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STUDIES OF THIN-FILM GROWTH OF SPUTTERED HYDROGENATED AMORPHOUS SILICON

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The role of a number of physical and chemical sputtering effects in the thin film growth of hydrogenated amorphous silicon has been investigated. Charged particle bombardment was found to affect the film microstructure more than neutral particle bombardment. The roles of electron and Ar^+ ion bombardment have been identified. Control of the hydrogen bonding is accomplished through bias sputtering. Positive substrate bias (electron bombardment) favors hydrogen in the 2000 cm^{-1} mode. Negative substrate bias (Ar^+ ion bombardment) favors the hydrogen in the 2100 cm^{-1} mode. However, the density of states in the middle of the gap and the recombination properties do not depend on the mode of the hydrogen bonding, but rather on the total amount of hydrogen in the film. Experimental evidence is produced that the SiH_x compound formation moves progressively from the substrate to the target as the hydrogen pressure in the discharge increases. Evidence of the importance of chemical etching of the growing film by H-plasma is produced.

1. Introduction

The anticipated potential use of hydrogenated amorphous silicon (a-SiH_x), or other related materials, for large area thin film device applications, has stimulated extensive research of these materials at a number of laboratories. Of the two plasma methods (glow discharge decomposition of silane, and sputtering from a silicon target in an $Ar + H_2$ plasma), the former has attracted considerably more attention since it was perceived as a more suitable technology for surface sensitive devices, and was assumed to lead to films with better optoelectronic properties. As a result this material has been extensively investigated through structural, optical, transport and recombination studies, which led to solar cell structures with efficiencies up to 8% [1]. Recent reviews in the physics and device areas have been published by Fritzsche [2] and Carlson [3].

It is widely believed that this rapid progress in the device area is the result of the understanding of the thin film growth conditions, which lead to material with much less structural and compositional inhomogeneity. Towards this end one needs to conceptualize and develop diagnostic tools to study the complex reactions in the plasma and in the surface of the growing film, and also develop an understanding of

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the thin film growth habit by studying the film's structure. Progress towards the first goal, which unravels the mechanism of hydrogen elimination, is slowly emerging [4], and towards the second goal the structural studies of Knights and Lujan [5] have led to the discovery that plasma deposition of a-SiH$_x$ films proceeds via nucleation and growth of island structures (average lateral dimensions $\approx$100 Å). The coalescence of these islands, if imperfect, leads to columnar morphology in subsequent growth. These authors report that growth of the films in pure silane, at low deposition rates, at large substrate negative biases, and deposition temperatures between 200 to 300 °C leads to much more perfect coalescence of the islands. The structural inhomogeneities, revealed by these studies, have been invoked to also interpret compositional inhomogeneities observed in NMR, neutron scattering and infrared vibrational studies [6–8]. Films showing columnar morphology are unstable upon exposure to atmosphere. The interstitial regions between the columns can be penetrated by active atmospheric impurities leading to post-deposition contamination effects. The electronic properties of such films are poor since the low density interstitial regions are correlated with electronically active defects [8].

The development of the reactive sputtering technology in depositing such films is proceeding along the same lines, namely through structural and optoelectronic studies of films deposited under a variety of deposition conditions. The properties of such films have recently been reviewed by Paul and Anderson [9] and earlier by the present author [10]. The device potential of this material has also come to age since films with very low density of states in the middle of the gap ($<10^{15}$ cm^{-3} eV^{-1}) and large collection widths [11, 12], as well as multilayer PIN devices with efficiencies up to 4% have been reported [13]. Although there is evidence that part of this lower value of the solar cell efficiency is related to practical problems, such as cross-contamination between the layers of the device [14], further optimization of the optoelectronic properties requires a better understanding of the critical parameters, which control the film growth.

The growth habit of the sputtered a-SiH$_x$ films is also columnar, as has been revealed by the extensive structural studies of Ross and Messier [15]. These authors find that films produced at high argon pressure have columnar microstructure, while those produced at low argon pressure show no noticeable microstructure. Their preferred interpretation for the lack of microstructure for the low argon pressure films is bombardment of the films by *positive Ar^+ ions* due to the substrate negative floating potential. However, these authors admit that the beneficial effects of this ion bombardment are partly offset by the simultaneous creation of atomic-scale electronically active defects. The Harvard group [16] attributes the microstructural changes with the pressure of argon to the bombardment of the film by the *neutral sputtered Si species* from which the film grows. They suggest that weak bombardment of the growing film might be beneficial in removing loosely bound material from the surface. At high argon pressures, this desirable bombardment is removed due to the thermalization of the Si species. Besides, the controversy

between these two models, the data indicate that even films which do not show microstructural imhomogeneity do show compositional inhomogeneity as revealed by Si–H vibrational studies. For example, the Si–H stretching vibration was found to be a doublet for films produced under a variety of deposition conditions [17, 18].

In this paper we present data which clearly indicate that charged particle bombardment rather than neutral particle bombardment is the cause of the observed microstructural changes as a function of argon pressure. In addition, we show how bias sputtering can be used to control compositional inhomogeneity through selective charged bombardment. Films produced with positively biased substrates (electron bombardment) have the Si–H stretching mode centered at 2000 cm^{-1}, while negative substrate bias (positive ion bombardment) favors the 2100 cm^{-1} mode. We also discuss experimental evidence that at low partial pressure of hydrogen, the SiH$_x$ compound is synthesized at the surface of the substrate, while at high partial pressure there is evidence of compound formation at the surface of the target. The importance of H-plasma etching effects of the growing film and target is also briefly addressed.

