning the nature of the states in the energy gap has been obtained from electron paramagnetic resonance (EPR) studies.¹⁴

The addition of hydrogen to a-Si to form a-Si:H markedly alters the optical absorption, defect structure, and conductivity. The role of hydrogen has been variously assumed to range from the passivation of Si dangling bonds to the formation of a fundamentally different structure¹⁵ for a-Si:H than for a-Si. Some of the effects of hydrogen on the commonly-studied properties of a-Si are summarized in Table I.

Initially, a-Si:H was prepared by deposition from a silane (SiH_4) plasma (glow discharge or plasma deposition). More recently, a-Si:H films prepared by sputtering in the presence of hydrogen¹⁶ and by ion implantation,¹⁷ or uhv evaporation of a-Si with subsequent exposure to an atomic hydrogen plasma,¹⁸ have been shown to have hydrogen-related effects similar to those for plasma deposited a-Si:H. Examples of the range in conductivity obtained for pure a-Si and for a-Si:H prepared by different techniques are illustrated in Fig. 1. A similar comparison for the optical absorption is shown in Fig. 2. As will be discussed below, wide variations in material properties such as hydrogen concentration and film microstructure can be obtained for different preparation conditions.

Although the best electrical performance and photovoltaic devices¹⁹ have been achieved to date with glow discharge deposited a-Si:H, the intrinsic complexity of the glow discharge process and the interrelations among the various deposition parameters have hampered studies of the basic material properties of films prepared by this technique. As a result, studies of films formed by other techniques are providing significant information on the basic structural properties of a-Si and a-Si:H. Particularly important structural information has been obtained from studies of films evaporated under uhv or formed by ion implantation. Similarly, ion implantation studies of sputter deposited films have yielded important new information concerning the bonding configurations for hydrogen in a-Si:H. Ion implantation affords the capability

for separate control of two important parameters in a-Si:H - namely disorder and hydrogen content - which cannot be independently controlled in plasma or sputter deposited materials.

Information on the structural properties of a-Si and the role of hydrogen in this structure will be discussed in the following Sections with emphasis on ion-implantation studies of a-Si:H.

III. STRUCTURAL PROPERTIES AND BONDING OF HYDROGEN

The amorphous phase of Si is a metastable state which can apparently be prepared with a range of structural configurations.¹² The addition of hydrogen stabilizes disorder²⁰ in Si and may further increase the structural configurations available. The structural properties of a-Si and the related material a-Ge have been studied by a variety of techniques. Galeener²¹ postulated that a-Ge contained voids and such voids were subsequently observed directly in TEM measurements.²² It has been shown by Messier and coworkers²³ that a-Si can contain similar voids with the void size decreasing with increasing deposition temperature if other deposition parameters are constant. These authors²⁴ also observed interconnected void networks in sputter-deposited a-Ge with void sizes ranging up to $\sim 50 \text{ \AA}$.

Recently, from measurements of epitaxial regrowth rates of a-Si evaporated onto room temperature substrates under uhv conditions, Bean and Poate²⁵ inferred the existence of an interconnected void network in evaporated a-Si. They found that the epitaxial growth rate for evaporated a-Si was significantly lower than that for ion-implantation produced a-Si²⁶ and that the growth rate was further reduced by exposure to air. Further evidence²⁷ for an interconnected void network in these films was obtained from SIMS measurements of atmospheric gases which had percolated in to depths of $\sim 1000 \text{ \AA}$ after exposure to air.

TEM measurements of the microstructure of a-Si:H prepared either by glow discharge²⁸ or sputter deposition²³ reveal wide variations in microstructure for variations in deposition conditions. Knights and coworkers²⁸ observed columnar structure in plasma deposited a-Si:H and concluded that film growth for this case proceeded via nucleation and island growth. For many combinations of deposition parameters, columnar growth was observed and attributed to growth conditions for which the ~ 100 Å wide islands did not coalesce into a homogeneous film. By changing the deposition conditions, however, they were able to prepare a-Si:H films without resolvable voids (resolution ~ 10 Å) at a substrate temperature of 230°C.

