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Properties of ion beam assisted, reactively evaporated a–Si:H

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Abstract. Films of a–Si:H have been prepared in a vacuum deposition system both with and without the help of low energy ion beam bombardment. Water vapour was introduced into the system in order to determine how it is incorporated into the Si film and to observe the effects of the ion beam on this process. Silane was used as the feed gas for the ion source and the ion beam enabled the oxygen to form only the bridging configuration between Si atoms. Without the ion beam, three oxygen related absorption peaks are obtained in the infra-red spectrum. Water-free films of a–Si:H were prepared to investigate the effects of ion beam voltage, ion beam intensity and substrate temperature on the resulting film photoconductivity. These parameters are interrelated and a maximum in the photosensitivity is found for rather narrow ranges of these parameters.

1. Introduction

When oxygen is incorporated into a–Si:H prepared in different ways, it alters many of the material's properties [1–5]. Oxygen enters the amorphous matrix predominantly in the Si–O–Si bridging configuration and probably serves as a network softener [1]. It has been reported that the presence of oxygen enhances the photoconductivity and photoluminescence [1–3], but it is detrimental to the photovoltaic performance of the material [2]. The effects of oxygen on the infra-red (IR) absorption spectra and hence the oxygen-bonding environments in a–Si:H, have been reported [3, 4, 12] and its effect on the electrical conductivity of reactively evaporated films was noted by Audas *et al* [5].

It is well known that energetic ion bombardment during the growth of a film can have a large effect on the properties of the layers. Among the many effects that are possible (see, for example Rossnagel and Cuomo [6]), the ion beam can influence the bonding configuration for H in a–Si:H [7] and the resulting properties of the layer.

In this study, a series of samples were prepared in which oxygen was added to a–Si:H by introducing water vapour into the vacuum chamber and bombarding the growing film with low energy ions in order to compare the results with those for films prepared in the same way but without the ion beam. In particular, we were interested in whether new oxygen related peaks might be seen in the IR transmission spectra.

The effects of substrate temperature [8] and some of the low-energy ion beam parameters [7, 9] on the properties of a–Si:H films have been reported. The most influential parameters include: the ion beam intensity, the ion beam energy, the discharge conditions for the plasma in the ion source, the substrate temperature, and the

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rate at which add atoms arrive from the evaporation source. The mass and the chemical nature of the ions used, can also play a major role if these are varied. In general, the interplay among these parameters is complex but they can be controlled separately in a vacuum deposition system equipped with a low-energy ion source. Here we report on the results of systematic studies designed to reveal some of this interplay by observing some of the properties of the resulting a–Si : H films. For which appears to be a critical range of substrate temperatures, ion beam energies and ion beam currents, we have studied the electrical conductivity and the ratio of the photoconductivity to the dark conductivity. We assume this latter quantity represents a quality measure for the film.

2. Experiment

Samples used in this study were fabricated in a vacuum deposition system (base pressures in the 10^{-7} Pa range) equipped with a high-intensity, low-energy ion source (MPS-3000FC Ion Tech) and films were deposited both with and without the help of the ion source. Silicon was evaporated from a vitreous carbon crucible and silane was used as the feed gas for the ion source. Films were deposited on Corning 7059 glass substrates and simultaneously on polished silicon wafers mounted on one corner of the glass substrate. Water vapour present in the system was maintained in the low 10^{-7} Pa range, when 'water-free' samples were prepared. In order to obtain oxygen contaminated films, water vapour was introduced into the system via a separate controlled leak to give water vapour partial pressures from 6.5×10^{-7} to 4×10^{-3} Pa. The flow rate of silane through the ion source (when used) was 4 cm^3 min^{-1} and this yielded a total system operating pressure near 2.7×10^{-1} Pa.

The ion source discharge voltage was set at 120 V, the accelerating voltage was set at 420 V and either the ion beam voltage or the ion beam current was varied.