2. Deposition system and experimental methods

The deposition system used in this study has stainless steel walls, held at ground potential, and electrically insulated cathode and anode assemblies. The water cooled target is a polycrystalline silicon disk, 5″ (13 cm) in diameter and $\frac{1}{4}$″ (0.64 cm) thick, and is supplied with an rf power at a frequency 13.56 MHz. The anode assembly was held 5 cm below the target and can be grounded, floated or supplied with rf or dc electrical bias. The substrates (quartz glass and high purity silicon single crystal wafer) were fastened with a stainless steel frame and molybdenum springs on the top of the anode assembly. An 0.005 cm thick Al foil is inserted between the anode and substrates to improve the thermal contact. The system was pumped by a combination of turbomolecular and mechanical pumps to a base pressure of about $1–2\times10^{-7}$ Torr and routinely checked for atmospheric leaks with a mass spectrometer. The systems total leak rate was approximately $1–2\times10^{-5}$ Torr l s^{-1}.

The parameter space investigated involved variation of the substrate temperature, the argon pressure, the hydrogen pressure, the substrate bias (self-induced or externally applied) and the power in the discharge.

Microstructural changes in the films were investigated through measurements of the index of refraction, post deposition oxidation effects and SEM microscopy. All of these properties are very sensitive to microstructural changes, and in particular the index of refraction and post deposition contamination effects can be measured accurately on thin films ($\approx1\,\mu$m). The index of refraction was determined by studying the optical densities of the films deposited on the quartz substrates in a Carry 17 spectrophotometer, using a 2 mm aperture to eliminate the possibility of

thickness gradients. The magnitude, ΔOD, of the interference fringes, which are displayed at wavelengths longer than the absorption edge, was used to calculate the refractive index at given wavelength. The post-oxidation effects were investigated by studying the optical densities of the films, deposited on the silicon substrates, using a Digilab FT Spectrophotometer set at a resolution of 4 cm^{-1}. Both type of measurements were made immediately after the films were removed from the deposition system and aging effects were followed up by repeating the measurements as a function of time.

The hydrogen contents of the films were measured by the nuclear reaction $^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma$ [19, 20]. These measurements were also correlated with the integrated intensities under the Si–H vibrational modes [20]. These modes were also used in identifying different bonding configurations of hydrogen.

The films were also characterized by measuring their optoelectronic properties such as, optical absorption constant, conductivity, photoconductivity, photoluminescence and density of states. Such data will be mentioned in this paper only to support observed trends in the film's growth.

3. Relation between microstructural changes and film bombardment by charged and neutral particles

In order to investigate the relation between the film's microstructure and bombardment by different particles in the discharge we deposited a number of films at fixed hydrogen partial pressure ($P_H = 0.7$ mTorr) and argon pressure varying between 5 to 40 mTorr. The substrates were electrically floated and held at a temperature of 275 °C. The target was supplied with a constant power of 200 W, which resulted in a deposition rate increasing monotonically with the pressure of argon from 2.2 to 2.7 Å/s. The hydrogen content of the films was found to be between 22 to 20 at%. The optical gaps of the films, measured immediately after removing the substrates from the deposition system, were found to decrease with the argon of pressure from 1.85 to 1.77 eV. The optical constants of the film produced at 40 mTorr were found to change with the length of time of air exposure.

Fig. 1 shows the dependence of index of refraction, n, measured immediately after the film deposition at wavelength $\lambda \approx 2.0\,\mu$m, on the argon pressure in the discharge. The value of n remains constant up to about 20 mTorr of argon and then it drops rather abruptly. The reduction of the index of refraction at high argon pressures is accompanied by post-deposition contamination. Fig. 2 shows the infrared vibrational spectral for samples deposited at 5, 10, 20 and 40 mTorr of argon. The films deposited at 5 and 10 mTorr of argon show the usual Si–H vibrations [17], while the samples deposited at 20 and 40 mTorr of argon additionally show Si–O ($\approx$1100 cm^{-1}), Si–N (880 cm^{-1}) and C–H ($\approx$3000 cm^{-1}) vibrations. In agreement with Freeman and Paul [18], we find that these additional vibrations are due to post-

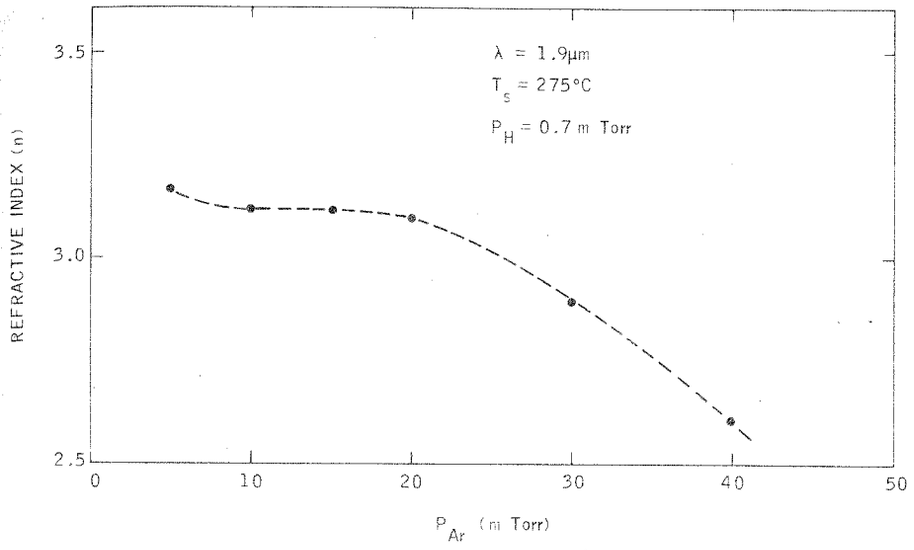

Fig. 1. The index of refraction, measured at $\lambda \approx 2.0\,\mu$m, vs. the argon pressure in the discharge.

deposition contamination and they grow as a function of time.