Models for the morphology of deposited films generally attribute columnar structure to nucleation at isolated sites²⁹ which can occur independent of the deposition technique. Columnar structure similar to that observed for plasma-deposited a-Si:H is as observed for sputter-deposited a-Si:H by Messier and coworkers.²³ An example of the differences in film morphology observed by Messier and coworkers²³ for different sputtering conditions is given in Fig. 3. For the case of a-Ge, these workers further find that the relatively large (~ 1 μ m) columns are comprised of smaller (~ 100 Å) columns. Furthermore, field ion microscopy studies (FIM) of this material reveal that there may also be ~ 100 Å diameter regions which actually contain less dense material rather than being true voids.³⁰ These wide variations in film morphology can easily account for the variations observed in film densities which range from ~ 5 to 30% lower than the density of crystalline Si.³¹ Microstructure resolvable from SEM or TEM measurements has not been reported for implantation-produced a-Si. This absence of observable voids or the columnar structure frequently observed in deposited a-Si films may account for the higher density frequently observed for implantation produced ($\sim 5\%$ less than the density of crystalline

Si) than in deposited a-Si. Similarly, the higher structural homogeneity of implanted a-Si compared to evaporated films may account for Foti and coworkers²⁷ suggestion that the structure of high purity a-Si films evaporated at room temperature differed from the structure of implantation-produced a-Si. From the decrease in void size with increasing deposition temperature for a-Si:H and a-Ge,^{23,30,32} it is probable that deposition at higher temperature or different deposition rates could yield evaporated films without an interconnected void network, similar to implantation produced films.

The hydrogen content of a-Si:H can be varied from 0 to ~ 50 at.% depending on the preparation conditions.³³ An illustration of the variation in hydrogen concentration with variations in deposition conditions is given in Fig. 4. The data in Fig. 4 show the hydrogen depth distribution, measured by nuclear reaction analysis techniques, for a-Si:H films deposited at a substrate temperature $T_s = 50^\circ\text{C}$ by magnetron sputtering with various partial pressures of hydrogen.³⁴ All deposition parameters except the Ar/H ratio were held constant. As can be seen from these data, the hydrogen concentration can be varied over wide ranges by variations in Ar/H. Similar changes in the hydrogen content can be obtained at a given Ar/H ratio by changing other deposition parameters such as substrate temperature, deposition rate, target-substrate separation, etc. These variations in hydrogen concentration are associated with variations in morphology and film stability. Low density films with significant columnar structure are unstable and susceptible to oxygen contamination after exposure to air.³⁵ Oxygen concentrations of several atomic percent can be absorbed and Si-O vibrations are readily observable in the ir absorption spectrum. These films also tend to contain large hydrogen concentrations (≥ 20 at.%).

Not only does the hydrogen concentration change with deposition conditions but the hydrogen bonding configurations also change. Although there is presently some controversy concerning specific assignments of some Si-H vibrational modes

observed in the ir, there is no doubt that a-Si:H can contain both monohydride SiH and dihydride SiH₂ bonding configurations.³⁶ The common assignment³⁶⁻³⁸ of the Si-H stretching vibrations attribute the stretching mode at 1985 cm⁻¹ to SiH₁ and the mode at 2085 cm⁻¹ to SiH₂ vibrations. However, recent studies have shown that a vibrational mode at 2085 cm⁻¹ may be present in a-Si:H in which no evidence for dihydride centers was found in the spectral region containing the "bending" and "wagging" modes (600 to 1000 cm⁻¹),^{39,40} indicating the possibility of more than one frequency for SiH₁ vibrations. An ir absorption feature at 2150 cm⁻¹ in high hydrogen content films which has also been assigned to SiH₃ or (SiH₂)_n units.³⁸

As noted above, the more porous films tend to have high hydrogen concentrations. In addition, these films also display large ir absorptions at 2095 cm⁻¹ which is commonly attributed to SiH₂. The high concentrations of SiH₂ and (SiH₂)_n units have been attributed to low density material in the interstitial regions separating the columns.²⁸ Because of the evidence for two distinct local environments for SiH₁ which give rise to two discrete vibrational frequencies in the ir, it may be that these modes also represent SiH₁ centers in the high density columnar regions and lower density interstitial regions. As might be expected, these high hydrogen content films display electrical and photovoltaic properties which are inferior to those of the lower hydrogen content films.