The concentrations of hydrogen (C_H) and oxygen (C_0) were estimated from IR transmission spectra obtained from films deposited on the crystalline silicon wafers. The calculation of the concentration of bound hydrogen follows that used in Zhang *et al* [8]. C_0 was estimated using the absorption band near 1040 cm^{-1} and the formula [2, 4, 10]

$$C_0\,(\text{at.\%}) = A \int \alpha \, \mathrm{d}(h\nu) \tag{1}$$

Here, A is a constant, $h\nu$ is the photon energy in eV, α is the absorption coefficient calculated from the transmission T using the equation

$$T = (1 - R)^2 \exp(-\alpha t)/[1 - R^2 \exp(-2\alpha t)] \tag{2}$$

where t is the film thickness, and R is the reflectance. The earlier workers have used three different values for A, i.e. 0.25 [2], 0.156 [4], and 0.064 [10]. Here we have used $A = 0.156$ to obtain a rough estimate for the concentrations of oxygen in our samples and we expect the relative concentrations among samples to be correct. The calculated values for both C_H and C_0 have not been checked using another technique.

All photoconductivity measurements were made using a solar simulator and set to give air mass 1 (AM 1) illumination on the sample in each case.

3. Results and discussion

3.1. The influence of oxygen

Here, we will discuss the effects of adding oxygen to a–Si:H and later we will investigate whether an ion beam can alter the way that oxygen is incorporated into the growing film and hence the film properties.

Control, or reference, films (i.e. no ion beam assist) were reactively deposited, either in the presence of silane with a silane partial pressure of 5×10^{-2} Pa to give a–Si:H, or films were prepared using only water vapour at a partial pressure of 2.7×10^{-4} Pa, to give a–Si:H:O. (This series of samples enabled us to observe some of the effects of adding oxygen to a–Si:H and also served as reference films to determine the effect of using low energy ion beam assisted deposition.) The substrate temperature was 120 °C and the deposition rate 8.5 nm min^{-1}. These conditions yielded the same hydrogen concentrations in both sets of samples and the IR absorption measurements show that this was 24 ± 2 at.%. Note the water vapour partial pressure needed to achieve this result is more than two orders of magnitude lower than that for silane. In addition to the fact that water has the larger sticking coefficient [11], this implies that the dissociation of the water is rather efficient when being incorporated into the silicon film. Figure 1 compares the Arrhenius plots for these two kinds of film. In each case the data are obtained *in situ* after annealing at 200 °C for 2 hr, following sample fabrication. The upper curve is representative of films made in a silane ambient, while the lower curve is representative of those made in a water-vapour ambient. From room temperature to 200 °C, (the range observed) the oxygenated sample has one order of magnitude lower conductivity and a slightly larger activation energy (0.9 compared with 0.8 ± 0.05 eV). Because the hydrogen concentrations are the same, the differences are attributed to the presence of oxygen.

The optical gaps (E_0) for the oxygenated samples (deduced from a Tauc plot) are typically 0.05 eV larger, and the ratio of photoconductivity to dark conductivity (σ_{ph}/σ_{RT}) an order of magnitude larger, than those for the samples made with silane. Again these differences can be attributed to the present of the oxygen.

Figure 2 shows IR spectra for a sample made with water vapour introduced into the system. The top trace was obtained about 20 min after the sample was taken from the deposition system. This shows that a large number of oxygen atoms have been incorporated into the film during the deposition (see the absorption peak near 1040cm^{-1}). The bottom traces in figure 2 were measured 3 days and 8 days after the sample was removed from the vacuum system. Note that the absorption peaks at 2240 and 1040 cm^{-1} increase with time when the sample is exposed to air. This indicates that these films are porous [8] and the uptake of oxygen continues after the sample is removed from the vacuum chamber. However, it was noted that the rate of uptake of oxygen, as indicated by IR absorption, is much slower for films made with water vapour present than for films made with silane as the ambient reactive gas. A porous film contains dangling-bond defects which act as recombination centres. The addition of oxygen reduces the dangling bond density [1], improves the photoconductivity, and makes the film less susceptible to oxygen uptake in air.