The reduction of the index of refraction for the films produced at high argon pressure can be accounted for as the result of the film's porosity (since n depends on

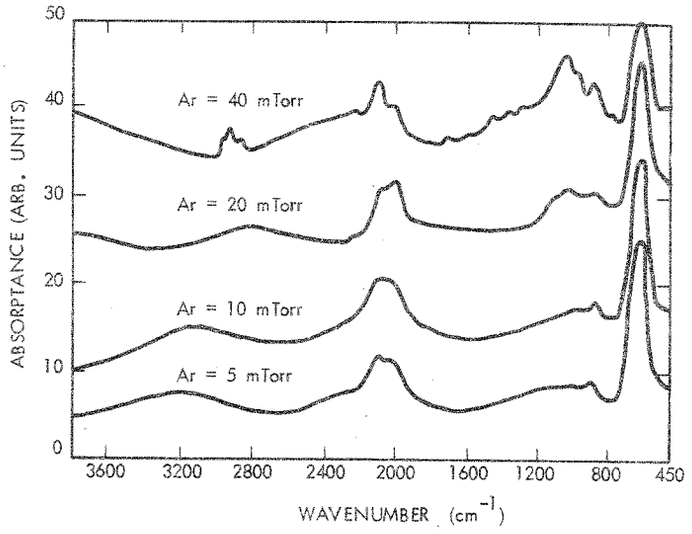

Fig. 2. Infrared vibrational spectra of sample deposited at argon pressure of 5, 10, 20 and 40 mTorr.

the density of the valence electrons), and the formation of low index of refraction coatings (SiO_x, SiN_x) in the internal surfaces of the voids. Therefore, the results of figs. 1 and 2 are consistent with the observations of Ross and Messier [15] that films grown at high argon pressure have a columnar morphology, and that under the described preparation conditions the coalescence of the island structure is imperfect for films grown at argon pressure higher than 20 mTorr.

In agreement with Knights [8] and Anderson et al. [10] we find that the films produced at high argon pressures have poor photoelectronic properties. As an illustration, fig. 3 shows the photoconductivity under AM1 illumination vs. the argon pressure in the discharge. The photoconductivity of the film produced at 40 mTorr

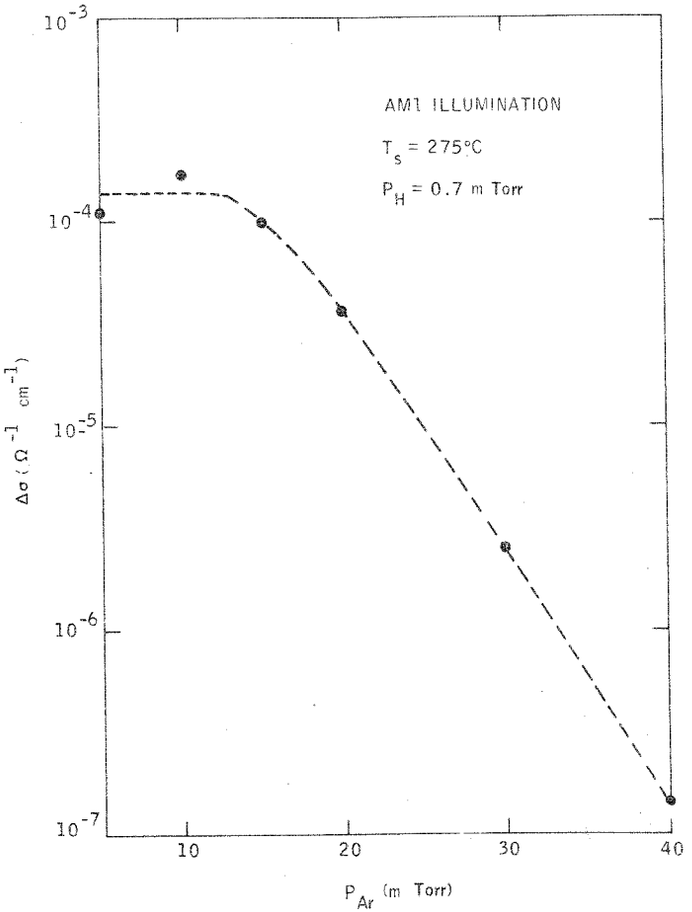

Fig. 3. The photoconductivity, measured under AM1 illumination, vs. the argon pressure in the discharge.

of argon is lower by three orders of magnitude from that of the films produced at low argon pressures.

In order to investigate whether these structural changes are the result of bombardment or lack of bombardment of the film by neutral or charged particles we determined the dependence of the self-bias potential of the substrates on the partial pressure of argon. The substrate self-bias voltage was measured with respect to the ground in a separate experiment, which simulated the conditions of the sample deposition. Fig. 4 shows the substrate self-bias potential, with respect to the ground, vs. the partial pressure argon in the discharge. The substrates are negatively biased at low argon pressures, because they are bombarded by more electrons than ions due to the higher electron mobility. At high argon pressures, on the other hand, the substrates have the same potential as the plasma (positive), and charged particles do not bombard but migrate to the substrates by thermal diffusion [21]. Ross and Messier [15] have measured, in addition, the plasma potential with a Lagmuir probe and they were able to calculate the floating potential of the substrates with respect to the plasma. Their data have the same functional behavior observed in fig. 4. We conclude from the data of figs. 1–4 that the change in the sign of self-bias potential with respect to the ground, occurs at exactly the same argon pressure where significant changes in the film's microstructure have been observed. Therefore, these data sug-