IV. ION IMPLANTATION STUDIES OF a-Si

Because the disorder and hydrogen content can be varied independently, ion implantation has proven to be a valuable technique for the study of a-Si. Comparison of the properties of a-Si produced by ion implantation with those

of a-Si formed by conventional techniques have shown wide-ranging similarities for materials prepared by the various techniques. In particular, the vibrational phonon spectra,⁴¹ defect configurations measured by EPR,⁴² optical absorption,⁴³ and conductivity⁴⁴ are similar for high purity a-Si produced by ion implantation or uhv evaporation. After the discovery of the role of hydrogen on the properties of a-Si, extension of ion implantation techniques to produce a-Si:H further revealed that the same qualitative changes in the conductivity observed with the inclusion of hydrogen during sputter deposition could be effected by ion implantation of hydrogen.⁴⁵ In addition, infrared studies of the Si-H bonding configurations of implanted hydrogen revealed that the prominent Si-H vibrational mode at 1985 cm^{-1} was preferentially populated⁴⁶ in implantation-produced a-Si:H.

To illustrate the control afforded by ion implantation, a typical depth profile of hydrogen implanted into high purity a-Si formed by Si-ion implantation is shown in Fig. 5. The hydrogen depth distribution was measured by resonant nuclear reaction analysis and the thickness of the amorphous layer produced by implantation of 1×10^{16} 250 keV Si/cm² was measured by 3 MeV ⁴He channeling.⁴⁶ The monoenergetic hydrogen implant at 20 keV yields an essentially Gaussian depth distribution centered at a depth of 2600 Å with a full width at half maximum of $\sim 900\text{ Å}$ and a peak hydrogen concentration of ~ 15 at.% for an implant of 1×10^{17} H/cm². Uniform hydrogen concentrations can be achieved either by using multiple implant energies or various sample tilt angles during implantation.

The implanted hydrogen was found to be chemically bonded to Si for all implantation fluences examined. Infrared absorption spectra for the spectral region containing the Si-H stretching vibrations are compared for implantation produced and sputter deposited a-Si:H in Fig. 6. As noted in Section III, two

vibrational modes are typically observed in sputter- or glow discharge-deposited a-Si:H, with the mode at $\sim 1985 \text{ cm}^{-1}$ assigned to an SiH_1 vibration and the $\sim 2090 \text{ cm}^{-1}$ mode to an SiH_2 vibration although there is continuing controversy over this latter assignment. As also noted in Section III, porous films which exhibit columnar structure generally contain a strong 2090 cm^{-1} absorption. For a-Si:H films which display the best photoconductivity properties,⁴⁷ the hydrogen is bonded predominantly in the SiH_1 site with absorption near 1985 cm^{-1} .

The hydrogen bonding configuration illustrated in Fig. 6 for implantation produced a-Si:H holds over a wide range of hydrogen concentrations as shown by the ir absorption data in Fig. 7. Although the absorption cross section changes with hydrogen concentration, which was also recently noted⁴⁸ for sputter-deposited a-Si:H, the monohydride absorption at $\sim 1985 \text{ cm}^{-1}$ predominates the spectra. Absorption at $\sim 2090 \text{ cm}^{-1}$, attributed to SiH_2 in these films, does not become observable until the local hydrogen concentration exceeds $\sim 15 \text{ at.}\%$; this $\sim 2090 \text{ cm}^{-1}$ absorption increases with increasing hydrogen concentration and becomes appreciable for $\geq 25 \text{ at.}\%$ hydrogen, which is taken to be an indication that SiH_1 is the lowest energy site and SiH_2 formation is not observed until the available SiH_1 sites are occupied. The maximum local hydrogen content which can be obtained by ion implantation into crystalline Si is $33 \text{ at.}\%$ (H/Si ratio of 0.5).⁴⁹

Although both glow discharge and sputter-deposited a-Si:H which contains only SiH_1 bonding with absorption at $\sim 1985 \text{ cm}^{-1}$ has been demonstrated to have superior photoconductivity and electrical properties, it is not known if the same conclusion holds for implantation-produced a-Si:H. It is of interest to note, however, that marked changes in the Si-H absorption spectra can be produced by ion implantation into sputter-deposited a-Si:H. For

material deposited with low ($\sim 3\%$) hydrogen content, the energy deposited into atomic processes by ^4He implantation effectively removes the Si-H bonding configurations responsible for the 2090 cm^{-1} absorption, as shown by the ir spectra in Fig. 8, with a corresponding increase in the SiH_1 configurations responsible for the 1985 cm^{-1} absorption. A similar implantation-induced increase in the 1985 cm^{-1} absorption is observed for films with high (~ 30 at.%) hydrogen content films without removal of the 2090 cm^{-1} absorption.⁵⁰ These studies on the high hydrogen content film were interpreted as indicating that the oscillator strengths of the Si-H modes are strongly dependent on the defect structure in the vicinity of the vibrating Si-H complex.