Using silane as the feed gas, a second series of a–Si:H films (0.5 μm thick) were made with a low-energy ion beam bombarding the substrate using the following conditions: a substrate temperature of 165 °C, an ion beam current of 9 mA, and an ion beam voltage of 100 V. All other deposition conditions were reproduced except that water vapour was

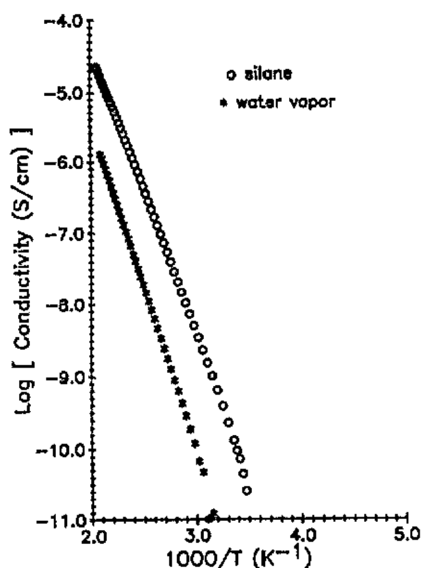

Figure 1. An Arrhenius plot for two samples. The sample represented by the top curve (O), (measured *in situ*) was made using silane as the reactive gas at a partial pressure of 5.2×10^{-2} Pa; the other, represented by the bottom curve (*), (also measured *in situ*) was made using water vapour as the reactive gas at a partial pressure 2.7×10^{-4} Pa. All other conditions were duplicated.

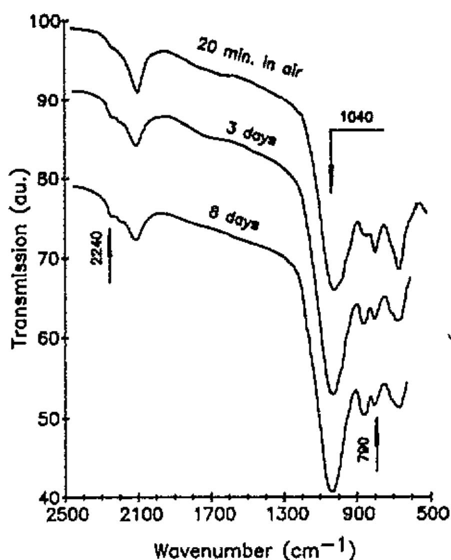

Figure 2. The IR spectra for the sample made with water vapour (partial pressure of 2.7×10^{-4} Pa) and no ion beam assistance. The top curve was measured 20 min after the sample was taken out of the deposition system. The bottom two curves were measured 3 and 8 days later, as indicated.

introduced at different partial pressures for the different samples. The IR transmission spectra for these samples are given in figure 3. These deposition conditions produced films with hydrogen concentrations of 24 ± 1 at.%, determined from the IR spectra. One unexpected result is the fact that the observed hydrogen concentration in these films shows no detectable dependence on the presence of the water vapour in the system. However, oxygen absorption peaks are noted near 1040 cm^{-1} (see figure 3) for the samples made with water vapour pressures of 4×10^{-3}, 1.3×10^{-3}, and 2.7×10^{-4} Pa. For the sample represented by the top trace, made in a water vapour partial pressure of 4.0×10^{-3} Pa, we find that it contains about 4 at.% oxygen, calculated using (1), and an absorption band at 1040 cm^{-1}. The sample represented by the second trace contains about 3 at.% oxygen.