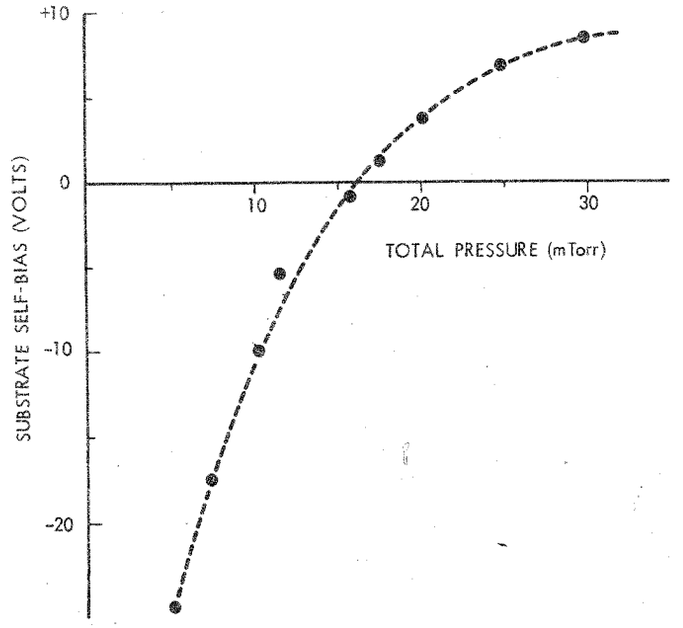

Fig. 4. The substrate self-bias voltage, measured with respect to the ground vs. the total pressure in the discharge.

gest that the coalescence of the island structure is the result of atomic rearrangement due to the bombardment of the growing film by charged particles. However, these data cannot differentiate the relative roles of electron or Ar^+ bombardment in the growth of the film. Ross and Messier [15] attribute the structural changes to the Ar^+ ion bombardment. However, in the next section we will show that electron bombardment may be as important in inducing structural changes. The correlations observed in figs. 1-4 cannot be explained on the basis of film bombardment by neutral species, as suggested by the Harvard group [16], since such species are unaffected by substrate bias.

4. Control of Si–H bonding through substrate biasing

In this section we address two issues concerning the Si–H bonding configuration in reactively sputtered a-SiH$_x$ films. The first issue deals with the ability to control the bonding of hydrogen in these materials, through external deposition parameters, and the second deals with the correlation between the hydrogen bonding and electronic properties of the films.

The Si–H vibrational spectra in reactively sputtered a-SiH$_x$ films were first reported by Brodsky et al. [17] and by Freeman and Paul [18]. Both of these extensive studies indicate that the Si–H stretching vibration is always a doublet for films produced under a variety of deposition conditions. This should be contrasted with the ease of controlling the H-bonding in a-SiH$_x$ films produced by the method of glow discharge decomposition of silane [17]. Although there are multiple opinions [22] as to the type of Si–H local environments which give rise to this doublet, it is evident that its existence indicates that these films are compositionally inhomogeneous. This appears to be the case even for films produced at low argon pressures, which do not show structural inhomogeneity. The inability to control the bonding of hydrogen in the sputtered material has led to the widespread belief that the sputtered films are inferior to those produced by decomposition of silane.

Jeffrey and co-workers [23] have demonstrated that sputtered a-SiH$_x$ films having only the 2000 cm^{-1} Si–H stretching mode can be made, if the substrates are inserted inside the plasma below the edge of the dark space. Based on photoconductivity studies, these authors report that films having only the 2000 cm^{-1} Si–H stretching mode have superior electronic properties than films with the Si–H stretching mode at 2100 cm^{-1}. The Harvard group [24], by adopting Jeffrey's method of film deposition, recently produced films having the Si–H stretching vibration at 2000 cm^{-1}. However, this group concluded that sputtered films having the stretching mode at 2000 cm^{-1} have inferior electonic properties than films having the stretching mode at 2100 cm^{-1}.

At our laboratory we have developed [25] bias sputtering as a means of controlling the bonding of hydrogen. We find that the maximum effect of external bias on

the films' microstructure occurs under deposition conditions which lead to substrate self-bias close to zero. We also find that positive bias favors the 2000 cm^{-1} Si–H stretching mode, while negative bias favors the 2100 cm^{-1} Si–H stretching mode. Fig. 5 shows the Si–H stretching vibrations of a number of films produced at substrate bias +50 V and at other deposition conditions as indicated in figure caption. Indicated next to the sample number is the hydrogen content in the films. Note that most of the hydrogen, up to 14 at%, is bonded in the 2000 cm^{-1} mode. The 2100 cm^{-1} mode acquires the same strength as the 2000 cm^{-1} mode for films having more than 20 at% H. For contrast we show in fig. 6 the Si–H stretching vibrations for a number of films produced under negative biasing conditions. The negative bias in these films is self-induced (−25 V), by sputtering the films at low argon pressure, $P_{Ar} = 5$ mTorr, and having all other deposition parameters the same. Note that although the hydrogen content of these films covers the same range as those of fig. 5, the 2100 cm^{-1} mode is present even at the lowest hydrogen content films and becomes progressively stronger as the hydrogen content increases.