For the ion implantation studies summarized above, the hydrogen content and depth distribution was controlled by the implantation parameters. An alternative approach which provides important insight into the nature of a-Si is to introduce atomic hydrogen into implantation-produced a-Si under thermodynamic equilibrium conditions. This technique allows a direct determination of the number of bonding sites available in high purity a-Si prepared in the absence of hydrogen and of the interrelation between hydrogen and disorder in silicon. As noted earlier, the disorder level, ranging from crystalline to amorphous can be controlled by ion implantation.

The depth distribution⁵¹ of ion-implantation-induced disorder is illustrated in Fig. 9 for 200 keV Si implantation into crystalline Si at fluences ranging from $3 \times 10^{14}\text{ Si/cm}^2$ to $5 \times 10^{15}\text{ Si/cm}^2$. The data in Fig. 9 were taken with 3 MeV ^4He channeling and show that the amorphous level is approached at the damage peak (maxima in the energy deposited into atomic processes) near $0.2\text{ }\mu\text{m}$ at a fluence of $1 \times 10^{15}\text{ Si/cm}^2$. As the fluence is increased, the width of the amorphous layer increases until a layer of a-Si $\sim 0.4\text{ }\mu\text{m}$ thick is formed at a fluence of $5 \times 10^{15}\text{ Si/cm}^2$.

Hydrogen was then introduced into the implanted Si by exposure to an atomic hydrogen plasma at various temperatures and the resulting hydrogen depth distribution measured with resonant nuclear reaction analysis. The hydrogen depth distribution obtained after 17 hour exposures at 300 and 375°C are shown in Fig. 10. As can be seen from these data, hydrogen diffuses into Si under exposure to the plasma and is trapped at the implantation-induced disorder.

Diffusion-limited hydrogenation is apparent for the a-Si layer at 300°C exposure, but saturation levels were reached for $T \geq 350^\circ\text{C}$ for 17 hour exposures. Two important features are evident from the data in Fig. 10. First, hydrogen is retained in Si only when disorder is present. Within the sensitivity of the measurements ($\lesssim 100$ ppm), no hydrogen was observed in the underlying, undamaged crystal. Secondly, defected crystalline Si can absorb more hydrogen than totally disordered (amorphous) Si. It should also be noted that the effective diffusion coefficient is larger in crystalline Si than in implantation produced a-Si. For example, after a 17 hour exposure at 300°C the hydrogen content of Si implanted with 5×10^{14} Si/cm² is approaching saturation whereas the hydrogen concentration in the a-Si is clearly diffusion limited. This lower hydrogen migration rate in a-Si is interpreted to be due to the diffusion of hydrogen in the presence of traps. These results can be compared with the differences in epitaxial regrowth rates for implantation-produced a-Si and a-Si produced by uhv evaporation onto room temperature substrates. From the rapid indiffusion of contaminants in evaporated a-Si, Bean and coworkers²⁷ inferred that evaporated a-Si deposited at low temperatures contained an interconnected void network that was not present in implantation produced a-Si. It would be of significant

interest to repeat the epitaxial growth rate measurements on a-Si evaporated onto higher temperature substrates.

Further insight into hydrogen incorporation in a-Si is obtained from ir measurements shown in Fig. 11 for a 350°C plasma exposure. The Si-H vibration spectra are dominated by the 1985 cm^{-1} SiH_1 mode for Si fluences $\geq 10^{15}\text{ Si/cm}^2$. (The absorption near 2100 cm^{-1} , present for all Si fluence levels, is associated with surface hydrogen⁵² and defects within the crystalline matrix.⁵³) The hydrogen bonding configuration is thus identical to that observed for implantation at comparable hydrogen concentrations and in contrast to the configuration frequently observed in sputter or glow discharge-deposited a-Si:H where both the 1985 cm^{-1} and 2090 cm^{-1} vibrations are observed. Thus, the predominance of Si-H bonded in the SiH_1 mode at 1985 cm^{-1} when the hydrogen is implanted into a-Si is not an artifact of the hydrogen implantation; rather, it reflects the available bonding configurations in high-purity implantation-produced a-Si.