Figure 4 shows the variation in the optical gaps E_0 and electrical activation energies E_a, for samples made with different water vapour pressures. These parameters change very little with the varying oxygen content introduced by changing the water vapour partial pressure over four orders of magnitude. However, the photoconductivity does change and this dependence is shown in figure 5. From this, one sees that the photoconductivity (AM 1 illumination) observed in the resulting film increases initially up to water vapour pressures near 9.3×10^{-5} Pa and then decreases as the water vapour pressure is increased above this value and more oxygen is incorporated into the film. This increase in the photoconductivity for small amounts of oxygen added to a–Si:H has also been reported in references [1–3]. Initially, small amounts of oxygen reduce the

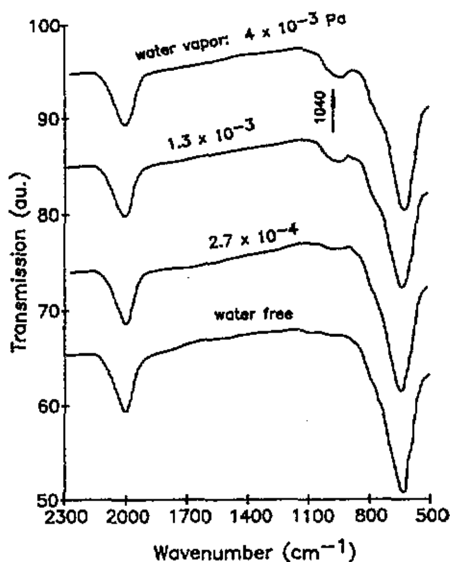

Figure 3. The IR spectra for four samples made with ion beam assistance. In the deposition of the samples represented by the top three curves, water vapour was intentionally introduced into the system at the pressures indicated.

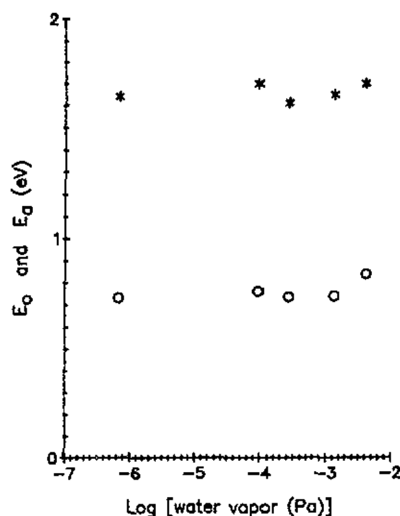

Figure 4. The dependence of the optical gap E_0 (*) and the electrical activation energy E_a (O), on the water vapour partial pressure for the samples made with ion beam assistance. The highest water vapour pressure used introduced about 4 at.% of oxygen into the film.

dangling bond density, but further increases in the oxygen concentration enhances the concentration of oxygen related defects, which appears to more than compensate for the oxygen's initial network softening effects [2].

Two samples were made in a water vapour ambient of 2.7×10^{-4} Pa, one with the ion beam bombarding the substrate and the other without the ion beam assist. The IR spectrum for the first sample shows only an oxygen related absorption peak at 1040 cm^{-1} associated with the Si–O–Si bridging configuration [12] and the film contains less than 3 at.% oxygen. The IR spectrum for the second film contains three oxygen related peaks, one at 1040 cm^{-1} as above, another at 2240 cm^{-1} associated with the stretching mode of $HSiO_3$ [3], and one near 790 cm^{-1}. Anderson [13] has associated this peak with the Si–O–Si–H structure at the surface of microvoids. This result is consistent with the porous structure observed for these films (see figure 2). This latter sample contains significantly more oxygen than that made with the ion source. However, it is difficult to obtain an accurate estimate of the oxygen content because it is difficult to select the correct base line for the analysis from this spectrum.

Like some others [1, 2] who have prepared a–Si:H:O, but using oxygen as the reactive gas, we do not see any peaks near 3700 cm^{-1}, associated with the O–H configuration in the IR transmission spectra of any of our samples. This suggests that most of the water dissociates into atomic oxygen and hydrogen, when it is incorporated into the film.

It is clear that the effects of the presence of water vapour in the deposition system on the properties of an a–Si:H film, are reduced substantially if an ion beam assisted deposition method is used. However, oxygen is still added to the matrix and its positive effect on the photoconductivity for small amounts of oxygen is still observed.