These structural variations associated with the substrate biasing can now be accounted for in the following way. Biasing the substrates to a positive voltage has two effects. One is electronic bombardment of the growing film, and the second is minimization of Ar^+ ion bombardment. Although electronic bombardment is thought to be undesirable in the growth of semiconductor material, our findings

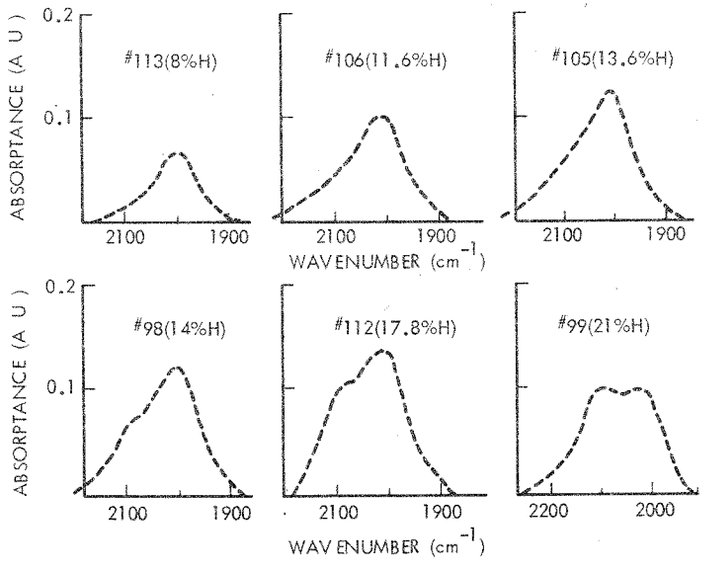

Fig. 5. The Si–H stretching vibrations for a number of films produced at positive substrate bias. Indicated next to the sample number is the hydrogen content in the films. (These films were produced at $T_s = 275$ °C, power = 200 W and $P_{Ar} = 15$ mT.)

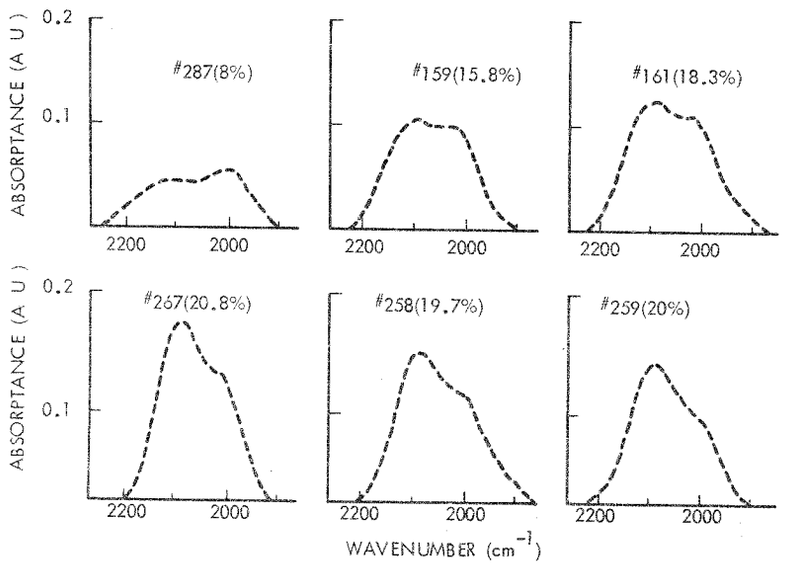

Fig. 6. The Si–H stretching vibrations for a number of films produced under negative bias conditions. Indicated next to the sample number is the hydrogen content in the films.

indicate that some electronic bombardment can have a favorable effect on the growth of structurally and compositionally homogeneous sputtered a-SiH$_x$ films. Under typical sputtering conditions, there are low energy and high energy electrons arriving at the substrate. The high-energy electrons have a sharp cut-off which corresponds to the cathode potential, and are the secondary electrons ejected from the target. Bombardment by these electrons can have profound effects on the film's chemistry and structure because it enhances adatom surface mobility through surface heating. We believe that this electron bombardment is responsible for the perfect coalescence of the island structure which leads to films having both structural and compositional homogeneity. The second effect of the positive bias, namely the minimization of the Ar^+ ion bombardment, is also highly desirable. These films contain much less argon since the Ar^+ ions require a certain threshold ($\approx$15 to 20 eV) in order to be implanted into the film [26]. Resputtering is also minimized under these conditions of film growth. Since resputtering by Ar^+ ions is likely to be anisotropic, i.e., with higher sputtering yield at the low density intercolumnar regions, there is a high possibility of microvoid formation during the film re-growth in these regions. Both argon incorporation and void formation lead to films with structural and compositional inhomogeneity. In fact there is some evidence [27, 28] that argon inhabits voids. We believe that such structural inhomogeneities result in the formation of a stretching vibration doublet.

Regarding the second issue, namely the correlation between hydrogen bonding

and electronic properties of the films, our data do not substantiate either the claims of Jeffrey et al. [23] or those of the Harvard group [24]. More specifically, we find that the states in the middle of the gap [11] and properties which are related to these states (recombination), do not depend on the hydrogen bonding, but rather on the total amount of bonded hydrogen. To illustrate this point we show in figs. 7 and 8 the photoconductivity and the density of states in the middle of the gap of the same films, whose Si–H stretching vibrations have been discussed in figs. 5 and 6 correspondingly.

The data of fig. 7 indicate that the photoconductivity increases by four orders of magnitudes as the hydrogen content increases from 8 to 14 at%. Sample #98 has as high photoconductivity as the best reported for glow discharge films [29]. This is contrary to the claim [24] that sputtered films with the 2000 cm^{-1} mode have inferior electronic properties. The second point to be made is that sample #99, in which the 2000 and 2100 cm^{-1} modes have the same strength, has exactly the same photoconductivity as sample #98. This contradicts the alternative claim [23] that films with the 2000 cm^{-1} mode have superior photoconductivity than those with the 2100 cm^{-1} mode.

The data of fig. 8, which were published earlier [11], demonstrate the same point through a direct measurement of the density of states in the middle of the gap by *C–V* and ESR techniques. The film with the lowest density of states (7×10^{14} cm^{-3} eV^{-1}) has a significant fraction of its hydrogen bonded in the 2100 cm^{-1} mode.