From the ir data of Fig. 11, it can be seen that the hydrogen content in the SiH_1 mode at 1985 cm^{-1} saturates with increasing Si implantation fluence. The opposite behavior is observed for the peak hydrogen content in the disordered region, however, as seen from the data in Fig. 10. In Fig. 12, the hydrogen content at the disorder maximum, measured by nuclear reaction analysis, is compared with the SiH_1 intensity measured by ir absorption. First consider the hydrogen content; the hydrogen concentration increases with increasing Si fluence (disorder) in crystalline Si until a-Si begins to form. As the Si implantation fluence is further increased above this level, the hydrogen content decreases as the material apparently reconstructs into the amorphous structure. These data alone demonstrate that a random network model in which the a-Si structure is considered to be an extension of highly

defected crystalline structure without reconstruction is incorrect. This conclusion is further supported by the ir data, also shown in Fig. 12. The fraction of hydrogen bonded in the 1985 cm^{-1} site of a-Si increases with increasing Si implantation fluence and attains its maximum value in the totally amorphous material. In fact, it is not until the material becomes amorphous, as measured by ion channeling, that appreciable hydrogen is bonded in this site.

Whereas conventionally prepared a-Si:H can have hydrogen concentrations of up to 50 at.%, the maximum hydrogen concentration observed for implantation produced a-Si in which the hydrogen is incorporated by exposure to an atomic hydrogen plasma is ~ 3 at.%. This concentration is quite comparable to the 3.5 at.% hydrogen concentration observed by Kaplan et al.¹⁸ for the hydrogen content of high purity a-Si prepared by evaporation and subsequently exposed to a hydrogen plasma. The observations suggest that the higher hydrogen concentrations commonly present in conventionally prepared a-Si:H are an artifact of the deposition conditions, and these latter materials do not represent "ideal" a-Si for which dangling or unsaturated Si bonds are passivated with hydrogen. Indeed, more desirable photovoltaic properties have been achieved to date in a-Si:H with ~ 5 -10% hydrogen rather than in materials with high ($\geq 20\%$) hydrogen content.

In the studies reviewed above, the uses of ion implantation to study the bonding configuration of hydrogen in ground state and the concentration of available bonding sites for hydrogen in high purity a-Si were illustrated. Ion implantation can also be used to study the interrelation between hydrogen and disorder in Si. Although the bonding configuration for hydrogen in implantation-produced a-Si, is independent of the order of the Si and hydrogen implantation, the presence of hydrogen stabilizes disorder in Si.²⁰ An

example of hydrogen stabilization of disorder is illustrated by the data in Figs. 13 and 14. The hydrogen depth distribution produced by implantation of 6×10^{16} H/cm² at 20 keV and the disorder introduced by this implant, as measured by 3 MeV ⁴He channeling, are shown in Fig. 13. Random yield disorder (+) is shown for comparison. This hydrogen implant deposits 1.5×10^{24} eV/cm³ in the damage peak near 0.2 μ m depth, which is less than the 2 to 3×10^{24} eV/cm³ required to convert Si from crystalline to amorphous for room temperature Si implantation.⁵⁴ We now wish to consider the effect of this hydrogen on the structure as additional disorder is introduced by Si implantation.

Figure 14 contains the channeling spectra for two samples implanted with 6×10^{16} H/cm² at 20 keV and 2×10^{14} Si/cm² at 200 keV. For this Si energy, the damage maximum from the Si overlaps the hydrogen distribution. The only difference between the two samples for which the channeling spectra are shown is the order in which the hydrogen and Si were implanted; however, the disorder level is a factor of ~ 4 higher for the case in which hydrogen was implanted before the Si, compared to the case in which the Si was implanted first. In fact, the channeling yield reached the amorphous yield after implantation of 2×10^{14} 200 keV Si/cm² in the sample containing hydrogen whereas the disorder for Si followed by hydrogen is comparable to that for hydrogen alone (Fig. 13). These data indicate that hydrogen stabilizes disorder in Si and assist the transition from crystalline to amorphous. With hydrogen present, a-Si is produced with only 5.6×10^{23} eV/cm³ deposited into atomic processes, or about 1/4 the energy required in the absence of hydrogen. This disorder stabilization presumably results from hydrogen bonding to defects to inhibit defect annealing.²⁰