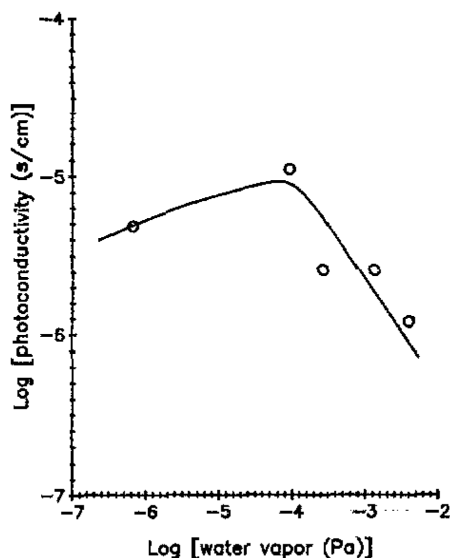

Figure 5. The dependence of photoconductivity on the water vapour pressure in the deposition system for samples made with ion beam assistance. All samples were illuminated with simulated AM 1 light.

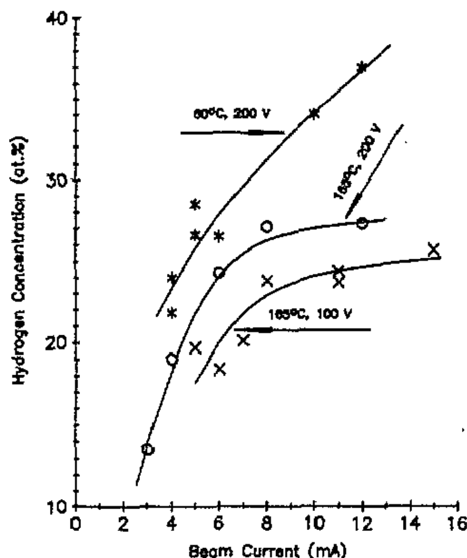

Figure 6. The dependence of hydrogen concentration on the beam current used. The films were made with two different ion voltages (100 and 200 V) and two different substrate temperatures (60 and 165 °C).

3.2. *Effects of varying selected deposition parameters*

When silane is used as the feed gas for the ion source, the amount of hydrogen incorporated into a pure a–Si : H film (all of the samples used in the rest of this study had no oxygen added) is influenced by the ion beam current and the substrate temperature. Figure 6 shows this relationship for two different substrate temperatures (60 and 165 °C) with the same beam voltage (200 V), and for two different ion beam voltages (100 and 200 V) when the substrate temperature is 165 °C. The deposition rates were 8.5 nm min^{-1}. Note that the concentration of hydrogen in the amorphous film tends to saturate when the higher substrate temperature is used. Rather large concentrations of hydrogen can be added when the substrate temperature is only 60 °C. The lower two curves in this figure show a difference in the hydrogen concentrations between samples made with an ion voltage of 100 V or 200 V, when the substrate temperature is 165 °C. A calibration using an ion probe mounted at the substrate position shows that, for the same current from the ion source, the ion density at the substrate is increased when a higher ion beam voltage is used. The difference in the measured hydrogen concentration correlates with the change in the ion beam density introduced by the ion voltages used.

Figures 7 and 8 show that the ratio σ_{ph}/σ_{RT} (observed at room temperature) has a maximum for a hydrogen concentration near 24 at.%, which is not very sensitive to the substrate temperature. Thus, all of the samples given in figure 8 contain approximately 24 at.% hydrogen. The effect of the ion beam voltage is dependent on the substrate temperature, and the maximum of the ratio σ_{ph}/σ_{RT} becomes sharp and shifts to lower beam voltages for higher substrate temperatures. In the group of samples deposited at 165 °C, the film with the highest ratio of σ_{ph}/σ_{RT} is made with an ion beam voltage of 100 V. This value is in the range (50 to 100 V) predicted by Drevillon *et al* [14], to yield