From these studies we conclude that in good electronic quality sputtered material (no visible microstructure), most of the defects, which contribute states in the middle of the gap, are coordination type defects and can be eliminated through hydrogen incorporation into the films. However, films with more structural inhomogeneity require more hydrogen in order to accomplish the same result. This point as well as other differences between films with the 2000 and 2100 cm^{-1} modes will be discussed in another paper [30].

5. The role of reactive sputtering effects in the synthesis of SiH$_x$ compounds

In this section we discuss experimental results related to the synthesis of the SiH$_x$ compound. Of the three possible places (target, gas phase, substrate) where the Si and H can react, the gas phase reaction can be ruled out. This is because the heat liberated in the chemical reaction cannot be dissipated in a two body collision. Simultaneous conservation of energy and momentum requires the reaction to occur at a surface [21]. The common experience in reactive sputtering is that, at very low reactive gas partial pressure and high target sputtering rate, virtually all of the compound synthesis occurs at the substrate. As the reactive gas partial pressure is increased or the sputtering rate is decreased, a threshold is reached at which the rate of target compound formation exceeds the removal rate of compound, and thus most

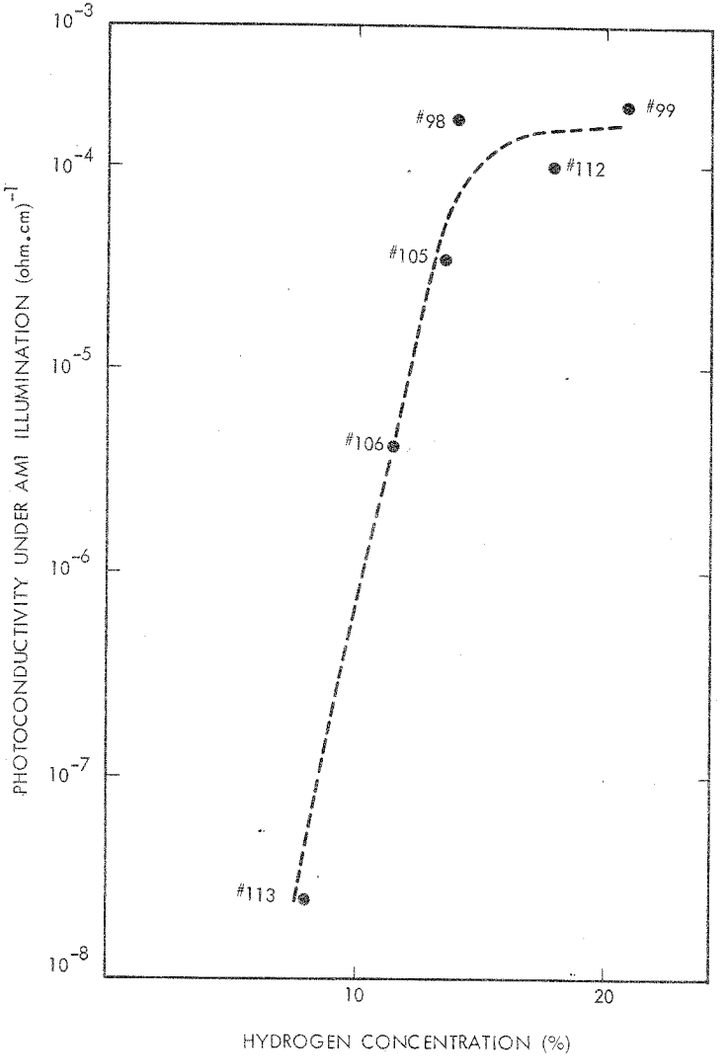

Fig. 7. The photoconductivity under AM1 illumination vs. hydrogen content for films produced under positive substrate bias. The infrared vibrational spectra of these films are shown in fig. 5.

of the compound synthesis occurs at the target [21].

In earlier papers [11, 20] we have published experimental results suggesting that, for films produced up to 20 to 30% hydrogen in the discharge, with deposition rates in the range of 1 to 4 Å/s, most of the compound formation occurs at the substrate. In this paper we give only a brief summary of these results. In order to investigate

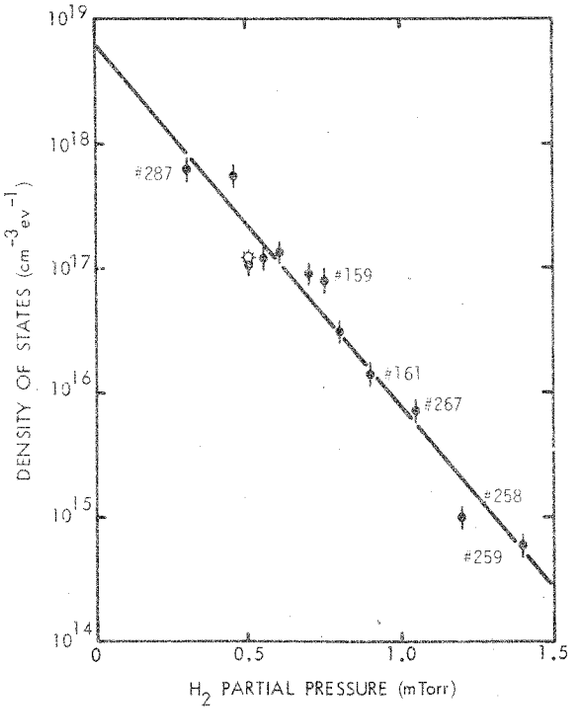

Fig. 8. Density of states in the middle of the gap as a function of hydrogen partial pressure in the discharge. The point indicated by the symbol (☼) is the ESR spin density (1.1×10^{17} cm^{-3}). The infrared vibrational spectra of some of these films are shown in fig. 6.