Three ir spectra are shown in Fig. 15: one for 6×10^{16} H/cm² alone, one for 6×10^{16} H/cm² followed by 2×10^{14} Si/cm² and one for 2×10^{14} Si/cm² followed by 6×10^{16} H/cm². As can be seen from the data, the hydrogen only implant and the Si implant followed by hydrogen yield essentially identical spectra and both are characteristic of hydrogen bonded in association with defects in crystalline Si. The 6×10^{16} H/cm² followed by 2×10^{14} Si/cm² implant, however, yields a spectrum characteristic of hydrogen in a-Si:H with the hydrogen bonded predominantly in the SiH₁ site with absorption at 1985 cm⁻¹. The intensity of this SiH₁ line is $\sim 75\%$ of what one would observe if the hydrogen were implanted into fully amorphous Si.

The results of the ion implantation studies of the interrelation between hydrogen and disorder lend further support to the conclusions noted above. Hydrogen stabilizes disorder in crystalline Si. If there is a similar hydrogen stabilization of disorder in a-Si:H, materials containing large hydrogen concentrations could be expected to contain more defects than the low hydrogen content material. If this speculation is correct, much of this hydrogen does not merely passivate dangling Si bonds; rather it is apparently trapped during deposition. Once trapped, the hydrogen inhibits defect annealing and prevents the Si from reconstructing into the lowest energy a-Si structure.

V. STRUCTURAL MODELS

A wide variety of models^{12,55-59} have been suggested to describe the structure of pure a-Si. These models range from microcrystallite models, through cluster models to random network models and random networks containing voids. The random network model with voids ("Swiss Cheese" model) was constructed to allow for an ideal amorphous state in which the a-Si has short range order with all bonds saturated but no long range order, while also

allowing for the voids observed in as-deposited films. Such a structure is metastable in that it corresponds to a local minimum in the free energy with respect to atomic rearrangements. Considering the wide variations in materials and materials properties which can be obtained for various preparation conditions, it is probable that materials which embody major characteristics of either model can be prepared.

With the addition of hydrogen to a-Si to form a-Si:H, two distinct conceptual frameworks for interpreting the structural properties emerged. One concept is that SiH_x units are present during deposition and govern the structure whereas the other concept is that an a-Si structure forms and hydrogen passivates the unsaturated Si bonds. The conceptual framework in which SiH_x units are present during deposition leads to a flexible bond model.¹⁵ These flexible bonds reduce strain in film, analogous to the case for SiO bonds in vitreous SiO_2 , and allow the formation of a continuous network. This type of model would be expected to be most applicable to high hydrogen content ($\geq 25\%$ H) a-Si:H were it not for the existence of inhomogeneous, columnar structure for this material.

The conceptual models based on hydrogen passivation of an intrinsic amorphous structure are extensions of the a-Si structural models noted above. These models include a continuous random network model⁶⁰ in which hydrogen is assumed to passivate dangling Si-bonds or to "heal" weak Si-Si bonds, for example, by breaking these bonds and saturating the broken bonds with hydrogen. Similarly, the "Swiss Cheese" model in which the a-Si structure was assumed to be comprised of a random network containing voids was extended to the microvoid model.⁶¹ In this model the hydrogen is assumed to be bonded on reconstructed surfaces in the voids and at dangling bond sites in the random network.

The microvoid model, or a model containing microvoids, is attractive for explaining many diverse experimental observations. For example, voids are commonly observed on a microscopic scale in a-Si:H, as discussed above. Measurements of microscopic properties also give evidence for void structures in crystalline Si which have EPR and hydrogen bonding configurations similar to those observed in a-Si:H. Brower⁶² showed from EPR studies of defects in crystalline Si that only the end atoms of a vacancy chain contribute unpaired electron spins, which could account for the difference in the number of paramagnetic spins in a-Si compared to the amount of hydrogen required to passivate those spins. Recently, Stein⁶³ found that hydrogen implanted into crystalline Si at low temperature was bonded in a site analogous to the SiH₁ site, with absorption at 1985 cm^{-1} , in crystalline Si. This result was interpreted to reflect hydrogen bonded to silicon in "microvoids" produced by the implantation which could not anneal because of the low temperature.