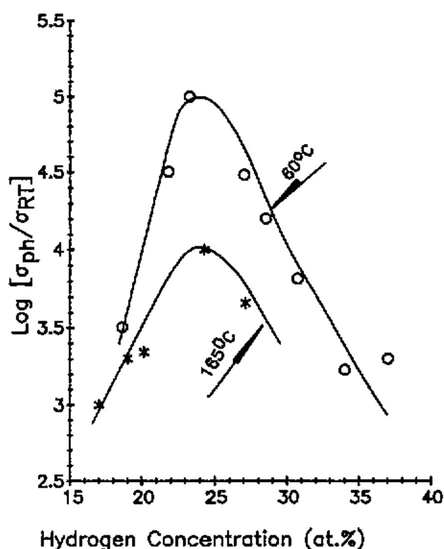

Figure 7. A plot of log $[\sigma_{ph}/\sigma_{RT}]$ against hydrogen concentration (AM 1 illumination) for samples made with an ion beam voltage of 200 V and a substrate temperature of 60 or 165 °C as indicated. No water vapour was introduced into the system.

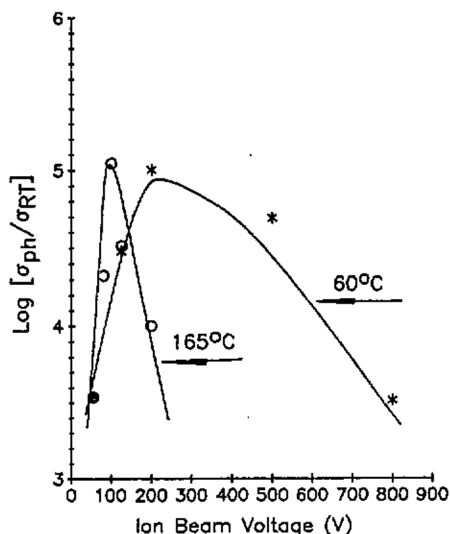

Figure 8. A plot of log $[\sigma_{ph}/\sigma_{RT}]$ against ion beam voltage (AM 1 illumination) for samples prepared with a substrate temperature of either 60 or 165 °C. All of these samples have the same hydrogen concentration (24 ± 1 at.%).

effective surface etching. This result also confirms the speculation by Zhang *et al* [9], that substrate temperature would alter the value of the optimum ion beam voltage needed.

At low substrate temperatures a film prepared with no ion beam bombardment is porous and contains a large number of dangling bonds. To obtain a better photoconductor, the film structure must be improved. An ion beam bombarding the growing surface with the appropriate energy and intensity, in relation to the deposition rate and substrate temperature, can improve the film structure. When the ion energy or ion beam density is too low, surface etching effects are reduced and the optimum improvement in the density is not achieved. When the ion energy is too high, the ion penetration into the film surface is probably too large and new defects are created which cannot be annealed out at the given substrate temperature. If the beam intensity is too high, it seems that too much hydrogen is incorporated into the film, particularly at the lower substrate temperatures, and this again introduces detrimental defects.

4. Conclusions

Water vapour can be a troublesome reactive contaminant in silicon deposition systems, particularly if the substrate temperature is low and ion beam bombardment of the growing film is not present. The water dissociates into oxygen and hydrogen and is incorporated into the film, forming Si–O and Si–H bonds in the structure. The oxygen introduced increases both the optical gap and the electrical activation energy as long as the film was prepared with no ion beam present. When ion bombardment occurs during

the deposition, under otherwise identical conditions, much less oxygen is incorporated into the film, and at these lower concentrations the photoconductivity is improved. Too much oxygen reduces the photosensitivity below the optimum value.

When the ion beam assisted reactive deposition method is used to prepare a–Si:H (without water or oxygen contamination), the photoconductivity can be optimized to obtain a ratio, σ_{ph}/σ_{RT}, of at least as large as 10^5 (under AM 1 illumination), by choosing a set of ion beam parameters and deposition conditions within relatively narrow limits. The most important parameters are: substrate temperature, ion beam intensity (i.e. hydrogen concentration) and ion beam voltage. These parameters are interrelated.

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