the Si and H reactions, we studied the density of states in the middle of the gap, which is related to Si dangling bonds, and the hydrogen content of the films. We find that both the density of states and the hydrogen content depend exponentially on the ratio of the flux of hydrogen atoms impinging on the substrate, and the deposition rate. These results are summarized in figs. 8 and 9. These data clearly indicate that the composition of the film depends on the relative rates of arrival at the substrate of Si and H atoms. In the substrate temperature range of 200 to 400 °C, where the electronic quality material is produced, we find that the Si and H reactions are kinetically controlled and that there is no evidence of thermodynamic equilibrium between the hydrogen in the film and the hydrogen in the plasma. From the kinetic model, for the Si and H reactions, we have deduced that there are two sites for hydrogen attachment and the hydrogen bonds to these sites with different efficiency. One site has been identified as a potential Si dangling bond and the second site has been speculated to be a potential reconstructed dangling bond in internal surfaces. The sticking coefficient of hydrogen to the second site is likely to

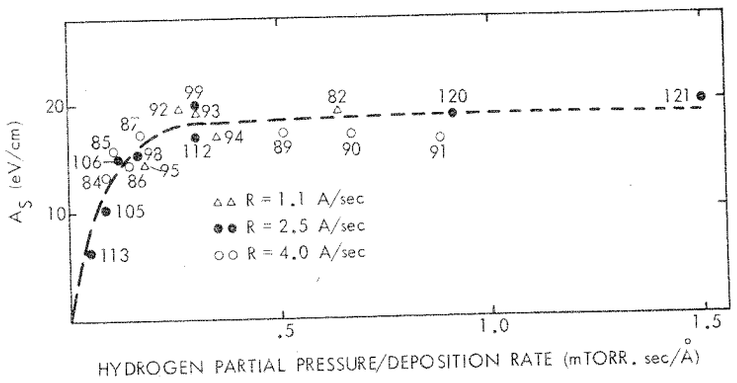

Fig. 9. Integrated infrared absorption under the Si-H stretching vibration vs. the P_H/R (deposition rate) for a number of films, deposited at $P_H \ll P_{Ar}$.

be smaller than for a true dangling bond, because the hydrogen incorporation involves bond breaking. The data also indicate that from the different species of hydrogen in the discharge (molecule, atom, ion) the atomic hydrogen incorporates far more efficiently than the most abundant molecular hydrogen.

We next discuss experimental data indicating that the SiH_x compound formation occurs at the target as the partial pressure of hydrogen increases. Fig. 10 shows the substrate self-bias potential vs. the total gas pressure in the discharge, as the ratio of H_2/Ar in the discharge increases from zero to ten. Note that the substrates are self-biased to more negative voltages as the hydrogen pressure in the discharge increases. In addition, the deposition rate decreases by about an order of magnitude with the hydrogen pressure in the discharge, even at a constant target voltage.

These results can now be accounted for as follows. The increase of the negative value of the self-bias voltage implies that the substrates are bombarded by more electrons as the hydrogen content in the discharge increases. This indeed is expected to be the case if the SiH_x compound formation occurs at the surface of the target. Compounds have higher secondary-electron emission yields than metal. The same effect can partly account also for the drop in the deposition rate since most of the energy of the incoming ions is used to produce and accelerate secondary electrons. The drop in the deposition rate could also partly be accounted for by the fact that compounds have generally lower sputtering yields than metals and by the fact that hydrogen as a lighter ion will carry a large fraction of the discharge current although contributing very little to the sputtering rate [21]. Therefore, this model of data interpretation suggests that the SiH_x compound formation moves gradually from the substrate to the target as the hydrogen pressure in the discharge increases or the deposition rate decreases. It should be emphasized, however, that the SiH_x compound in the target may or may not sputter stoichiometrically, because ion bombardment can result in chemical dissociation. The film growth under such conditions

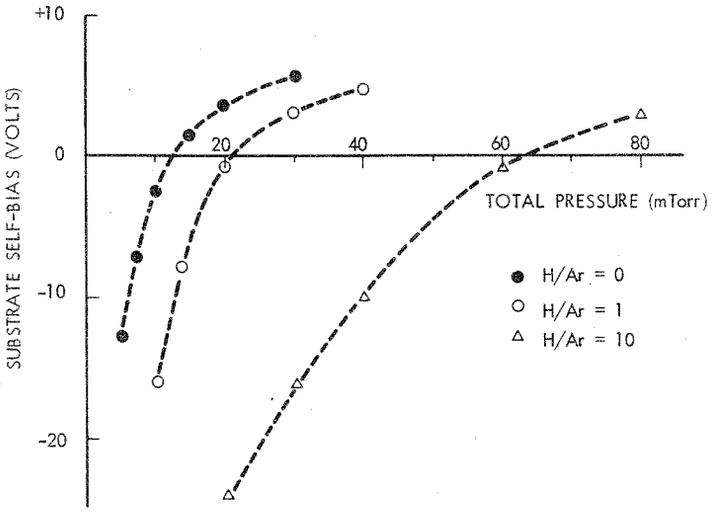

Fig. 10. The substrate self-bias voltage, measured with respect to the ground, vs. the total gas pressure in the discharge. The three curves correspond to H/Ar ratios of 0, 1 and 10.

would be greatly influenced by the fluxes of the products of the chemical dissociation arriving at the substrate.

This model of SiH_x compound formation could perhaps account for the controversial results of the two existing spectroscopic studies of the sputtering plasmas [31, 32]. In one study the results suggest that SiH_x molecules exist in the sputtering plasma, while in the other study SiH_x species have not been detected.

6. The role of chemical sputtering effects in the synthesis of SiH_x compounds

Up to this point we have discussed the effects of physical sputtering processes on the growth of a-SiH_x films. There is a high possibility, however, that in addition to these processes the film growth is influenced by chemical sputtering effects of the target or the growing film. As an example, the H-plasma may react with the surface of the target or the growing film and forms volatile SiH_x compounds, which may either be pumped out or may undergo plasma decomposition. Since such etching process of the growing film may be anisotropic, its influence on film structure may be significant.