A viable model for the structure of a-Si:H must be able to explain quantitatively several general experimental observations for a-Si and a-Si:H. Some of the more striking of these observations include 1) the lower density of a-Si or a-Si:H compared to crystalline Si; 2) the large changes in electrical conductivity upon hydrogenation; 3) saturation of the dangling bonds requires over an order of magnitude more hydrogen than the observed number of paramagnetic spins and 4) high purity a-Si prepared by evaporation or ion implantation and hydrogenated by subsequent exposure to an atomic hydrogen plasma takes on only 3 to 4 at.% hydrogen.

While the random-network and microvoid models discussed above may be able to explain these observations qualitatively, unfortunately they have no predictive capabilities. Phillips⁶⁴ has recently proposed a self-limited cluster model that does have predictive capability which we now discuss

briefly. In this model he postulated that a-Si is comprised of clusters of five-, six-, and seven-membered rings of Si and that the cluster size was limited by surface strain. The growth rate of a cluster decreases as the size, and attendant surface strain, increases; hence the cluster size becomes self-limiting. In this picture, the a-Si is composed of clusters with some size distribution and voids between the clusters. The void network arises because the cluster growth rates for different bonding directions (e.g., $\langle 111 \rangle$ -like versus $\langle 100 \rangle$ -like) are assumed to have anisotropy similar to the growth rates for these same bonding directions in crystalline Si. The result is an a-Si structure with connected clusters of a-Si and an interconnected void network. By further assuming that the Si bonds on the internal void surfaces reconstruct in a manner similar to the reconstruction observed on analogous crystalline Si surfaces, the model yields a paramagnetic center/hydrogen-bonding site ratio of $\sim 1:100$ for reasonable parameters.

This self-limited cluster model is consistent with many of the structural features observed in high purity a-Si produced by ion implantation or evaporation. For example, both evaporated and implantation-produced a-Si hydrogenated by exposure to an atomic hydrogen plasma absorb ~ 3 to 4 at.% hydrogen. Furthermore, the hydrogen is bonded predominantly as SiH_1 with ir absorption at 1985 cm^{-1} for both cases. Although there was no evidence for the void network being interconnected in implantation-produced a-Si, evidence for an interconnected void network has been observed in high purity evaporated a-Si. More work is required to determine if the large change in electrical properties on hydrogenation, which are assumed to be controlled by bridges connecting the clusters, can be adequately accounted for by this model.

If this model is correct, it has important implications concerning "ideal" a-Si:H. In particular, the desired hydrogen concentration would be $\lesssim 5$ at.% with the hydrogen bonded in monohydride sites. The role of hydrogen is passivation of Si dangling bonds, as initially suggested, and hydrogen in excess of the ~ 5 at.% could be expected to degrade the electrical properties of a-Si:H. Similarly, significant concentrations of hydrogen bonded in polyhydride sites would represent defects incorporated as an artifact of the deposition conditions. Many of these speculations are in agreement with the experimental results reviewed earlier, but much more research is required to completely understand the structure of a-Si:H and the interrelation between the structure and the electrical and optical properties.

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- Figure 1. Electrical conductivity for a-Si and a-Si:H films prepared by various techniques. II - ion implanted; Sp - sputtered; IT + 1% H - ion implanted with 1% H implanted and Sp-700°K - Sputtered with H, annealed 700°K; GD - Glow Discharge. (After Müller and Kalbitzer, Ref. 45.)
- Figure 2. TEM photographs illustrating the different structural morphology for sputtered a-Si obtained for different Ar pressures. (After Messier, et al. Ref. 23.)
- Figure 3. Optical absorption for a-Si and a-Si:H prepared by different techniques. A.-Sputtering, $T_s = 25^\circ\text{C}$; B.-Ion Bombardment; C.-Sputtering, $T_s = 200^\circ\text{C}$; D.-Evaporation, $T_s = 20^\circ\text{C}$; E.-Sputtering, with $0.16 \mu\text{H}$, $T_s = 200^\circ\text{C}$; F.-CVD from SiH_4 , $T_s = 650^\circ\text{C}$; G.-Glow discharge of SiH_4 , $T_s = 195^\circ\text{C}$; H.-Sputtering, $0.44 \mu\text{H}$, $T_s = 200^\circ\text{C}$; I.-Crystalline Si. (After Freeman and Paul, Ref. 13).
- Figure 4. Nuclear reaction analysis measurements of the hydrogen concentrations in magnetron sputtered a-Si:H for various Ar/H ratios.
- Figure 5. Backscattering yield showing the depth of the bombardment-produced amorphous Si layer on $\langle 111 \rangle$ Si and implanted-hydrogen concentration profile within the amorphous layer determined by $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ nuclear reaction analysis. (After Stein and Peercy, Ref. 46.)
- Figure 6. Comparison of the vibrational spectra for ion implantation-produced and sputter-deposited a-Si:H.
- Figure 7. Infrared absorption of chemically bound hydrogen implanted into Si after amorphization with 10^{16} 250-keV Si^+ ions/ cm^2 . Results are shown for several different hydrogen atom fluences and compared to those for a sputter-deposited a-Si film with ~ 3 at.% hydrogen partitioned between SiH_1 and SiH_2 centers. (After Stein and Peercy, Ref. 46.)