Since direct observation of such processes are difficult, we have investigated this effect indirectly. We have first grown an a-SiH_x film and then exposed it to a hydrogen plasma. The surface morphology of this film, as revealed by SEM microscopy, is shown in fig. 11. Details of these etching studies will be published elsewhere [33]. At this point we want to emphasize that such processes participate during the film

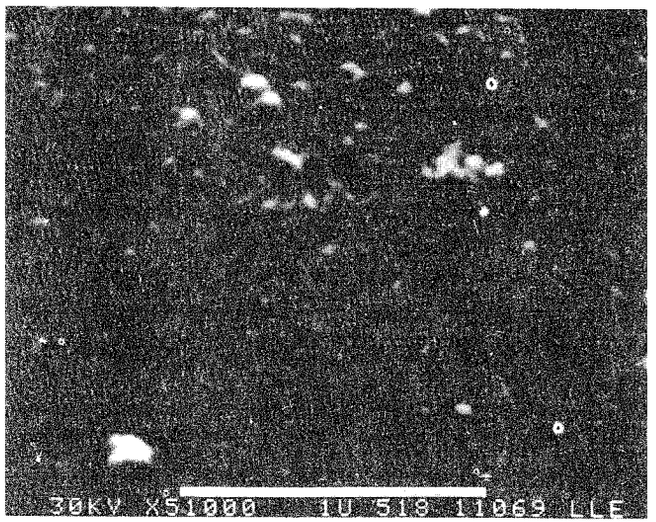

Fig. 11. SEM micrograph of the surface morphology of an a-SiH$_x$ film exposed to a hydrogen plasma [33].

growth. Of course they become far more important as the hydrogen pressure in the discharge increases.

7. Conclusions

In conclusion we have presented experimental results showing the role of different physical sputtering and chemical sputtering effects on the growth of hydrogenated a-SiH$_x$ films. These results can be summarized as follows:

In agreement with Ross and Messier [15], we demonstrated that the coalescence of the island structure is influenced primarily by charged rather than neutral particle bombardment. However, in disagreement with these authors, we proposed that the beneficial effects arise from the electron bombardment, while Ar^+ ion bombardment leads to undesirable effects, such as Ar incorporation and void formation.

We demonstrated that control of the hydrogen bonding, and thus the formation of compositionally homogeneous films can be accomplished through bias sputtering. Positive substrate bias (electron bombardment) favors hydrogen in the 2000 cm^{-1} mode while negative substrate bias (Ar^+ ion bombardment) favors the hydrogen in the 2100 cm^{-1} mode. This mode is correlated with Ar incorporation and microvoid formation in the film.

We have shown that the density of states in the middle of the gap, and related phenomena, such as recombination, do not depend on the bonding of hydrogen in the 2000 or 2100 cm^{-1} modes but they depend on the total amount of hydrogen in the film.

We produced evidence that the SiH$_x$ compound formation occurs in the substrate at low hydrogen partial pressures, while at high hydrogen pressure, compound formation at the target becomes important.

Finally, the effects of etching of the growing film by the H-plasma have been pointed out through indirect etching studies of already formed SiH$_x$ films.

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DEPENDENCE OF HYDROGEN EVOLUTION FROM a-Si : H ON BORON DOPING AND SUBSTRATE POTENTIAL

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The dependence of the hydrogen effusion rate h on temperature T reflects the two-phase compositional inhomogeneities observed by proton NMR spectroscopy in plasma-deposited hydrogenated amorphous Si. We studied $h(T)$ of 1 μm thick a-Si : H films prepared in an rf diode plasma reactor at 260°C from a $SiH_4/Ar = 0.1$ mixture doped with $10^{-7} < B_2H_6/SiH_4 < 10^{-4}$. We find that $h(T)$ depends on the self-bias potential V_s of the substrate with respect to the plasma. For $V_s < 130$ V, $h(T)$ peaks at two temperatures. The lower peak temperature decreases from 570 to 350°C and the higher one from 620 to 450°C with increasing boron concentration. Near $B_2H_6/SiH_4 = 5 \times 10^{-5}$ one finds changes in film morphology because of boron-induced weakening of hydrogen-bonding configurations. We associate the low and the high temperature hydrogen evolution peaks with the hydrogen concentrated and hydrogen dilute phases of the material. We conclude that boron doping and ion bombardment during growth strongly affect the film structure and the hydrogen bonding and hence fundamental properties of the amorphous film. Since V_s is more negative for cathode films than for anode films, their properties are different.

1. Introduction

Hydrogenated amorphous silicon, either with or without additional fluorine (a-Si : F : H or a-Si : H) has become the prototype amorphous semiconductor because it is the only one which can be doped efficiently [1] and which shows electronic characteristics useful for device applications [2]. Since the discovery by effusion measurements [3] that plasma-deposited a-Si : H films contain substantial amounts of hydrogen, it has been clear that hydrogen plays a vital role in reducing the density of gap states by compensating potential dangling bonds. However, since the typical hydrogen content of 5–15 at% is about 100 times larger than needed to satisfy the dangling bond concentration ($\approx 10^{20}$ cm^{-3}) of hydrogen-free a-Si [4], the hydrogen modifies the whole structure of a-Si : H. Infrared absorption studies revealed that the hydrogen may be bonded as monohydride, dihydride, and in various polyhydride modifications depending on the preparation conditions [5, 6].

Proton resonance experiments have shown recently that a-Si : H contains structural and compositional inhomogeneities [7–9]. It consists of two phases. In one, about 3.5 at% H is essentially randomly distributed and bound as monohydride. In

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