Figure 8. Infrared absorption spectra for SiH stretch modes in sputter-deposited amorphous Si before and after He ion bombardment.

(After Stein and Peercy, Ref. 20.)

Figure 9. Channeling spectra in Si^+ -implanted crystalline Si showing the disorder produced by various Si^+ fluences. (After Peercy, Stein, and Ginley, Ref. 51.)

Figure 10. Hydrogen depth distributions for different disorder levels, measured by nuclear reaction analysis, obtained after 17-h H exposures at 300 (a) and 375°C (b). (After Peercy, Stein, and Ginley, Ref. 51.)

Figure 11. Infrared absorption spectra for the spectral regions containing the Si-H stretching vibrations after a 17-h H exposure at 350°C. Data are shown for Si^+ fluences of 0.3, 0.5, 1, 3, and $5 \times 10^{15} \text{ Si}^+/\text{cm}^2$. (After Peercy, Stein, and Ginley, Ref. 51.)

Figure 12. Comparison of the hydrogen concentration at the disorder maxima for various Si implantation fluences with the SiH_1 ir absorption after a 17 hr H plasma exposure at 400°C.

Figure 13. The hydrogen depth distribution for $6 \times 10^{16} \text{ 20 keV H/cm}^2$ measured by nuclear reaction analysis, and backscattered He spectra from Si after this hydrogen implantation. Also included is the backscattering spectra from (100) Si after amorphization by $5 \times 10^{15} \text{ 200 keV Si/cm}^2$. (After Stein and Peercy, Ref. 20.)

Figure 14. He backscattering spectra for Si illustrating hydrogen enhancement of disorder produced by $2 \times 10^{14} \text{ 200 keV Si/cm}^2$. (After Stein and Peercy, Ref. 20.)

Figure 15. Infrared absorption spectra for SiH modes in Si illustrating hydrogen enhancement of amorphization by 2×10^{14} 200 keV Si/cm².

(After Stein and Percy, Ref. 20.)

Table I. Comparison of electrical and optical
properties of a-Si and a-Si:H

	a-Si	a-Si:H
$\sigma(\text{R.T.})$	$10^{-3}-10^{-4} (\Omega \text{ cm})^{-1}$	$\sim 10^{-10} (\Omega \text{ cm})^{-1}$
$E_G(\text{optical})$	absorption into ir	$\sim 1.7 \text{ eV}$
Paramagnetic Centers	$\sim 5 \times 10^{19} / \text{cm}^3$	$\sim 10^{16} / \text{cm}^3$
Gap States	$\sim 10^{20} / \text{cm}^3 \text{ eV}$	$\sim 10^{17} / \text{cm}^3 \text{ eV}$

5MTORR Ar(.22%H)

20MTORR Ar(.22%H)

40MTORR Ar(.22%H)

70MTORR Ar(.22%H)

FRACTURED EDGES OF UNETCHED (TOP) AND ETCHED (BOTTOM) A-Si:H AT FOUR DIFFERENT SPUTTERING CONDITIONS

Figure 2 - Peercy
Hydrogen in Amorphous Silicon

Figure 4 - Percy
Hydrogen in Amorphous Silicon

Figure 6 - Peercy
Hydrogen in Amorphous Silicon

Figure 8 - Percy
Hydrogen in Amorphous Silicon

Figure 9 - Percy
Hydrogen in Amorphous Silicon

Figure 14 - Percy
Hydrogen in Amorphous Silicon